A manual of chemical analysis as applied to the examination of medicinal chemicals : a guide for the determination of their identity and quality, and for the detection of impurities and adulterations : for the use of pharmacists, physicians, druggists, manufacturing chemists, and pharmaceutical and medical students / by Frederick Hoffmann and Frederick B. Power.

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To Henry S. Wellcome. Esq

with the sincere regards of his friends

The Authors.

A
MANUAL
OF
CHEMICAL ANALYSIS

AS APPLIED TO THE

EXAMINATION OF MEDICINAL CHEMICALS.

A GUIDE FOR THE DETERMINATION OF THEIR IDENTITY AND QUALITY,
AND FOR THE DETECTION OF IMPURITIES AND ADULTERATIONS.

FOR THE USE OF

PHARMACISTS, PHYSICIANS, DRUGGISTS, MANUFACTURING
CHEMISTS, AND PHARMACEUTICAL AND
MEDICAL STUDENTS.

THIRD EDITION,

THOROUGHLY REVISED AND GREATLY ENLARGED.

BY

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PHILADELPHIA:
HENRY C. LEA'S SON & CO.
1883.

COLLINS, PRINTER.

PREFACE TO THE THIRD EDITION.

THE third edition of this work has been thoroughly revised and to a large extent re-written, in order to make it comply with the present compass of chemical knowledge, as also with the recently issued new editions of the Pharmacopœias of the United States of America and of the German Empire.

The general and original plan and character of the work have been retained; the first part has been much enlarged, so as to afford an explicit and comprehensive guide and work of reference to both student and expert. All the articles of the second part have been carefully revised and greatly enlarged, many new ones added, as also the most approved methods for the separation, identification, and, in most cases, for the quantitative estimation of the chemical poisons likely to be met with in forensic research.

As in former editions, the aim has been to render each article complete in text and illustrations, so as to avoid, as far as possible, references to other articles. The German, French, and Spanish names have been added, as also a large number of new illustrations of apparatus and forms of crystals.

The senior author desires to express his obligations and thanks to his friend and associate Dr. FREDERICK B. POWER, to whose efficient and able assistance all credit for the superiority of the present edition is due.

NEW YORK, February, 1883.

PREFACE TO THE FIRST AND SECOND EDITIONS.

Although the preparation of most medicinal chemicals has passed away from the laboratory of the pharmacist, and is successfully conducted on a commercial scale in manufacturing establishments, yet the responsibility for the identity and quality of medicines, and of the substances used in their preparation, rests properly and legally with those who prepare, compound, and dispense them. It is therefore the duty of the pharmacist and the dispensing practitioner of medicine, as also, to a considerable extent, of the druggist and the manufacturing chemist, to examine the medicinal chemicals of commerce as to their identity, quality, and purity. In the exercise of this duty, they have frequent occasion to resort for information to references now widely scattered through chemical, pharmaceutical, and medical manuals and journals; since our literature, although of vast and increasing extent, and crystallizing more and more into distinct branches, is still wanting in a special guide for ready reference in the application of chemical analysis to such examinations.

In the present volume I have endeavored to supply this want, in a manner and to an extent which, it is hoped, will confine the work within the precise limits of requirement, without detracting from its general scope and its practical usefulness.

Since chemical tests and examinations bear upon and involve the methods of systematic chemical analysis, and as these cannot be described in each particular instance, I have deemed it expedient to preface the volume with a few notes on operations and reagents, and on a few important general tests, and to present a brief outline of a simple course of qualitative analysis for the systematic and progressive recognition of such substances as are met with in the medicinal chemicals. A brief guide has also been added for the volumetric estimation of those compounds to which this mode of examination is especially applicable.

Upon these preliminaries is based the subsequent description of the physical and chemical properties and relations of the medicinal chemicals and their preparations, and of the methods employed for establishing their identity, and for ascertaining their quality and purity. It has been compiled with special reference to the recent editions of the Pharmacopœias of the United States, of Great Britain, and of Germany, and has been brought within the briefest possible compass, with the view to furnish a concise and trustworthy guide, combining easy execution, simple apparatus, and economy of time, with the greatest attainable accuracy.

In preparing this compendium, I have consulted, and at times made free use of, a number of standard works, and periodicals of the kindred literature. I have, however, felt compelled, not without hesitation, to omit the introduction of references, which would have required much space, and would have greatly increased the size of the volume, without affording a corresponding advantage.

Though well aware of the shortcomings and imperfections of the work, I nevertheless venture to hope that it will meet with kind consideration, and will prove both serviceable and stimulating in a province not yet duly appreciated or deservedly cultivated. This hope is the stronger, as the work appears at a time when the rapid advance of both sciences and arts, the drift of public sentiment, and the consequently increasing obligations of the pharmaceutist and the physician, all tend toward higher qualifications, and necessitate also, among other attainments, a more extended exercise of knowledge and skill in chemical and microscopical investigation.

New York, February, 1873.

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OPERATIONS.

THE operations involved in the application of simple tests and chemical examinations must be supposed to be familiar to the pharmacist, the druggist, the pharmaceutical or chemical manufacturer, and the physician. For the student and the less experienced operator, however, the following preliminary explanations and descriptions relating to the more important simple operations are considered to be of sufficient practical value to merit a brief notice.

Solutions.—With regard to the nature of the product, two kinds of solution are distinguished, *simple* and *chemical*. In a "simple solution" the dissolved body retains all of its original properties, with the exception of its physical form, and may be obtained again in its former state on the removal of the solvent by evaporation: for instance, solution of ferrous sulphate in water. It is "saturated" when the solvent ceases to take up any more of the dissolved body; but as the coefficient of solubility of most substances is increased by heat, the expression of saturation will therefore always relate to the temperature at which the solution has been formed. A "chemical solution" is one in which the dissolved body no longer retains its original qualities, but, through the action of the solvent, has become converted into a new substance, possessing variously modified chemical and physical properties: for instance, solution of ferrous carbonate in dilute sulphuric acid.

Solutions for testing are best prepared in test-tubes, or in small flasks or beaker-glasses.

Increase of the surfaces of contact by comminution, agitation, and increase of temperature, as is well known, aid and accelerate the process of solution, as well as of chemical reaction; and one or both of these auxiliaries may be employed, unless the nature of the substance or the effect of heat upon it is such as to exclude their application.

The common solvent, water, has to be used distilled, and this fact is to be understood throughout this work; neither rain-water nor spring-water, however pure it may appear to be, can be used indiscriminately as a solvent or for edulcoration in chemical investigations.

To effect the solution of substances insoluble in water, for the purpose of chemical examination, or where the aid of an acid is required, only such acids as are found by the operator himself to be chemically pure should be employed.

Precipitation.—The formation of an insoluble body from a solution can be effected either by a change or modification of the solvent, or by the production of one or more new bodies, insoluble in the solvent. An instance of the first case is an aqueous solution of barium chloride, which will be precipitated by the addition of concentrated hydrochloric acid, or a solution of calcium sulphate, which will be precipitated by alcohol; in both these instances the solvent power of the liquid is lessened, and solution may be re-established by the addition of a sufficient quantity of water. Instances of the second case of precipitation are a solution of calcium hydrate precipitated by sodium carbonate, and a solution of magnesium sulphate precipitated by barium hydrate.

Precipitation is resorted to as the most important mode of detecting and discriminating bodies by their physical and chemical properties, and of effecting their separation. According to the nature or appearance of the precipitates, they are variously distinguished; thus "flocculent," when forming flock-like masses; "crystalline," if, when magnified, the small particles are seen to be composed of minute but distinctly formed crystals; "gelatinous," if jelly-like; or "curdy," if separating in the form of a curd, etc.

The terms "turbidity" and "cloudiness" designate the formation of a precipitate so insignificant in quantity, or so finely divided, or so light in weight, that the suspended particles only impair the transparency of the fluid, and require a certain amount of time to subside in the form of a precipitate. If the transparency of a colorless or nearly colorless liquid becomes so slightly impaired upon the addition of a reagent as not to become distinctly turbid, but displays a reflection of pearly light, and thus presents an opal-like appearance, the minute degree of precipitation thus produced is designated as "opalescence."

Filtration and Decantation.—The separation of the supernatant liquid from a precipitate is effected either by filtration and subsequent washing of the precipitate upon the filter by means of a wash-bottle (Figs. 1 and 2), or, where the precipitate speedily and completely subsides, by decantation. As a rule, funnels and filters must be small, and proportionate to the amount of the precipitate and the liquid requiring filtration.

Filters employed in analytical operations should be as free as possible from inorganic substances, especially such as become dissolved by the action of acids, as calcium salts, ferric oxide, etc., and for the collection of precipitates should be smooth, so placed in the funnel as to fit closely on all sides, and cut so as not to project over the rim; it is also advisable always to moisten the filter upon the funnel with distilled water, by means of the wash-bottle, previous to the collection of the precipitate, or to filtration.

FIG. 1.

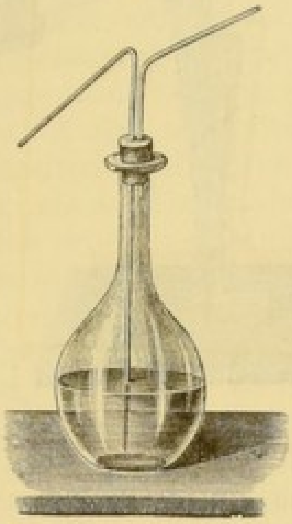
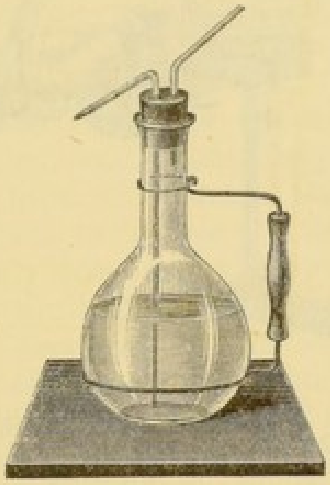
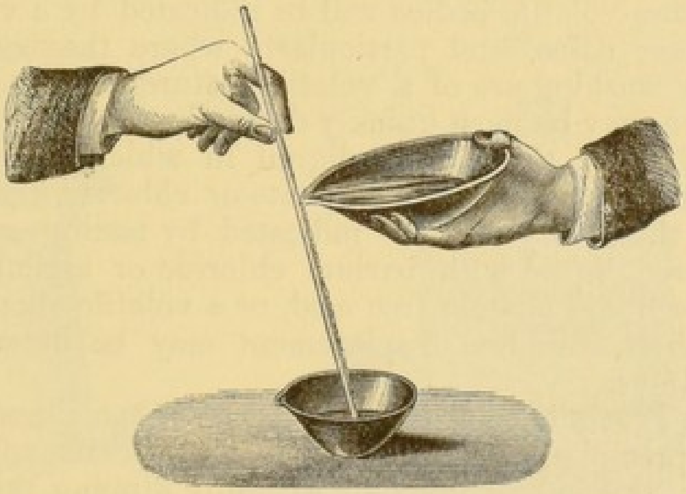


FIG. 2.



Decantation is effected either by pouring off the supernatant clear part of the fluid by simply inclining the vessel, and allowing the fluid to flow down a glass rod (Fig. 3), or by drawing it off by means of a small glass siphon or a pipette (Figs. 4 and 5).

FIG. 3.



Washing Precipitates.—In either mode of separation the precipitate, in most instances, must be thoroughly freed from the adhering liquid by washing with water, either on the filter or by decantation. As a rule, the washing of precipitates is most thoroughly and quickly effected by means of hot water; for this purpose nothing more is required than the ordinary wash-bottle,

FIG. 4.

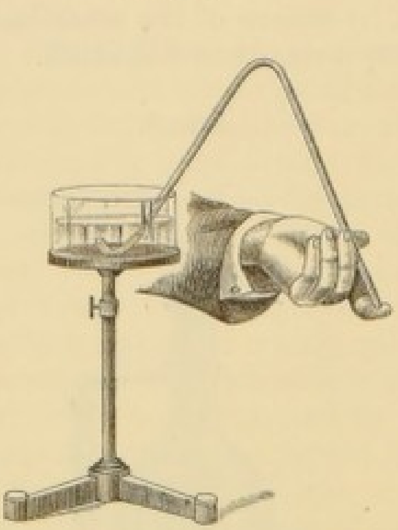


FIG. 5.

which, however, for convenience in holding, is provided either with a wooden handle, attached by means of a strong wire to the flask (Fig. 2), or the neck of the flask may be covered with a thick circular strip of cork, or tightly bound with twine.

In order to ascertain whether a precipitate has been sufficiently or thoroughly washed, a few drops of the liquid, as it escapes from the funnel, may be collected from time to time on platinum foil, and subsequently slowly evaporated, whereby the presence of soluble, non-volatile bodies will be indicated by a visible residue. In some cases, and particularly where the bodies to be removed by washing are of a volatile nature, the completion of the operation may be most quickly determined by the application of chemical tests; thus, if the liquid in which the precipitate has been produced contains a sulphate or chloride, the complete removal of these salts will be indicated by testing a few drops of the filtered liquid with barium chloride or argentic nitrate, whilst if the liquid contain free acid, or a volatile alkali, such as ammonia, their complete displacement may be determined by means of litmus.

Removing Precipitates from the Filter.—When a small quantity of a moist precipitate has to be taken from the filter for further examination, this is best done by carefully dipping the end of a thin glass rod into it, and subsequently detaching the adherent part of the precipitate upon a watch-glass, the interior of a small test-tube, or the microscopic glass slide.

If a precipitate is to be removed from the filter as completely as possible, this may be accomplished either by puncturing the point of the filter by means of a glass rod, and subsequently washing the precipitate with a fine stream of water or other liquid from a wash-bottle into a receptacle beneath, or the funnel may be held in a horizontal position, so that its rim projects inside the edge of a porcelain dish or beaker, when by directing a fine stream of water against the sides of the filter by means of a wash-bottle, the precipitate may be removed without breaking the filter.

If, however, it is not desirable to add a liquid to the precipitate, the filter with its contents is first allowed to drain thoroughly in the funnel, and is then opened and placed upon a glass plate or upon several layers of bibulous paper, when the moisture will have soon become sufficiently absorbed to permit the ready removal of the precipitate with a glass rod or a spatula. When it is desired to dissolve a precipitate on the filter, the solvent should, when admissible, be first heated, and gradually poured upon the precipitate, and the filtrate, which will contain the precipitate in solution, collected in a test-tube or beaker; if the precipitate does not thus become completely dissolved, the filtrate is again heated, and returned to the filter until complete solution is effected, which may be finally aided, if necessary, by the addition of a fresh portion of the solvent. If the precipitate should be considerable in amount, the larger portion may be first removed by means of a spatula, and transferred to a porcelain dish or beaker, and the residue upon the filter subsequently dissolved by the aid of the proper solvent.

Drying Precipitates.—When a precipitate is required in a dry condition, it is first allowed to drain as completely as possible on the filter, and the funnel and filter are then placed in a hollow tin cone or cylinder (Fig. 6), which is supported on a piece of wire gauze over a moderate gas flame, being careful to so regulate the heat as not to char the filter. The operation may also be accomplished still more quickly by opening the filter and spreading it with its contents upon a porcelain plate or watch-glass, which is placed upon a piece of wire gauze over a low flame, the proper precautions being observed to prevent excessive heat. In either

FIG. 6.

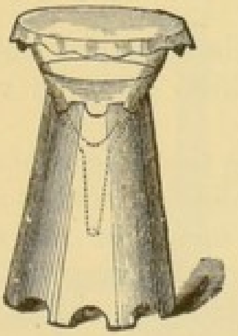
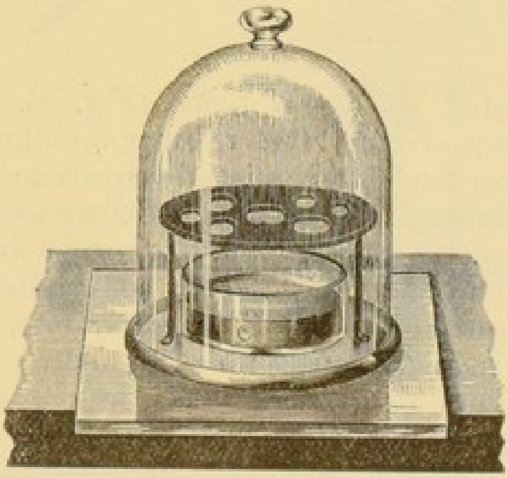


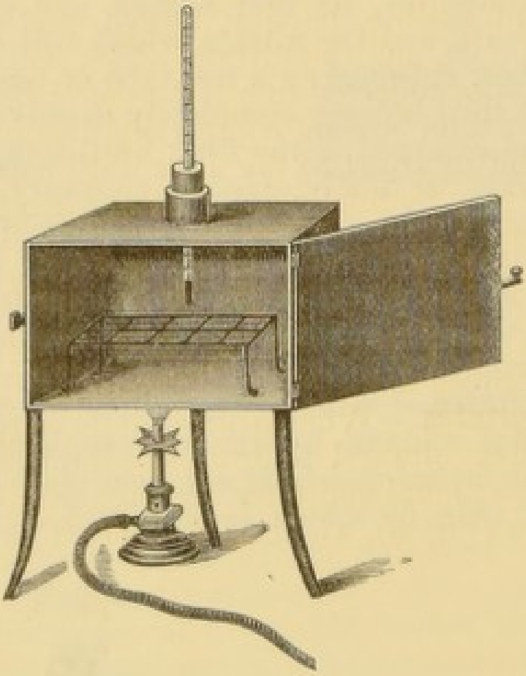
FIG. 7.



case, the precipitate may be first partially dried by opening the filter, and placing it with its contents upon several folds of bibulous paper.

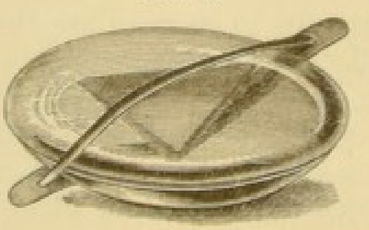
In the more exact requirements of analysis, the precipitate or other substance requiring desiccation may be placed under a bell-jar containing concentrated sulphuric acid or fragments of fused calcium chloride (Fig. 7), or in an air-bath or drying oven, provided with a thermometer, and the temperature of which is regulated by a gas flame (Fig. 8). By this means a uniform temperature may be readily maintained, which may be varied in accordance with special requirements.

Fig. 8.



Weighing Precipitates.—Before ascertaining the weight of a precipitate, it is usually required to be first completely dried at a definite temperature. This is accomplished by means of the above illustrated air-bath. The precipitate, after partial drying upon the filter in the funnel, is placed upon a watch-glass, which, together with another glass of the same size and a small brass clamp, has been previously accurately weighed. During the process of drying the glasses are placed one within the other, so that the moisture from the precipitate contained on the uppermost glass may readily escape. When the precipitate has become sufficiently dry, it is removed from the air-bath, the lower watch-glass placed upon the upper, and the whole secured by means of the brass

Fig. 9.



clamp (Fig. 9), in order that on cooling no moisture shall be absorbed by exposure to the air. The glasses, with the inclosed precipitate, as indicated in the figure, are brought upon the balance, and the weight finally determined. In order to ascertain that no further loss takes place upon drying, the glasses are again opened, placed in the air-bath as before, and the operation repeated until two successive weighings prove the weight to remain constant.

Ignition.—The process of ignition refers to the subjection of solids to a more or less elevated temperature, and is employed for various purposes, but has, usually, for its object, the separation of a volatile from a less volatile or non-volatile body, when the latter alone is required; it is also frequently employed for ascertaining the effect of strong heat upon a substance. In the latter case the substance is heated in a bent glass tube (Fig. 10), whereby the nature of the evolved gases or sublimate produced may be observed, whereas, if it be required simply to ascertain or confirm the volatile or non-volatile nature of a substance, it is heated on platinum foil, in the non-luminous flame. For the ignition of precipitates, however, the substance is placed in a porcelain or platinum[1] crucible of convenient size (Fig. 11), supported on a wire triangle, and heated in the non-luminous gas flame, or, if a higher temperature be required, by means of the blowpipe or gas blast-lamp.

Fig. 10.

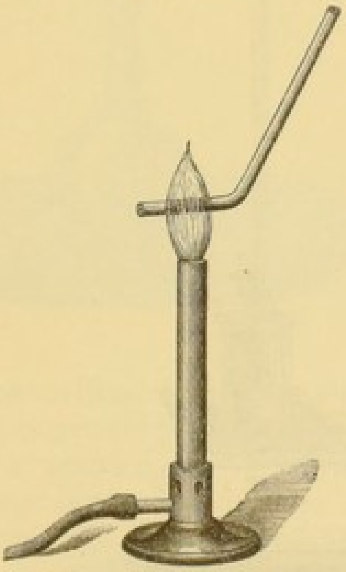
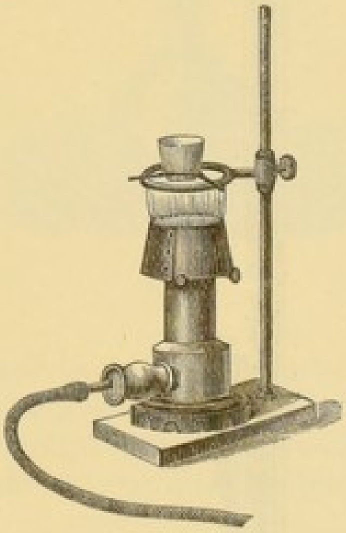


Fig. 11.



Determination of the Melting and Boiling Point.—The melting and boiling point of bodies under normal atmospheric pressure

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[1] The use of platinum vessels should be avoided for heating substances which develop chlorine, the alkaline hydrates, nitrates, and cyanides, metallic sulphides, readily reducible metallic oxides, salts of the heavy metals with organic acids, or phosphates in the presence of organic compounds.

FIG. 12.

being contant and unchangeable, the determination of these factors is an operation which is frequently resorted to for the purpose of establishing the identity of a substance, and for affording confirmatory evidence of its purity.

The *melting point* is determined by bringing a very small portion of the substance into the lower part of a capillary glass-tube (Fig. 12), and attaching the latter by means of a small rubber band to a thermometer, so that the substance will be on the same level and in the most direct possible contact with the thermometer bulb (Fig. 13). The thermometer, thus arranged, is then suspended, and the bulb and the capillary portion of the tube allowed to dip below the surface of water or sulphuric acid, contained in a beaker; the liquid employed being adapted to the melting point

FIG. 13.

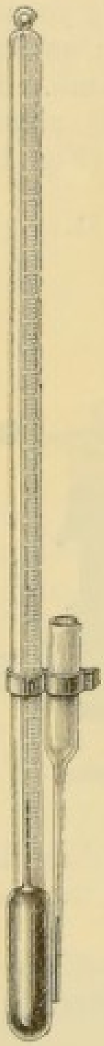
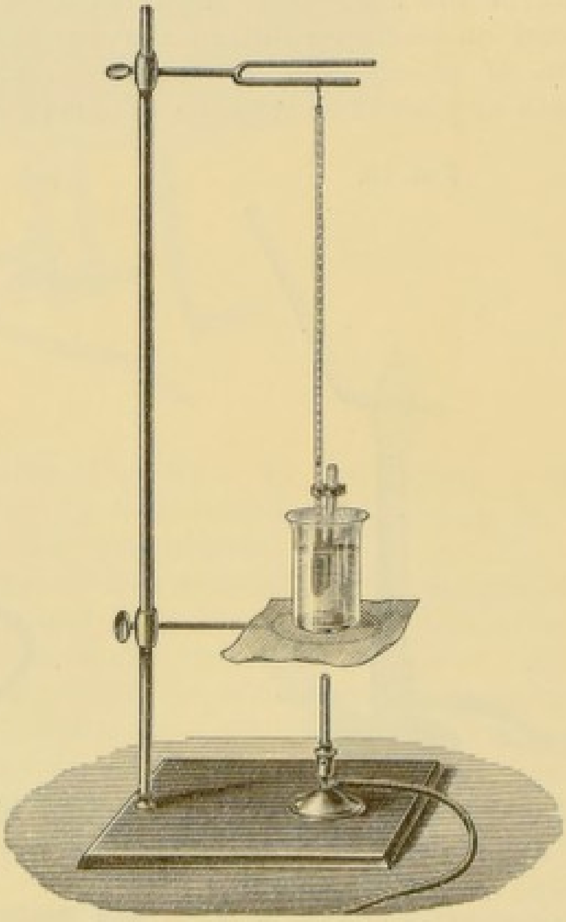


FIG. 14.



of the substance. The liquid is then very gradually heated by means of a carefully regulated gas flame (Fig. 14), and the moment when the body melts in the capillary tube is accurately observed and the temperature noted.

The *boiling point* is determined by bringing the liquid into a vessel adapted for fractional distillation (Fig. 15), or into an ordinary glass flask provided with a doubly perforated cork (Fig. 16), in one orifice of which the thermometer is inserted, while the other is provided with a bent glass tube, which may be connected with a condenser. The thermometer should not be allowed to become immersed in the liquid, but should simply project so far into the interior of the flask as to be surrounded by the vapor of the boiling liquid. On the application of heat, the boiling point will be indicated by the height of the mercurial column when the liquid is in a state of active ebullition.

FIG. 15.

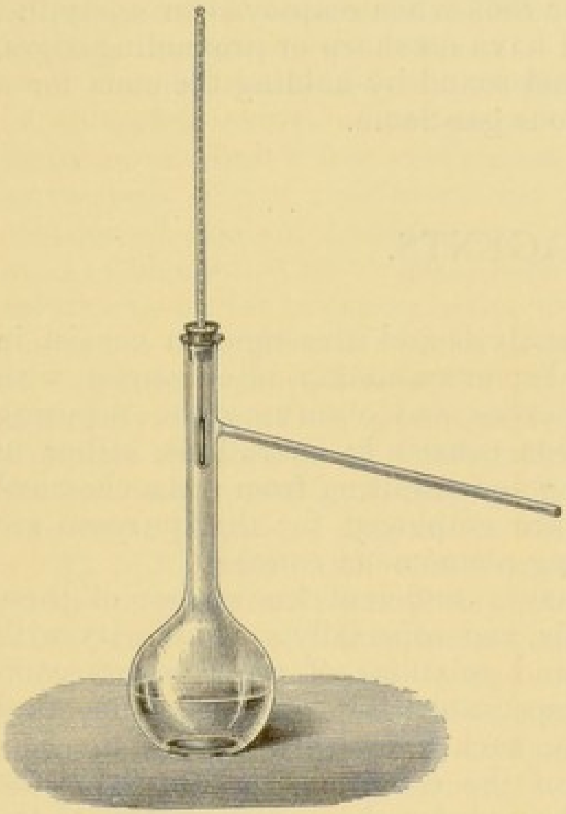
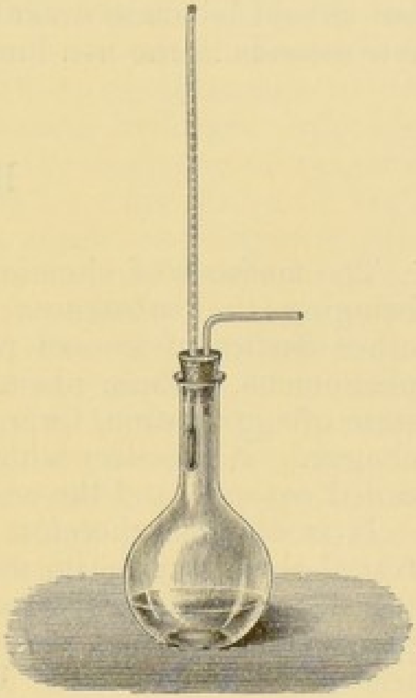
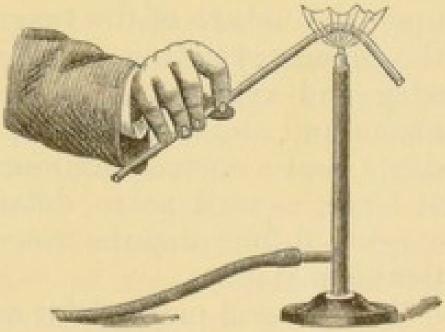


FIG. 16.



Bending of Glass Tubing.—Glass tubing may be regularly and uniformly bent in any desired shape

FIG. 17.



by the use of the upper edge of the common fish-tail gas-flame; the flame of the Bunsen gas-lamp cannot be well employed, producing unsatisfactory curves. The tube is held in a horizontal position in the flame at the point requiring to be bent, so that it becomes entirely enveloped by the illuminating portion; it soon becomes covered with a deposit of soot, and, when sufficiently heated, bends itself by the weight of the unsupported end (Fig. 17). The bend, if properly made, will form a symmetrical curve, without diminishing the calibre of the tube at any point, and will be free from sharp angles. Glass tubing or rods when employed in analytical or chemical operations should have no sharp or protruding edges, but should be made smooth and round by holding the ends for a few seconds in the non-luminous gas-flame.

REAGENTS.

The methods of chemical analysis and investigation consist in bringing the substances under examination into contact with other bodies of known properties, and observing the resulting phenomena. These phenomena consist in alterations, either in state of aggregation, form, or color, resulting from some chemical change. All bodies which are employed for this purpose are called *reagents*, and the ensuing phenomena *reactions*.

It is obvious, therefore, that a sufficient knowledge of theoretical chemistry in its details, and especially a familiarity with the deportment, properties, and relations of the common compounds and reagents, are indispensable to the pursuit of chemical tests and examinations. Upon such knowledge depend the conception and comprehension of the conditions necessary for the formation of new compounds, and for the manifestation of the various reactions, as well as the correct inference from the observations and results of all investigations; and without it they will remain unavailing and uncertain.

No special and definite rules can be assigned for the application of reagents in each instance, with respect to their proportion and quantity. These must depend upon the quantity and nature of the substance under examination and its solution, as well as upon the nature of the reagent, the strength of its solution, and the processes taking place in each particular reaction. Knowledge and reflection, as well as a ready comprehension of the object and aim of each test, of its issues, and of the possible incidents, and a correct inference from all phenomena, must decide at large, as well as in detail, not only what reagents should be employed, but also the amount and the conditions in each particular instance.

The general method for ascertaining the sufficient or slightly excessive amount of a reagent, as has to be done before proceeding in the systematic course of analysis, is to add a few drops more of the reagent to the clear liquid obtained either by allowing the precipitate to subside, or by filtering off a small quantity of it; if any further precipitate is formed, the filtered portion must be returned, more of the reagent added, and the clear liquid again examined with a few additional drops of the reagent, until no further precipitate is produced. With some reagents, as, for instance, with hydrogen sulphide or ammonia water, this method of procedure is rendered unnecessary, an excess being indicated by their characteristic odor.

A common error, and an obstacle to the less skilled, is the use of an undue excess of reagents. There are reagents which in many cases admit a free application without disadvantage to the correctness of the result—as, for instance, hydrogen sulphide, solution of calcium hydrate, etc.; but the majority of reagents need to be applied in common tests only by a few drops of their solutions—as, for instance, baric, ferric, cupric, and argentic solutions, etc. On the other hand, there are not unfrequently errors arising from an insufficient amount in the application of reagents, especially with dilute solutions, or in those cases in which the complete elimination of a substance by precipitation is required for the subsequent examination for other bodies: for instance, hydrogen sulphide, applied in a limited quantity, produces a white precipitate with solutions of mercuric salts; applied in excess, it gives a black precipitate. There are other instances where an excess of the solution under consideration, as well as of the reagent, may redissolve, and consequently destroy, the precipitate whereon the reaction is based.

In operations of chemical analysis it must always be borne in mind and well understood that, in the processes and phenomena taking place between the reagents and the substances acted upon, as in all chemical changes and reactions, certain laws and definite limits exist between cause and effect, and that the ability of correctly applying knowledge, judgment, and skill, and of drawing the right inference from necessary as well as from casual reactions and phenomena, must rule and guide the methods and operations of the investigator, and carry them beyond mere conjecture and empiricism.

It is beyond the scope of this work to describe the mode of preparing the reagents, their use and application, and their deportment with the common compounds, or to dwell upon the general rules of systematic methods, accuracy, order, neatness, and cleanliness to be observed in the execution of analytical work. For such information reference must be had to the text-books of applied and analytical chemistry. From a practical point of view, only the usual strength of the solution of the reagents, as best suited for the common tests and examinations, and the mode of preparing a few of the rarer or special reagents, or of such as are not included among the medicinal chemicals considered in this volume, have been stated.

As regards the strength of the solutions of reagents, unless otherwise stated, the test solutions described upon the following pages are invariably understood to be used wherever the name of the reagent only is stated.

It hardly needs to be mentioned that all reagents must consist purely of their essential constituents, and must contain no admixture of any other substance; it must, therefore, be an invariable rule to test the purity of the reagents before they are employed.

The reagents and their solutions must be preserved according to their nature; of those whose solutions are liable to alteration or decomposition only small quantities must be kept, and always in tightly closed glass-stoppered bottles.

REAGENTS AND TEST SOLUTIONS.

Acetic Acid.—Spec. grav. 1.048.

Acetic Acid, Diluted.—Obtained by mixing 1 part of acetic acid with 4 parts of water.

Hydrochloric Acid.—Spec. grav. 1.16; containing 32.2 per cent. of absolute acid.

Hydrochloric Acid, Diluted. — Spec. grav. 1.049; containing about 10 per cent. of absolute acid. Obtained by mixing 6 parts of hydrochloric acid with 13 parts of water.

Hydrosulphuric Acid. See Hydrogen Sulphide.

Nitric Acid.—Spec. grav. 1.42; containing 69.4 per cent. of absolute acid.

When concentrated acids are applied in small tests only by the drop, as, for instance, in testing alkaloids, etc., they are taken from the bottle by dipping a glass rod into the acid and allowing the drop or drops to fall upon the substance to be acted upon, or better by means of a kind of pipette consisting of a thin, strong glass tube, adjusted at one end to a small caoutchouc bulb, and contracted at the other extremity to a capillary end. The fluid is drawn into the tube, and delivered again by gentle pressure of the bulb (Fig. 18).

FIG. 18.

Nitric Acid, Diluted.—Spec. grav. 1.059; containing 10 per cent. of absolute acid. Obtained by mixing 1 part of nitric acid with 6 parts of water.

Nitro-hydrochloric Acid (Aqua Regia).—4 parts by weight of nitric acid, spec. grav. 1.42, are gradually added to 15 parts by weight of hydrochloric acid, spec. grav. 1.160, in a capacious, open glass vessel, and, when effervescence has ceased, the product is transferred to glass-stoppered bottles, which should be not more than half filled, and preserved in a cool place.

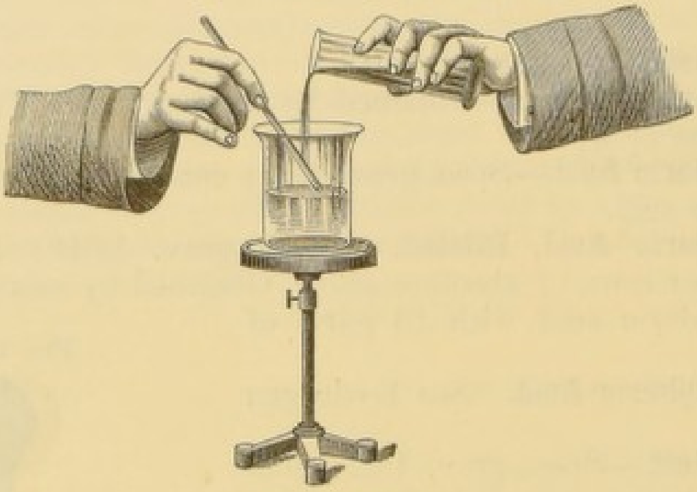
Oxalic Acid.—Solution of 1 part of crystallized oxalic acid in 10 parts of water.

Picric Acid.—Saturated aqueous solution of picric acid.

Sulphuric Acid, Concentrated.—Spec. grav. 1.84; containing 97 per cent. of absolute acid.

Sulphuric Acid, Strong.—Spec. grav. 1.64; containing 72.75 per cent. of absolute acid. Obtained by carefully mixing, in a flask or beaker, 3 parts of concentrated acid with 1 part of water (Fig. 19).

FIG. 19.



In diluting concentrated sulphuric acid with water, the acid should invariably and gradually be added to the water, and in vessels which are either placed in cold water or which are not liable to crack from the heat evolved.

Sulphuric Acid, Diluted.—Spec. grav. 1.068; containing about 10 per cent. of absolute acid. Obtained by mixing 1 part of concentrated acid with 9 parts of water.

Sulphurous Acid.—Spec. grav. 1.046. An aqueous solution of sulphurous acid gas, saturated at 15° C. (59° F.), containing 36 times its volume, or about 9.5 per cent. by weight of the gas.

Tannic Acid.—Solution of 1 part of tannic acid in a mixture consisting of 18 parts of water and 2 parts of alcohol.

Tartaric Acid.—Solution of 1 part of crystallized tartaric acid in 5 parts of water.

Albumen.—The white of one egg is triturated with 100 cubic centimeters of water, and is then filtered through cotton previously moistened with water.

Alcohol.—Spec. grav. 0.820; containing 91 per cent. by weight or 94 per cent. by volume of absolute alcohol.

Alcohol, Absolute.—Spec. grav. 0.795.

Alcohol, Amylic.—Spec. grav. 0.816 to 0.818.

Aluminium.—Metallic aluminium in the form of wire or ribbon.

Ammonia Water (Aqua Ammoniæ).—Spec. grav. 0.959. An aqueous solution of ammonia, containing 10 per cent. by weight of the gas.

Ammonia Water, Stronger (Aqua Ammoniæ Fortior, U. S. P.).—Spec. grav. 0.900. A nearly saturated aqueous solution of ammonia, containing 28 per cent. by weight of the gas.

Ammonium Carbonate.—Solution of 1 part of uneffloresced ammonium carbonate in a mixture of 4 parts of water and 1 part of ammonia water.

Ammonium Chloride.—Solution of 1 part of crystallized ammonium chloride in 10 parts of water.

Ammonium Molybdate.

Ammonium Molybdate in Nitric Acid.—Solution of 1 part of ammonium molybdate in 10 parts of water, to which 10 parts of nitric acid, spec. grav. 1.2, are subsequently added.

Ammonium Oxalate.—Solution of 1 part of crystallized ammonium oxalate in 20 parts of water.

Ammonium Phosphate.—Solution of 1 part of ammonium phosphate in 15 parts of water.

Ammonium Sulphide.—A solution of ammonium sulphide in water; it is obtained by saturating, at 15° C. (59° F.) or a lower temperature, 3 parts of Aqua Ammoniæ Fortior, U. S. P., with hydrogen sulphide gas, and by subsequent addition of 2 parts of ammonia water. It is best preserved in small vials, tightly corked, and in a cool place. This solution, being concentrated, has to be employed, in the common tests, only in small quantities, mostly by drops.

When hydrogen sulphide is at hand, ammonium sulphide may, in many of its applications, be produced by saturating the liquid under examination with the gas, and by the subsequent addition of ammonia water; or, in ammoniated solutions, if dilution does not interfere with the reaction, by the addition of an aqueous solution of hydrogen sulphide.

Aniline Sulphate.—Solution of 5 drops of aniline in 25 cubic centimeters of diluted sulphuric acid.

Argentic Nitrate.—Solution of 1 part of crystallized argentic nitrate in 20 parts of water.

Argentic Nitrate, Ammoniated.—Solution prepared by adding ammonia water, spec. grav. 0.959, in drops, to test-solution of argentic nitrate, until the precipitate at first formed is very nearly all redissolved, and filtering.

Argentic Sulphate.—Solution of 1 part of argentic sulphate in 250 parts of water.

Auric Chloride.—Solution of 1 part of auric chloride in 20 parts of water.

Barium Chloride.—Solution of 1 part of crystallized barium chloride in 10 parts of water.

Barium Hydrate (Baryta-water).—Saturated aqueous solution of barium hydrate, containing about 5 per cent. of the hydrate.

Barium Nitrate.—Solution of 1 part of crystallized barium nitrate in 20 parts of water.

Benzin (Petroleum Benzin or Petroleum Ether).—Spec. grav. from 0.670 to 0.675, and boiling at 50 to 60° C. (122 to 140° F.).

Benzol.—Spec. grav. 0.885.

Borax.

Bromine Water.—A saturated solution of bromine in water.

Calcium Chloride.—Solution of 1 part of pure crystallized calcium chloride in 10 parts of water.

Calcium Hydrate (Lime-water).—Saturated aqueous solution of calcium hydrate.

Calcium Sulphate.—Saturated aqueous solution of calcium sulphate, containing about 0.2 per cent. of the salt.

Carbon Bisulphide.—Spec. grav. 1.272.

Chlorine Water.—A saturated aqueous solution of chlorine, containing about 0.4 per cent. by weight of the gas. For analytical use, this solution is best preserved in small vials, tightly corked and sealed, in a cool place, and protected from the light.

Chloroform.—Spec. grav. 1.480.

Cobaltous Nitrate.—Solution of 1 part of cobaltous nitrate in 10 parts of water.

Copper.—Metallic copper in slender wire, or thin foil cut into strips.

Cupric Sulphate.—Solution of 1 part of crystallized cupric sulphate in 10 parts of water.

Cupric Sulphate, Ammoniated.—Solution prepared by adding ammonia water, spec. grav. 0.959, in drops, to test-solution of cupric sulphate, until the precipitate at first formed is very nearly all redissolved, and filtering.

Cupric Tartrate, Alkaline Solution of, (Fehling's Solution).—17.32 grams (267.3 grains) of pure crystallized cupric sulphate are dissolved in 100 cubic centimeters (about 3 fluidounces) of water; and 85 grams (2 ounces and 457 grains) of pure crystallized potassium and sodium tartrate are dissolved in 300 cubic centimeters (about 10 fluidounces) of a 10 per cent. solution of sodium hydrate. The cupric solution is then gradually added to the alkaline solution, and, having been well mixed, so much water is added as to make the whole measure 500 cubic centimeters (16 fluidounces). The solution should be free from yellowish-brown sediment, and should deposit none upon boiling.

Ether.—Spec. grav. 0.750.

Ferric Chloride.—Solution of 1 part of ferric chloride in 10 parts water.

Ferric Dinitrosulphide.—Obtained by adding, drop by drop, a solution of ferric chloride or sulphate, with constant stirring, to a mixture consisting of equal parts of strong solutions of potassium nitrate and ammonium sulphide, heating the liquid to boiling for a few minutes, and filtering while hot from the sulphur. The deep-colored liquid deposits, on cooling, black, needle-shaped rhombic prisms of ferric dinitrosulphide; these are dissolved 1 part in 10 parts of water, to give the required solution.

Ferrous Sulphate.—Solution of 1 part of ferrous sulphate, obtained by precipitation with alcohol, in 10 parts of water.

Ferrous sulphate is best obtained by pouring an aqueous solution of freshly prepared crystallized ferrous sulphate, saturated at the boiling-point, into strong alcohol, collecting the precipitate upon a filter, washing with a little alcohol, drying by pressing between filtering-paper, and by immediately filling the humid salt into small warm vials, which are corked and sealed while warm. The absence of ferric sulphate may be ascertained by testing the solution with potassium ferrocyanide; no blue turbidity, or only a very slight one, should occur.

Gelatin.—Solution obtained by digesting 1 part of isinglass (ichthyocolla) with 50 parts of water, on a water-bath, for half an hour, and subsequently filtering through cotton, moistened with water.

Gold.—Metallic gold in the form of leaf.

Hydrogen, Nascent, is a very delicate means of detecting arsenic. The test depends upon the production of hydrogen arsenide (arseniuretted hydrogen), whenever arsenic is present in any soluble form, in which hydrogen is being evolved by the action of dilute sulphuric or hydrochloric acid upon zinc or magnesium. From the hydrogen arsenide the arsenic can be separated in a characteristic and unmistakable form, either as metal, or by leading the gas into a solution of an easily reducible metallic salt, as, for instance, argentic nitrate, in which case the silver is precipitated and a solution of arsenious acid is obtained.

$$AsH_3 + 3H_2O + 6AgNO_3 = H_3AsO_3 + 6HNO_3 + 3Ag_2.$$

Marsh's Test.—Of the different methods for the application of this test, the one long and commonly known as *Marsh's test* is pre-eminently adapted for the recognition, as also for the quantitative estimation of small amounts of arsenic.

A complete and simple form of apparatus for the application of Marsh's test is represented in Fig. 20. It consists of a gas generating flask or Woulff's bottle (A), of about 300 to 400 cubic centimeters (10 to 14 ounces) capacity, provided by means of a peforated cork or rubber stopper with a funnel tube (*b*), and a drying tube (*a*), loosely stopped at each end with a small plug of cotton, and partially filled with dry calcium chloride in small fragments, followed by a layer of small pieces of dry potassium hydrate; the latter serving to retain any acid which may accidentally be carried over with the gas, as also any trace of hydrogen sulphide. The end of this tube is connected with a reduction tube (*d*), of hard German glass, narrowly drawn out in one or more places, and at the end into a capillary point, and bent up so as to form a vertical jet, as shown in Fig. 20.

The test consists in introducing into the flask (A) pure granulated zinc or magnesium, and adding gradually, by means of the funnel tube, a cold mixture of one part of sulphuric acid and three parts of water, when the hydrogen is more or less quickly evolved. When perfectly pure zinc is employed, the development of gas takes place very slowly, and may be hastened by the addition of a few drops of test solution of platinic chloride.

FIG. 20.

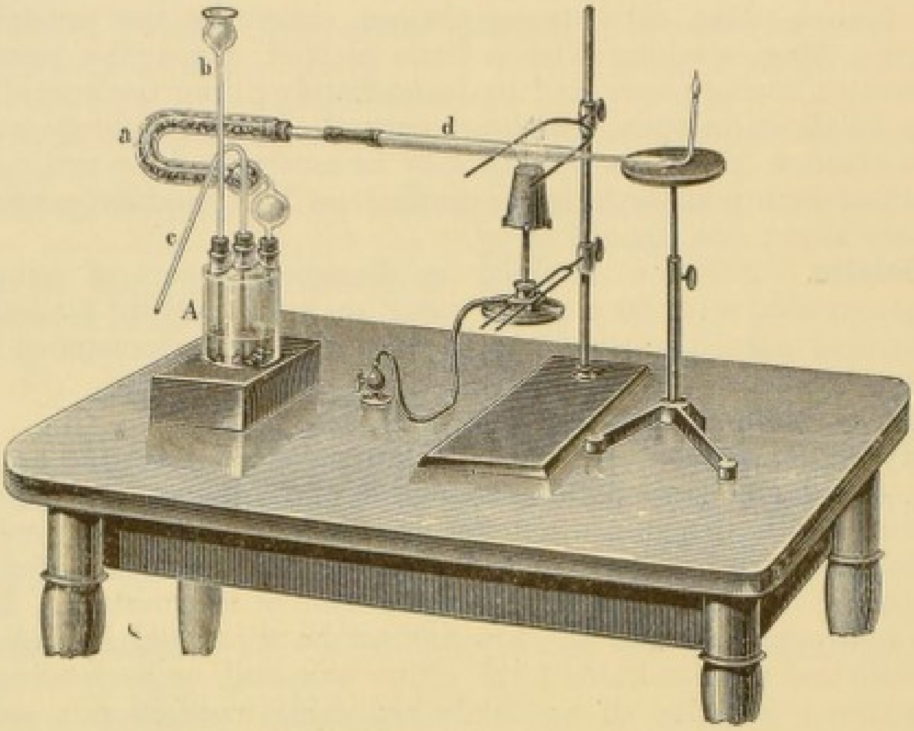
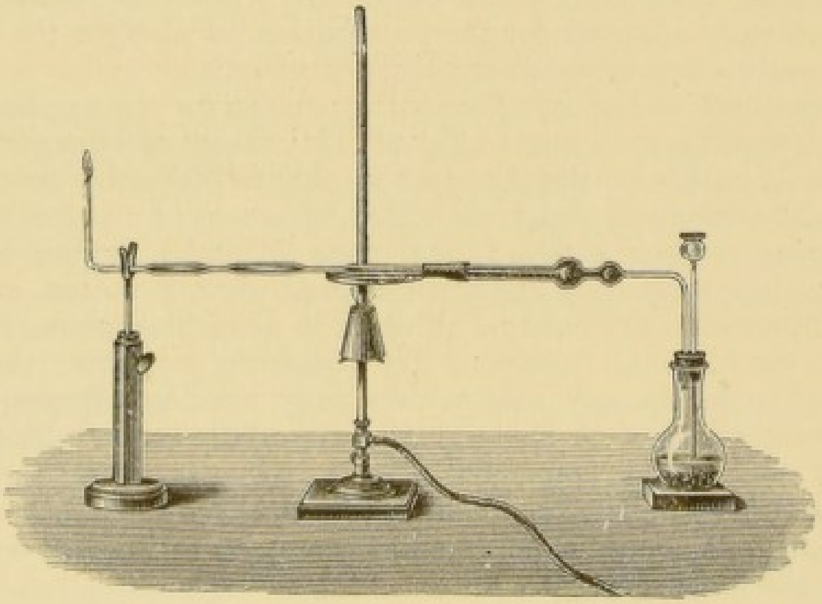


FIG. 21.



It is of primary importance in each case where the test is applied to first ascertain the absolute purity of the zinc or magnesium and acid employed.

After the evolution of gas has continued long enough to expel the atmospheric air,[1] the reduction tube (*d*) is heated to redness in the part indicated in the figure for about ten minutes, the escaping gas is lighted, and a piece of white porcelain is held in the flame. If no dark deposit takes place, either in the tube or on the porcelain, the reagents may be considered pure, and the liquid to be tested may then be added through the funnel tube (*b*), first in small amounts, and the operation continued in the manner described.

If arsenic-spots or mirrors are obtained in the tube, a number of them may be produced by heating the tube in at least two places, at distances of about three inches, or if an approximately quantitative estimation of the arsenic is desired, all the arsenic may be obtained by the employment of a larger reduction tube and several flames (Fig. 21). The obtained arsenic mirrors may be examined for identification, or quantitatively determined by subsequently removing the tube and determining the increase in weight.

In cases where it is desirable to estimate the entire amount of arsenic, and guard against possible loss, instead of allowing the developed gas to burn, it is preferable to conduct it into a solution of argentic nitrate, in which case any arsenic which may have escaped reduction in the glass tube will be recovered, and contained in the solution as arsenious acid, together with the excess of the undecomposed silver salt.

As is well known, certain compounds of antimony, when brought into Marsh's apparatus, give rise to the formation of hydrogen antimonide (antimoniuretted hydrogen), analogous in composition to hydrogen arsenide, which, when subjected to the same process of reduction as above described, produces black spots of metallic antimony. These spots are so different in their physical appearance and properties as to be readily distinguished by the experienced operator, and, when subjected to chemical tests, display so marked a difference that their discrimination from those of arsenic is readily effected.

To enumerate in detail all the special tests for each of these two metals would lead beyond the scope of this work; the principal distinctive characters, however, will be briefly described.

The mirror of arsenic, as obtained in the reduction-tube, when gently heated during the simultaneous development of a current of hydrogen, can easily be driven from one place to another, and, if the gas be allowed to escape at the exit tube, the development of the arsenical or garlic-like odor can at the same time be observed; whilst antimony, on account of the much higher temperature required for its volatilization, cannot be so readily

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[1] This may be determined by holding an inverted dry test-tube over the point of exit of the gas for a few seconds, and then bringing the mouth of the test-tube in contact with the flame; if the air be entirely expelled from the apparatus, the gas burns quietly, if not, a slight explosion ensues.

removed from the place in which it was deposited, and the escaping gas is quite odorless.

The spots of arsenic, obtained by holding the cold surface of a piece of white porcelain in the flame during the development of the hydrogen arsenide, have a bright metallic lustre, whilst the spots of antimony have a dull velvety black appearance. When touched with a solution of sodium hypochlorite or chlorinated lime, the arsenic spots become immediately dissolved, whereas the spots of antimony remain unaffected; by this means arsenic can be detected, even when accompanied by antimony.

The spots of arsenic, when touched with a drop of a solution of ammonium sulphide, and gently warmed, become completely dissolved, and, on being allowed to dry, display the bright yellow color of arsenious sulphide; antimony under the same circumstances gives an orange-red coloration of antimonious sulphide. The yellow arsenious sulphide remains unaffected upon the addition of a drop of hydrochloric acid, whilst antimonious sulphide is readily dissolved; and inversely a solution of ammonium carbonate dissolves the arsenious sulphide, but does not act upon the antimonious sulphide. These few points of distinction in relation to this important and characteristic test are sufficient in the majority of cases to render possible a prompt determination, as to the presence or absence of one or both of these metals, and to effect their discrimination.

Precautions to be observed in the Application of Marsh's Test for Arsenic.—Although this test is so delicate as to render possible the detection of exceedingly small amounts of arsenic, certain precautions are necessary, which, if not observed, may prove a source of serious error, and lead to incorrect inferences.

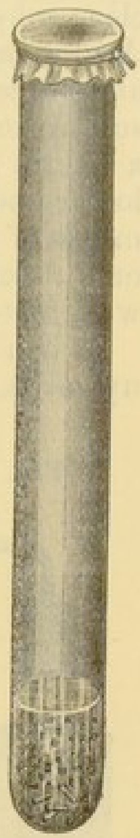
The sulphuric acid employed for generating the hydrogen gas should be free from the lower oxy-acids of sulphur and selenium, of the proper dilution, and cold; for if concentrated and warm, sulphurous-acid gas will be produced, which, combining with the nascent hydrogen, forms hydrogen sulphide, and a precipitation of arsenic as insoluble sulphide would result.

Nitric acid and nitrates, free chlorine and other similar oxidizing agents must be rigidly excluded in the application of the test, as preventing the formation of the gaseous hydrogen arsenide. Hydrochloric acid can also not be substituted to advantage for the sulphuric acid for the generation of the hydrogen, for although it does not interfere with the formation of hydrogen arsenide, yet on account of its greater volatility, and tendency to the production of the so called *zinc spots*, the presence of arsenic might be erroneously inferred.

Another test which may be employed for the detection of small amounts of arsenic, and which commends itself for convenience of application, is that known as:

Fleitmann's Test.—This consists in the generation of hydrogen by the action of a strong solution of potassium or sodium

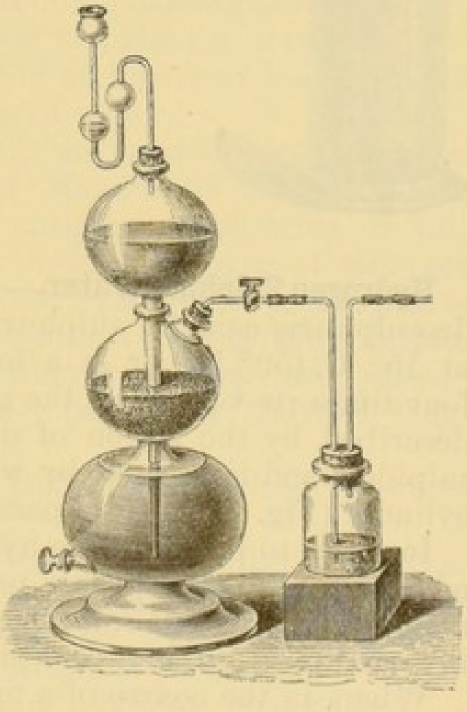
FIG. 22.



hydrate on metallic zinc or aluminium, by the aid of heat. The operation may be performed quickly in a long test-tube, taking care that the tube is only filled to about one-tenth of its capacity. As soon as the gas is generated, the solution to be tested is cautiously added to the alkaline liquid, and a cap of white filtering paper, moistened with a drop of solution of argentic nitrate, placed over the tube (Fig. 22). If arsenic is present, a purplish-black spot, due to the reduction of the argentic nitrate to metallic silver, will be produced upon the moist paper cover. This reaction is of particular importance and value, for while antimony combines with hydrogen evolved from dilute acids and zinc, it does not combine with hydrogen evolved by the action of an alkali on the same metal.

Hydrogen Sulphide (Hydrosulphuric Acid, or Sulphuretted Hydrogen).—Obtained by the action of diluted sulphuric or hydrochloric acids upon ferrous sulphide. Among the several convenient forms of apparatus for the continuous preparation of the gas and to keep it ready for use, the one represented in Fig. 23 is frequently employed. It consists of three glass bulbs, the two lower ones being a single piece, and the upper one, prolonged by a tube reaching to the bottom of the lower, being ground air-tight into the neck of the second. Through the tubulure of the middle bulb the ferrous sulphide is introduced, and the tubulure then closed by a cork containing a wide glass tube provided with a stopcock, or with a rubber tube, closed by a Mohr's wire clamp (see p. 74). The acid is poured in through the safety-tube, runs into the bottom globe, and rises to overflow the ferrous sulphide in the middle one. When the air has been allowed to escape through the delivery-tube, and this is closed, the pressure of the accumulating hydrogen sulphide forces the liquid from the second bulb down into the lower, and thence into the upper bulb, thus stopping the action, and preserving a volume of the gas ready for use.

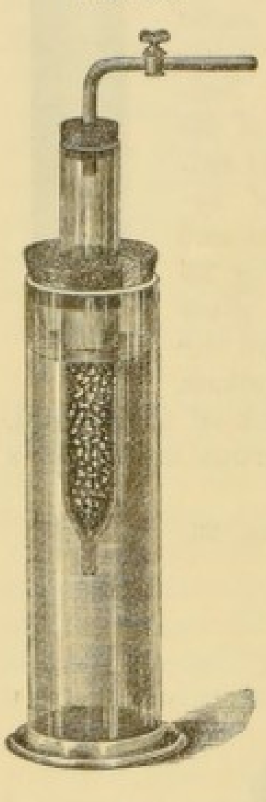
FIG. 23.



Another form of apparatus, which is recommended for simplicity of construction and the facility with which it may be cleansed or supplied with fresh material, is represented in Fig. 24. A glass cylinder, about 40 centimeters (nearly 16 inches) high, and 12 centimeters ($4\frac{3}{4}$ inches) wide, is partially filled with diluted sulphuric acid. It is closed with a cork or rubber stopper having a lateral notch, and carrying a rather long tube, drawn out at its lower end to a small point. This tube is filled with coarse fragments of ferrous sulphide, and is closed with a tightly fitting cork or rubber stopper, through which the delivery-tube (provided with a stop-cock) passes.

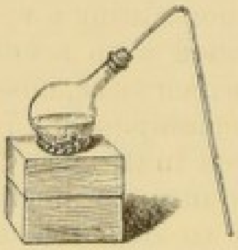
When the apparatus is not in use, the inner cylinder is drawn upwards, until its point merely is immersed in the liquid. When the gas is required, the tube is depressed to the position shown in the figure, and the stop cock opened. The acid then enters from below, and generates a more or less rapid current of the gas, which may be regulated by means of the stop-cock. When the latter is closed, the pressure of gas inside the inner tube forces the liquid back into the glass cylinder.

FIG. 24.



When the above described forms of apparatus are not at hand, hydrogen sulphide may be generated, in small tests, from a little flask or test-tube (Fig. 25), taking care that none of the contents of the flask pass through the delivery-tube into the liquid under examination.

FIG. 25.

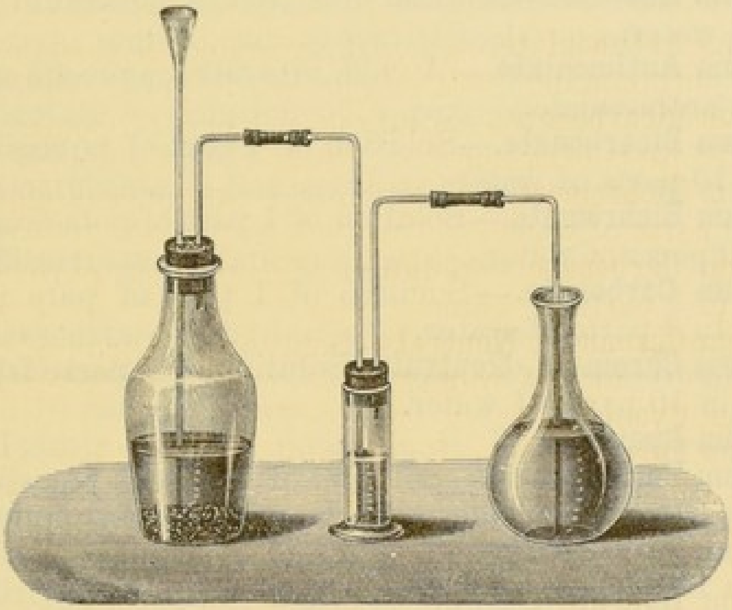


Hydrogen Sulphide Water.—A solution of hydrogen sulphide (hydrosulphuric acid, or sulphuretted hydrogen) in water, saturated at 15° C. (59° F.), or at a lower temperature, containing about four times its volume of the gas. The gas is obtained, as above described, by the action of diluted sulphuric acid upon ferrous sulphide, and is washed by water, contained in a small flask or cylinder (Fig. 26), before passing it into water for absorption.

In order to preserve the hydrogen sulphide in this form, it is advisable to fill the freshly-prepared saturated solution immediately into small vials, and to place them, tightly corked, in an inverted position, in a cool place.

When, in the course of a test, a solution has to be acted upon for some time by hydrogen sulphide, a test-tube or flask may be employed, of such size as nearly to be filled by the liquid. It may then be tightly stoppered, allowing sufficient escape of air before corking, if it has to be warmed.

FIG. 26.



Indigo Solution (Solution of Indigo in Sulphuric Acid).—1 part of finely powdered indigo is gradually added to 6 parts of fuming sulphuric acid; the mixture, after having been well stirred, is then allowed to repose in a covered vessel for about two days, when it is poured into 20 times its volume of water, the solution well mixed, filtered, and preserved for use in a glass-stoppered bottle.

Iodine Water.—A saturated solution of iodine in water.

Iodinized Potassium Iodide.—Solution of 1 part of iodine and 3 parts of potassium iodide in 60 parts of water.

Magnesium.—Metallic magnesium in the form of wire or ribbon.

Magnesium Mixture (Ammoniated Magnesium Sulphate).—A solution of 11 parts of crystallized magnesium chloride or sulphate and 14 parts of ammonium chloride in 70 parts of stronger ammonia water and 130 parts of water. (Magnesium chloride is to be preferred to the sulphate in the preparation of the solution, as having less tendency in its application to produce basic salts.)

Magnesium Sulphate.—Solution of 1 part of crystallized magnesium sulphate in 10 parts of water.

Mercuric Chloride.—Solution of 1 part of crystallized mercuric chloride in 20 parts of water.

Mercuric Oxychloride (*Bohlig's* Reagent).—To a dilute solution of mercuric chloride in water (1 : 30) a dilute solution of potassium carbonate (1 : 50) is added, drop by drop, with constant agitation, until a perfectly neutral solution is obtained.

Phosphorous Salt (Sodium-ammonium-hydrogen Phosphate).

Platinic Chloride.—Solution of 1 part of platinic chloride in 20 parts of water.

Plumbic Acetate.—Solution of 1 part of crystallized plumbic acetate in 10 parts of water.

Plumbic Nitrate.—Solution of 1 part of crystallized plumbic nitrate in 10 parts of water.

Potassium Acetate.—Solution of 1 part of potassium acetate in 5 parts of water.

Potassium Antimoniate.—A cold, saturated, aqueous solution of potassium antimoniate.

Potassium Bicarbonate.—Solution of 1 part of potassium bicarbonate in 10 parts of water.

Potassium Bichromate.—Solution of 1 part of potassium bichromate in 10 parts of water.

Potassium Carbonate.—Solution of 1 part of pure potassium carbonate in 3 parts of water.

Potassium Chromate, Neutral.—Solution of 1 part of potassium chromate in 10 parts of water.

Potassium Cyanide.

Potassium Ferricyanide.—Solution of 1 part of potassium ferricyanide in 10 parts of water. To be prepared as required.

Potassium Ferrocyanide.—Solution of 1 part of potassium ferrocyanide in 10 parts of water.

Potassium Hydrate (Liquor Potassæ, U. S. P.).—Containing 5 per cent. of potassium hydrate.

Potassium Iodide.—Solution of 1 part of potassium iodide in 20 parts of water.

Commercial potassium iodide occasionally contains traces of potassium iodate, and this should be eliminated by dissolving the salt in boiling alcohol, to saturation, filtering the hot solution, and, when cool, collecting and drying the separated salt.

Potassium Mercuric Iodide.—A solution of 1.35 grams of mercuric chloride and 4.98 grams of potassium iodide in 100 cubic centimeters of water.

Potassium Mercuric Iodide with Potassium Hydrate (*Nessler's* Test).—10 grams of potassium iodide are dissolved in 10 grams of hot water, and a hot solution of 5 grams of mercuric chloride added until the precipitate of mercuric iodide ceases to be dissolved. The mixture is then filtered, the filtrate mixed with a concentrated solution of 30 grams of potassium hydrate, and diluted to the measure of 200 cubic centimeters. To this solution 5 cubic centimeters of the above-prepared mercuric chloride solution are subsequently added, and the liquid, after having been allowed to become perfectly clear by standing, preserved in well stoppered bottles.

Potassium Nitrate.

Potassium Nitrite.

Potassium Permanganate.—Solution of 1 part of potassium permanganate in 1000 parts of water.

Potassium Sulphate.—Solution of 1 part of potassium sulphate in 15 parts of water.

Potassium Sulphocyanide.—Solution of 1 part of potassium sulphocyanide in 20 parts of water.

Soda-Lime.—Quicklime is slaked with a solution of sodium hydrate, of such a strength that about 2 parts of quicklime are mixed with 1 of sodium hydrate; the product, after drying, is heated to bright redness, subsequently finely powdered, and preserved in tightly stoppered bottles.

Sodium Acetate.—Solution of 1 part of crystallized sodium acetate in 5 parts of water.

Sodium Bicarbonate.—Saturated aqueous solution of sodium bicarbonate.

Sodium Bitartrate.—Saturated aqueous solution of sodium bitartrate.

Sodium Carbonate.—Dehydrated by exsiccation.

Sodium Carbonate.—Solution of 1 part of crystallized sodium carbonate in 10 parts of water.

Sodium Hydrate (Liquor Sodæ, U. S. P.).—Containing 5 per cent. of sodium hydrate.

Sodium Hyposulphite.—Solution of 1 part of crystallized sodium hyposulphite in 10 parts of water.

Sodium Molybdate.

Sodium Phosphate.—Solution of 1 part of crystallized sodium phosphate in 10 parts of water.

Stannous Chloride.—Saturated solution of real and pure tinfoil in concentrated hydrochloric acid, with subsequent addition of a little concentrated hydrochloric acid.

Starch Mucilage (Gelatinized Starch).—1 part of finely powdered starch is triturated with a little water, the mixture diluted with about 100 parts of water, and subsequently heated to the boiling-point; after cooling, and having been allowed to subside, the clear liquid is decanted. The reagent should be freshly prepared, when required.

Zinc.—Metallic zinc in slender sticks, or small fragments, or in thin disks, prepared by melting and pouring in a thin stream into water.

PREPARATION OF TEST PAPERS, ETC.

Neutral Litmus Solution is prepared by digesting 1 part of commercial litmus with alcohol, with the aid of a gentle heat, for about fifteen minutes; the alcoholic liquid, which contains objectionable coloring matters, is decanted, and the litmus subsequently extracted with about 10 parts of water, by digestion on the water-bath, and filtered.

The filtrate thus obtained is divided into two equal parts; to one of them, by means of a glass rod, very dilute sulphuric acid is added, with constant stirring, until the liquid turns faintly red;

the red liquid is then added to the reserved blue portion, and the whole well mixed.

If it is desirable to preserve the solution for any length of time, about 5 per cent. of alcohol should be added, or it must be kept in bottles provided with a perforated stopper, through which a bent glass tube may be inserted, or loosely stopped with cotton, in order to admit access of air, and exclude dust; if these precautions be neglected, the solution soon becomes mouldy or discolored, and unfit for use.

Blue Litmus-Paper is prepared by drawing unsized white paper (Swedish filtering-paper) through the above neutral liquid.

Red Litmus-Paper is prepared by drawing unsized white paper (Swedish filtering-paper) through the acidulated reddened part of the litmus solution, as obtained and described above, in the preparation of neutral litmus solution.

The paper thus prepared is dried in warm air by suspension over a thread, and for ready use is cut into strips about one-third of an inch wide and four inches long, and preserved inclosed in paraffin-paper, or in tightly corked bottles, protected from the light.

In reactions of neutralization, where carbonic aid gas is evolved, this substance acts on litmus, and may impair the correctness of the test; in such operations it is therefore better, if admissible, to operate on warm solutions, in order quickly to expel the carbonic acid gas; if heat be incompatible, turmeric-paper may be used instead of litmus-paper.

Turmeric Solution.—Obtained by digestion of 1 part of powdered turmeric in a mixture of 4 parts of alcohol and 3 parts of water. After one or two days, the liquid is filtered off and preserved.

Turmeric-Paper is prepared from this tincture by steeping in it white unsized paper (Swedish filtering-paper). The paper need not be preserved from the action of the atmosphere, since it remains unchanged by carbonic acid.

Alkanet-Paper is prepared like litmus-paper, by saturating unsized paper with a solution of the alkanet-red. This is obtained by extracting dry alkanet root with ether; the filtered solution is ready for use.

The blue paper may be obtained from the red one by dipping it into an aqueous solution of sodium carbonate (1:500). A neutral paper, answering for the alkaline as well as the acid test, may be prepared by dividing the ethereal solution of alkanet-red into two equal parts; to one is added, drop by drop, an aqueous solution of sodium carbonate, until the red is just changed to a distinct blue tint; then both liquids are mixed and used for the preparation of the paper.

Plumbic Acetate-Paper serves for the detection of hydrogen sulphide, and is prepared by dipping white unsized paper (Swedish filtering-paper) into a solution of plumbic acetate, and, when dry, cutting into strips of a convenient size, which may be preserved inclosed in paraffin-paper.

A SYSTEMATIC COURSE

OF

QUALITATIVE CHEMICAL ANALYSIS.

CHEMICAL tests and examinations must be founded upon a thorough knowledge of the nature and relations of the reagents, and of their deportment with the common compounds, and also upon a certain fixed order and methodical system in their application. These attainments, and the necessary skill, experience, and judgment, are requisite for every one who enters upon testing and investigation with a chance or claim of accuracy or certainty.

It is advisable in analytical work to enter the result of each test as soon as satisfactorily completed into a note-book, whereby the brief symbolic notation may be used to advantage; the analysis is thus recorded, step by step, as it progresses until completed.

It may also be stated here that a reasonable economy with the substance under examination, especially if only of a small quantity, and with its solutions is necessary, so as to leave enough of the former for unseen contingencies and for confirmatory tests, as well as to repeat or verify any and all results of the examination. All tests and reactions are, therefore, performed on as small a scale as is reasonable and appropriate in the particular case; and all operations should proceed accordingly, and with constant observance of the principles and processes whereon they depend.

The following brief outline of a simple progressive course ot qualitative chemical analysis depends, first, upon the successive elimination of groups of elementary compounds which possess certain common chemical properties, and, finally, upon the recognition of each member of such groups; it may therefore serve as a guide whenever, in the course of investigation, recourse is to be had to such a systematic method of analysis.

When the object of the examination is only to establish the presence or absence of some particular substance, the characteristic reagent may be employed at once, provided there be no other substance present which would interfere with, or exclude, the direct application of the test; but, if a qualitative analysis is required, the substance, if a solid body, may be subjected first to a preliminary examination in the dry way, by which means approximate information as to its composition may be obtained; after this, it is dissolved and examined. The course of qualitative analysis, therefore, consists of three parts:—

I. Preliminary examination in the dry way.
II. Solution, or conversion into the liquid form.
III. Analysis of the solution.

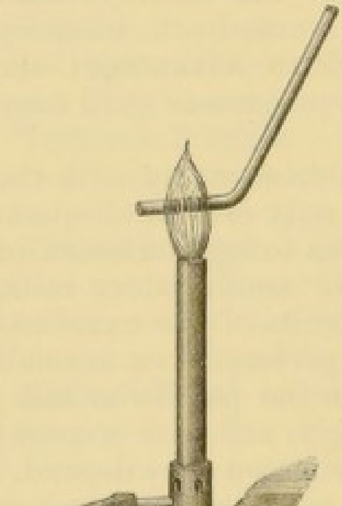
I. PRELIMINARY EXAMINATION.

This consists in an accurate observation, often by the aid of a lens or a microscope, of the physical properties of the substance, its form, color, hardness, gravity, and odor, and of its deportment at a high temperature, either alone, or in contact with some chemical compound which produces decomposition.

1. The substance is heated in a dry narrow tube open at both ends (Fig. 27).

(*a*) The *substance remains unaltered;* indicating absence of organic matter, of salts containing water of crystallization, and of volatile compounds.

Fig. 27.



(*b*) Non-volatile organic substances *carbonize* and *blacken*, evolving empyreumatic, inflammable gases.

(*c*) The *substance fuses, expelling aqueous vapors*, which condense in the cooler parts of the tube; indicating salts with water of crystallization (these will generally resolidify after the expulsion of the water), or decomposable hydrates, which often give off their water without fusing. The acid or alkaline reaction of the condensed vapors should be determined by means of litmus-paper.

(*d*) *A change of color takes place;* zinc oxide assumes a yellow color while hot, which disappears again on cooling; mercuric oxide shows a transitory brown coloration, followed by the sublimation of metallic mercury; mercuric iodide sublimes with a yellow color; chromates, and the oxides of lead and bismuth are colored brown.

(*e*) *Gases or fumes are evolved;* iodine or bromine vapors would indicate their respective compounds, and may be recognized by the violet or brownish-red color and characteristic odor of the vapor; sulphur dioxide is often produced by the decomposition of sulphates; nitric peroxide arises from the decomposition of many nitrates, and is recognized by its brownish color and suffocating odor; cyanogen is recognized by its odor, and would indicate such cyanogen compounds as are decomposable by heat (mercuric cyanide); ammonia vapors may arise either from the decomposition of ammonium salts, cyanogen compounds, or from nitrogenous organic compounds; in the latter case carbonization takes place, and either cyanogen or empyreumatic fumes escape with the ammonia.

(*f*) *Sublimates are formed* by volatile substances, such as sulphur, ammonium salts, compounds of mercury, arsenic, and antimony, and some organic acids (benzoic, succinic, oxalic, salicylic, etc.). Sulphur sublimes in reddish-brown drops, which, upon cooling, assume a yellow or yellowish-brown color; metallic mercury forms globules, which are sometimes only distinguishable by the aid of a lens; mercuric chloride melts before volatilizing, and mercurous chloride sublimes without previously melting; when touched with a solution of potassium hydrate the sublimate assumes a yellow color with mercuric, a black one with mercurous salt; metallic arsenic forms the well-known mirror, arsenious acid small octahedral crystals, and the sulphides of arsenic a reddish-yellow, or, when cold, yellow sublimate; antimonious oxide melts first to a yellow liquid, and then sublimes in bright, shining needles.

2. THE SUBSTANCE IS MIXED WITH SODA-LIME, AND HEATED IN A DRY GLASS TUBE (Fig. 28).

The development of ammonia vapors will indicate ammonium salts, or nitrogenous compounds.

FIG. 28.

3. THE SUBSTANCE IS MIXED WITH DRIED SODIUM CARBONATE, AND HEATED ON CHARCOAL IN THE REDUCING FLAME OF THE BLOWPIPE (Fig. 29).

(*a*) *Fusion and absorption* into the coal indicate alkalies, or their salts.

(*b*) An *infusible white residue*, either at once or after previous fusion in the water of crystallization, indicates compounds of calcium, barium, strontium, magnesium, aluminium, zinc, or tin.

(*c*) A *reduction to the metallic state* takes place, *without* formation of a *peripheric incrustation* upon the charcoal. Compounds of tin, silver, and copper, give malleable shining scales. Compounds of iron, manganese, cobalt, and nickel, are reduced to a gray infusible powder; all visible upon cutting the fuse from the coal, and triturating and levigating it in an agate mortar (Fig. 30).

FIG. 29.

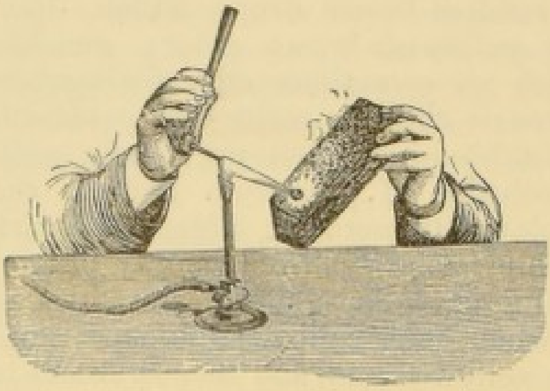
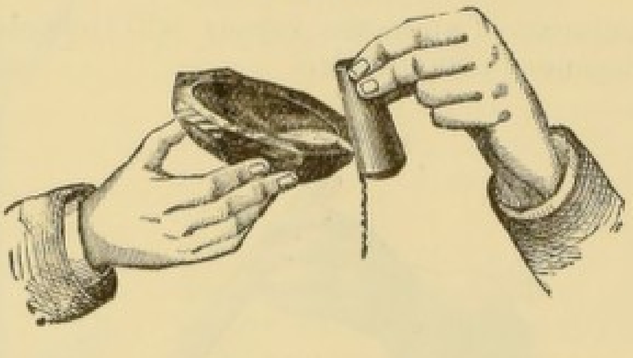


FIG. 30.



(*d*) *Reduction with incrustation:* Antimony compounds give a brittle metallic globule and a white incrustation; bismuth, a brittle globule and a brown-yellow incrustation; lead, a malleable globule and a yellow incrustation; zinc and cadmium are not reduced, but give, the former, a white incrustation, not volatile in the oxidizing flame, the latter, a brown-red incrustation.

(*e*) Arsenic compounds evolve the smell of garlic.

(*f*) Borax and alum intumesce, and lose their water of crystallization.

(*g*) All sulphur compounds give an alkaline sulphide, which, when moistened upon a clean silver plate, produces a black stain, and with acids develops hydrogen sulphide.

(*h*) If deflagration takes place, nitrates, chlorates, iodates, or bromates are indicated.

4. THE SUBSTANCE, CONTAINED ON THE LOOPED END OF A MOUNTED PLATINUM WIRE (Fig. 31), IS HEATED IN THE UPPER REDUCING PORTION OF THE NON-LUMINOUS GAS FLAME.

(*a*) A violet color imparted to the flame indicates potassium salts. As this reaction may be perfectly concealed by the presence of sodium salts, the flame should be observed through blue glass.[1]

FIG. 31.

(*b*) A yellow color imparted to the flame indicates sodium salts.

(*c*) The substance is moistened with hydrochloric acid, and the color of the flame observed; a purplish-red color indicates strontium, a carmine-red, lithium, and a yellowish-red color, calcium salts; a green coloration indicates either copper or barium salts, more evident with the former than with the latter.

(*d*) The substance is first heated to deprive it of moisture, then moistened with a drop of strong sulphuric acid, and the color of the flame observed; a green coloration may indicate phosphoric or boric acid, which, however, particularly when sodium compounds are present, is only of transient duration.

(*e*) A blue coloration imparted to the flame may indicate arsenic, antimony, or lead compounds.

5. A SMALL AMOUNT OF POWDERED BORAX IS MELTED ON THE LOOPED END OF A PLATINUM WIRE, BROUGHT IN CONTACT WITH A TRACE OF THE SUBSTANCE TO BE TESTED, AND HEATED:

(*a*) In the outer blowpipe flame, or in the lower oxidizing portion of the non-luminous gas flame.

A blue glass or bead indicates cobalt.

An amethyst-red colored glass indicates manganese.

A green glass indicates chromium or copper (the copper bead becomes blue on cooling, the chromium bead yellowish-green).

A brown-red glass indicates nickel or iron (the iron bead, when cold, is often of a yellowish color).

A yellow glass indicates uranium or lead.

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[1] The blue glass, which is tinted with cobalt monoxide, possesses the property of absorbing the yellow rays of light, and permits only the blue and violet rays of the spectrum to pass through it.

A colorless glass indicates molybdic acid, tin, antimony, and bismuth, as also the alkaline earths; the latter, however, becoming opaque on cooling.

(*b*) In the inner blowpipe flame, or in the lower reducing portion of the non-luminous gas-flame.

A blue glass indicates cobalt.

A yellow or brownish-red glass indicates copper or molybdenum.

A green glass indicates chromium, iron, or uranium.

A gray glass indicates nickel, bismuth, silver, or antimony.

A colorless glass indicates manganese, as also the alkaline earths; the latter showing the same behavior in both the reducing and the oxidizing flames.

The operation of reduction is usually more easily accomplished by the use of phosphorous salt, instead of borax; the former producing in the oxidizing flame with the oxides of manganese, cobalt, chromium, copper, iron, nickel, antimony, and molybdenum, and in the reducing flame with the oxides of cobalt, iron, uranium, chromium, copper, bismuth, and silver, the same results as with borax; the oxides of bismuth and silver, however, yield a yellow colored glass. With either phosphorous salt or borax, and heated in the oxidizing or reducing portion of the flame, silica and silicates produce a skeleton in the bead.

II. SOLUTION OF SOLID BODIES.

After having ascertained, by the preliminary examination, to what class of bodies the substance under consideration belongs, it has then to be brought into the liquid form—in other words, to be dissolved. The usual solvents which are employed are water, hydrochloric, nitric, and nitro-hydrochloric acids. The finely powdered substance is first boiled with from 12 to 20 times its weight of distilled water, in order to ascertain its complete or partial solubility, or its insolubility therein. If it be not completely dissolved, the portion insoluble in water is collected upon a filter, and is then treated successively with dilute and concentrated hydrochloric acid; by this process carbonates evolve carbonic-acid gas, with effervescence; peroxides, chromates, and chlorates, evolve chlorine; cyanides give hydrocyanic acid; many sulphides, hydrogen sulphide; sulphites and hyposulphites, sulphurous acid.

If hydrochloric acid does not completely dissolve the substance, it generally effects the separation of one or more of its constituents; for this reason the solution should be separated from the residue and examined apart. The residue may consist of compounds undecomposable by hydrochloric acid, which existed in the original substance; or of insoluble compounds formed by the decomposition of the original substance by hydrochloric acid. Thus sulphur is separated from polysulphides, and pulverulent or gelatinous silica from silicates; or, if lead, silver, or mercurous salts be present, insoluble chlorides of these metals will be formed. In this latter case, argentic chloride may be distinguished by its solubility in ammonia water, and mercurous chloride by its conversion by ammonia into the gray colored dimercurous ammonium chloride, or its reduction by potassium or sodium hydrate to black mercurous oxide; while plumbic chloride is characterized by its solubility in hot water, from which it separates in a crystalline form on cooling.

If the substance is not completely soluble in hydrochloric acid, the insoluble residue is treated successively with nitric and nitrohydrochloric acids, which either act as mere solvents or exert an oxidizing action.

When a finely powdered substance is not dissolved by successive treatment with either of these solvents, it must be rendered soluble by other means, in order that its constituents may be determined. This is generally accomplished by fusion with 3 to 4 parts by weight of alkaline carbonates, in the case of the sulphates of barium, strontium, calcium, and lead, and also of silica and silicates, or by fusion with acid potassium sulphate in the case of alumina or aluminates.

In the process of fusion with alkaline carbonates, as above described, in cases where arsenic or an easily reducible metal (antimony, tin, lead, bismuth, etc.) is present, the application of platinum crucibles should be avoided (see note on page 23).

III. QUALITATIVE ANALYSIS OF SOLUTIONS.

I. Examination for Bases.

In the systematic course of examination for metals, now generally employed, use is made of the analogy in physical and chemical properties, and especially in the solubilities of certain classes of compounds; the reagents which give rise to the formation of these compounds are: hydrochloric acid, hydrogen sulphide, ammonium sulphide, ammonium carbonate, and ammonium phosphate. Their application depends upon the different solubility and insolubility of metallic chlorides and sulphides, and of the carbonates or phosphates of the alkaline-earthy and alkali metals. By means of these general reagents, the metallic compounds are divided into several groups, and are successively eliminated from their solutions, whereby the detection of each individual member of such groups is considerably facilitated.

Group I.

Metals whose chlorides are insoluble, or nearly so, in water and dilute acids:

Silver,	white,	completely precipitated.
Mercurous salts,	white,	
Lead,	white,	incompletely precipitated.

Group II.

Metals whose sulphides are insoluble, or nearly so, in water and dilute acids: They are all precipitated from their acid solutions by hydrogen sulphide. They are divided into two subdivisions according to their deportment with ammonium sulphide.

A. Metals whose sulphides are sulpho-acids, forming with sulpho-bases, soluble sulpho-salts:

Antimony,	orange.	Molybdenum,	black-brown.
Arsenic,	yellow.	Gold,	black-brown.
Stannous salts,	brown.	Platinum,	black-brown.
Stannic salts,	yellow.		

B. Metals whose sulphides do not possess acid properties, not combining with, and therefore insoluble in, alkaline sulphides:

Lead,	black.	Copper,	black.
Mercuric salts,[1]	black.	Cadmium,	yellow.
Bismuth,	black-brown.	Palladium,	black,

Group III.

Metals whose sulphides form soluble sulpho-salts, which consequently are not precipitated by hydrogen sulphide from neutral or acid, but partially from alkaline solutions; which, however, are completely precipitated by ammonium sulphide from neutral as well as from alkaline solutions. These are, again, subdivided into two groups:

A. Metals which are precipitated as sulphides:

Zinc,	white.	Nickel,	black.
Iron,	black.	Uranium,	black-brown.
Manganese,	flesh-colored.	Thallium,	black.
Cobalt,	black.	Indium,	yellow.

B. Metals which are precipitated as hydrates:

Aluminium,	colorless and transparent.	Chromium,	grayish-green.
		Cerium,	white.

The oxalates, phosphates, and borates of barium, calcium, strontium, and magnesium, being soluble in dilute acids and insoluble in water, are similarly precipitated by ammonium sulphide.

Group IV.

Metals whose sulphides and hydrates are soluble in water; and which, therefore, are not precipitated by hydrogen sulphide nor by ammonium sulphide. These are subdivided according to their deportment with ammonium carbonate in the presence of ammonium chloride.

A. Metals whose normal carbonates are insoluble in water or in solution of ammonium chloride:

Barium, Calcium, Strontium.

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[1] Mercuric sulphide is slightly soluble in potassium sulphide, and cupric sulphide in ammonium sulphide.

B. Metals whose carbonates are soluble in water or in solution of ammonium chloride:

Magnesium, Potassium, Sodium,
Lithium, Ammonium.

When entering upon the examination of a solution, the results of the preliminary examination should be taken into due consideration, as they often will indicate the number and kind of bases present. If then a precipitate is caused by one of the general reagents, the solution should be examined for every member of that particular group. It is also evident that when the presence of one or several bases has been ascertained, the systematic and successive course of examination, as described hereafter, should be pursued, so as to exclude beyond doubt the presence of any not-detected metal.

The precipitation by each general reagent must be complete. To insure this, they must be employed in the order above stated, and must be added gradually, allowing the precipitate to subside between each addition, until no further precipitate is produced. In the case of hydrogen sulphide, the precipitation is complete when the solution, after agitation, still smells strongly of the gas. Gentle heat generally facilitates the separation of precipitates. Each group, when precipitated, must be thoroughly freed, by washing with water, from all members of the subsequent groups, which may be contained in the solution. After the precipitation of each group, it is advisable to ascertain the presence or absence of any members of the succeeding groups, by evaporating on platinum-foil a few drops of the filtrate; if, after ignition, there is no distinctly visible residue, non-volatile substances need not be looked for further. It is obvious that, if complete precipitation and thorough washing be neglected, metals belonging to one group are liable to be found among those of another group; and, consequently, as the analysis proceeds, reactions will be obtained which will be a source of perplexity and errors.

Hereupon the following course of analysis may be pursued, involving the systematic investigation of the several groups:

Group I.

A portion of the solution is acidulated with hydrochloric acid. An ensuing **precipitate,** which may be marked **No. 1,** would indicate lead, silver, or mercurous chlorides. In this case the precipitate is collected on a filter, washed and subsequently boiled with water, and the solution filtered while hot.

Lead chloride is soluble in hot water, and can be precipitated from its solution as yellow lead chromate on the addition of potassium chromate. **Silver** and **mercurous chlorides** are insoluble in water; the former, however, is readily soluble in ammonia water, from which solution it is again precipitated on the addition of an excess of nitric acid, whilst mercurous chloride in contact with ammonia is colored black.

Group II.

The liquid, acidulated with hydrochloric acid, or, if a precipitate was produced by the latter, the filtrate therefrom, is saturated with hydrogen sulphide. If no precipitate ensues, the reagents indicated in the next following group may at once be employed; if, however, a precipitate has been formed, indicating bases of group II, this is collected on a filter, well washed with water, and the filtrate and washings, which may be marked **Filtrate No. 2**, reserved for further examination. The **precipitate**, which may be marked **No. 2**, is then examined as follows: If it is of a light yellowish-white color, it may consist simply of sulphur, which may be recognized by its volatility when heated in a small glass tube, or by the formation of an alkaline sulphide when heated with a little exsiccated sodium carbonate on charcoal, before the blow-pipe. The precipitation of sulphur results from the presence of ferric salts, chromic acid, or chromates; in the first case, the ferric is reduced to ferrous salt, and in the latter, the chromic acid to chromic oxide, which imparts a green color to the solution. When considerable free nitric acid is present in a solution, sulphur may also be precipitated by the decomposition of hydrogen sulphide.

A *yellow* precipitate is produced when arsenious or arsenic acid, stannic acid, or cadmium salts are present in the solution. If arsenic is present in the form of arsenic acid, the solution must be heated before or during the time of saturation with the gas, and subsequently allowed to stand for a few hours in a closed flask or test-tube, in order to insure its complete precipitation.

An *orange*-colored precipitate is produced when antimony is present.

A *brown* precipitate is produced by stannous salts, and the salts of bismuth and molybdenum.

A *black* or blackish-brown precipitate is produced by mercuric salts, lead, copper, gold, platinum, and palladium, as also by silver and mercurous salts, in case the two latter were previously not completely precipitated by hydrochloric acid.

It is evident that when several metals precipitable by hydrogen sulphide are present, the color of the precipitate will be unavailable as a criterion for the recognition of any one substance.

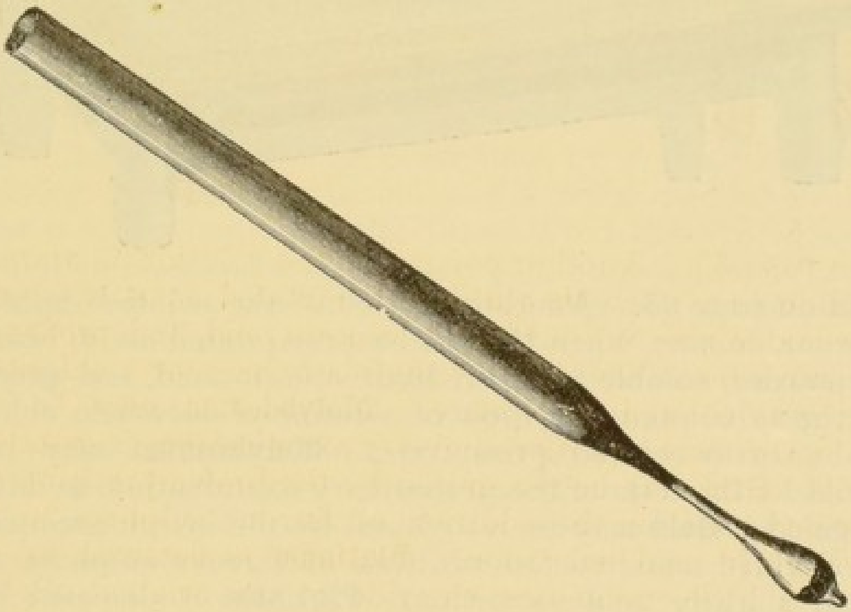
The metallic sulphides precipitated by hydrogen sulphide are distinguished by their deportment with ammonium sulphide, being soluble or insoluble therein, and may thus be resolved into two classes.

The precipitate No. 2, collected upon a filter and well washed with water, is digested with ammonium sulphide, by the aid of a gentle heat, and filtered. The solution may be marked **A**, and any insoluble residue upon the filter, **B.**

The obtained solution **A** contains those metals whose sulphides are sulpho-acids, combining with alkaline sulphides or sulphydrates to form soluble sulpho-salts. These are: arsenic, antimony, tin, molybdenum, gold, and platinum. In order to effect their separation, several methods may be employed, only one of which, however, need be here described.

The solution A is acidulated with dilute sulphuric acid, and the resulting precipitate (if not consisting only of sulphur) very slightly warmed with a concentrated solution of ammonium carbonate. **Arsenic** is thereby dissolved, and, upon supersaturating the solution with hydrochloric acid, and warming, is reprecipitated as arsenious sulphide, and may then be reduced to the metallic state by heating in a small glass tube with a mixture of potassium cyanide and exsiccated sodium carbonate (Fig. 32), or

FIG. 32.

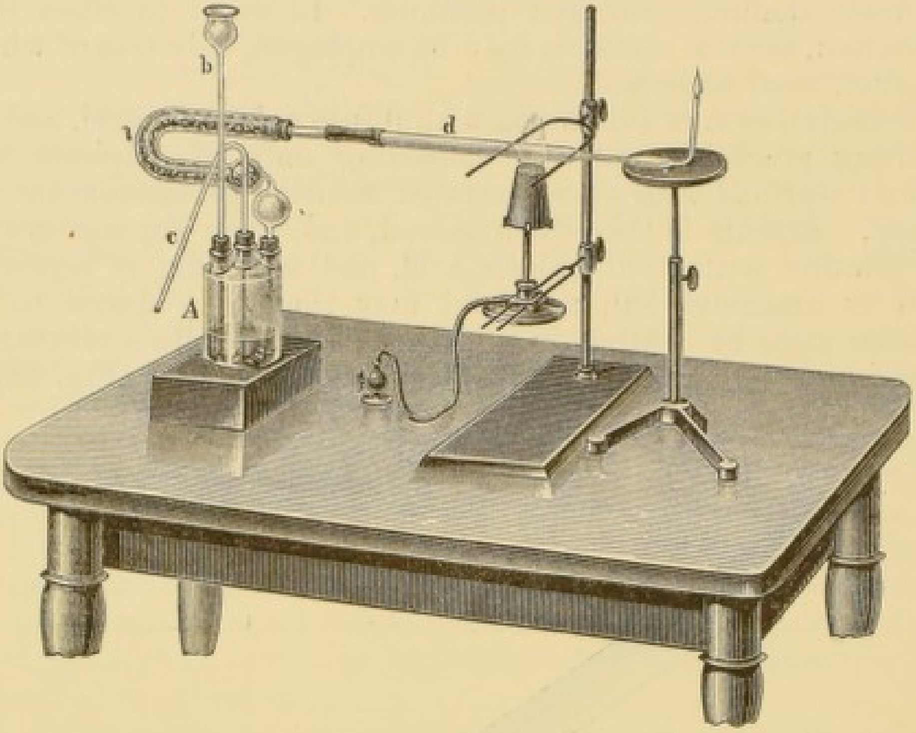


it may be dissolved by gently heating with hydrochloric acid and a little potassium chlorate, when upon the subsequent addition of test magnesium mixture, a white crystalline precipitate of ammonio-magnesium arseniate will be obtained.

Traces of arsenic may be more readily detected, after the above treatment, by examining the solution in Marsh's apparatus (Fig. 33), as described on pages 33 to 36.

The portion undissolved by ammonium carbonate is dissolved in hydrochloric acid, with the addition of a small amount of potassium chlorate, and gently heating, and the solution thus obtained tested as follows: A few drops are brought upon platinum-foil, together with a fragment of metallic zinc, when, if **antimony** is present, a deep black spot will be produced upon the foil, or the solution when brought into Marsh's apparatus, will develop hydrogen antimonide, which may be recognized by the method described on page 35. Another portion of the solution is warmed with metallic zinc, when **tin** will be precipitated as a black metallic powder, soluble in warm hydrochloric acid, and producing upon the subsequent addition of solution of mercuric chloride a white or gray-colored precipitate. **Molybdenum** may be best detected by the tests of the preliminary examination, as described on page 48. **Gold** may be recognized by the brown precipitate of finely divided metal on the addition of ferrous sulphate to the original slightly acid solutition. **Platinum** is detected by the addition of a little ammonium chloride to the original, slightly acid solution, evaporating nearly to dryness, and treating with strong alcohol; a yellow, crystalline precipitate, consisting of the double chloride of platinum and ammonium, and reducible by heating to black metallic platinum, will thus be formed.

FIG. 33.



The portion of the hydrogen sulphide precipitate **B,** insoluble in ammonium sulphide, contains those metals whose sulphides do not possess acid properties, not combining with, and therefore insoluble in, alkaline sulphides or sulphydrates. These are: lead, bismuth, copper, cadmium, and mercuric salts, also mercurous salts and silver, in case nitric instead of hydrochloric acid was employed for acidulating the original solution, before precipitating with hydrogen sulphide. The precipitate B is washed, subsequently treated upon the filter with concentrated nitric acid, and the filtrate examined as follows:

(1) *Portion soluble in nitric acid.*

Lead, which can be present in but small amount if the original solution was acidulated with hydrochloric acid, as described under group I. page 51, may be detected by neutralizing the solution with ammonia water, evaporating to a small volume, and acidulating with sulphuric acid; a white precipitate will thus be produced, which is soluble in basic ammonium tartrate, and may be again precipitated from this solution on the addition of potassium chromate. The latter precipitate, when mixed with exsiccated sodium carbonate, and heated upon charcoal, yields a soft metallic bead.

Silver can only be present when hydrochloric acid was not employed for acidulating the original solution, as directed under group I. page 51. It may be detected in the filtrate from the just-mentioned lead sulphate precipitate by the addition of hydrochloric acid, when a white curdy precipitate, soluble in ammonia water, will be produced.

Bismuth may be detected in the filtrate from the preceding silver precipitate by the addition of ammonia water, when a white precipitate, insoluble in an excess of the reagent, will be formed. The solution of the precipitate in a small amount of hydrochloric acid, becomes turbid on the addition of much water.

Copper is recognized when the filtrate from the preceding bismuth solution possesses a blue color, and, after acidulating with hydrochloric acid, by a reddish-brown precipitate on the addition of solution of potassium ferrocyanide.

Cadmium may be recognized, when the solution of the preceding test remains colorless upon the addition of ammonia water, by a yellow precipitate upon saturation with hydrogen sulphide. If, however, both copper and cadmium are present in the solution, then the ammoniacal liquid from the above-mentioned bismuth precipitate is supersaturated with hydrochloric acid, the solution concentrated by evaporation, and ammonium carbonate in excess added, when cadmium will be separated as a white precipitate, whilst copper, remaining dissolved, imparts a blue color to the liquid. The separation may also be effected by adding potassium cyanide to the ammoniacal liquid from the bismuth precipitate until the solution appears colorless; upon subsequent saturation with hydrogen sulphide cadmium will be precipitated as yellow cadmium sulphide, while copper remains in solution.

Palladium may be detected in the original solution of the substance under examination by the formation of a black precipitate on the addition of solution of potassium iodide.

(2) *The portion of precipitate B insoluble in nitric acid* may consist *of sulphur*, which is recognized by its yellowish or gray-

ish-yellow color,[1] as also by its complete volatilization when heated in a small glass tube, or the formation of an alkaline sulphide, when heated with exsiccated sodium carbonate on charcoal, before the blow-pipe. *Lead sulphate* forms a heavy, white precipitate, and results from the action of the nitric acid on the lead sulphide. In this case lead will usually be found and recognized also in that portion of the precipitate B which is soluble in nitric acid, page 55.

Mercury, in the form of mercuric salt, is recognized as a black, flocculent precipitate, which, when mixed with sodium carbonate, and heated in a glass tube, yields a sublimate of metallic mercury. Lead sulphate may be separated from mercuric sulphide by digesting with a solution of basic ammonium tartrate, in which lead sulphate is soluble, and may be subsequently recognized by a black precipitate with hydrogen sulphide, or a yellow one with potassium chromate. The washed mercuric sulphide may be dissolved in nitro-hydrochloric acid, the excess of acid removed by evaporation, and the solution tested, either with stannous chloride, which will produce a white precipitate, or by immersing a piece of bright copper foil in the liquid, when a coating of metallic mercury will be deposited.

Group III.

Filtrate No. 2, page 52, is supersaturated with ammonia water, and ammonium sulphide added, in an amount sufficient to effect complete precipitation, if any reaction is produced. If no precipitate is formed by the addition of these reagents, the solution may be further examined as directed under group IV., page 59. If, however, a precipitate is produced, it is collected on a filter, well washed with water, and the **filtrate,** which may be marked **No. 3,** reserved for the examination of the bases of group IV. This **precipitate,** marked **No. 3,** may contain iron, nickel, cobalt, manganese, zinc, uranium, chromium, and aluminium, as also calcium, barium, and strontium oxalates and phosphates and magnesium phosphate. A brown color of the filtrate from precipitate No. 3 would indicate the presence of nickel.

A *black* precipitate will indicate iron, cobalt, nickel, uranium, or one or all of these combined with other members of the group.

A *greenish* precipitate will indicate chromium.

A *flesh-colored* precipitate will indicate manganese.

A *white* precipitate is dependent in its character as to whether the original substance was soluble in water, or whether in order to effect its solution the aid of an acid was required. In the former case, it may consist of zinc or aluminium, either alone, or combined with manganese and chromium; in the latter case it

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[1] The sulphur frequently incloses particles of mercuric sulphide, which imparts to it a brown color.

may also contain magnesium, barium, calcium, or strontium, in combination with phosphoric or oxalic acids.

Precipitate No. 3 (page 56) is examined as follows:

(**a**) It is first digested with cold, dilute hydrochloric acid. This dissolves all the oxides and sulphides of the group, with the exception of the sulphides of cobalt and nickel, which, if present, are separately examined as directed under (**c**). The acid solution or filtrate thus obtained is first heated, in order to remove the hydrogen sulphide, filtered, and solution of sodium hydrate, in considerable excess, added. If a precipitate is formed, it is examined as directed under (**b**), whilst the alkaline solution or filtrate is examined as follows: It is first boiled for some time, when **chromium** will be precipitated; its identity may be confirmed by fusing it, on platinum-foil, with an equal weight of exsiccated sodium carbonate and potassium nitrate, dissolving the fused mass in water, and, after acidulating with acetic acid, testing with plumbic acetate, when a yellow precipitate will be produced. A portion of the filtrate from the first chromium precipitate is then saturated with hydrogen sulphide, when an ensuing white precipitate will indicate **zinc**; this may be confirmed by moistening part of the precipitate, on the looped end of a platinum-wire, with a drop of solution of cobaltous nitrate, and heating in the non-luminous flame, when a green color will be imparted to the bead. If the hydrogen sulphide has produced no precipitate in the alkaline solution, then another portion of the latter is supersaturated with hydrochloric acid, and subsequently made slightly alkaline with ammonia water, when an ensuing transparent, flocculent precipitate will indicate **aluminium**; this may be confirmed by moistening the precipitate, on the looped end of a platinum-wire, with a drop of solution of cobaltous nitrate, and heating in the non-luminous flame, when a blue color will be imparted to the bead.

(**b**) The precipitate, undissolved by solution of sodium hydrate, as directed under (**a**), may contain the oxides or hydrates of iron, manganese, and uranium, the phosphates and oxalates of the alkaline earths, calcium fluoride, and possibly traces of zinc. It is redissolved in dilute hydrochloric acid, ammonium chloride added, and subsequently ammonia water in slight excess. By this means the above-mentioned metals are again precipitated, with the exception of manganese and zinc, which remain dissolved, and are separated as follows: From the ammoniacal solution the manganese and zinc are again precipitated by ammonium sulphide; a portion of this precipitate is heated, on platinum-foil, with a mixture of potassium nitrate and exsiccated sodium carbonate, when a green color of the fused mass will indicate **manganese**; the remaining portion of the precipitate is dissolved in hydrochloric acid, sodium acetate in excess added, and the solution subsequently saturated with hydrogen sulphide, when an ensuing white precipitate will indicate **zinc.**

The precipitate, as above obtained by the addition of ammonium chloride and ammonia water, is digested with a concentrated solution of ammonium carbonate, when uranium and cerium will be dissolved.

Uranium is recognized by a brown precipitate on supersaturating the solution with hydrochloric acid, and the subsequent addition of potassium ferrocyanide.

Cerium is recognized by the formation of a difficultly soluble double salt with potassium sulphate. The precipitate which remains undissolved by the above treatment with concentrated solution of ammonium carbonate, is dissolved in dilute hydrochloric acid, and the solution tested, in separate portions, as follows:

Iron is recognized by a blue precipitate on the addition of solution of potassium ferrocyanide.

Barium or **strontium** by a white precipitate on the addition of solution of calcium sulphate.

Calcium by a white precipitate on the addition of sodium acetate, in slight excess, and solution of ammonium oxalate.

Magnesium.—Sodium acetate, in slight excess, is added to the solution, and subsequently ferric chloride until a red coloration is produced. The liquid is then heated to boiling, filtered, and the filtrate completely precipitated by ammonium carbonate. The filtrate from the latter precipitate is finally tested with ammonium phosphate, when an ensuing white, crystalline precipitate will indicate magnesium.

Phosphoric Acid is recognized by an ensuing white precipitate of ferric phosphate, when to the cold solution sodium acetate, in slight excess, and subsequently a few drops of solution of ferric chloride are added; or, if on the addition of solution of ammonium molybdate in nitric acid, and gently heating, a yellow, crystalline precipitate is produced.

Oxalic Acid, as calcium oxalate, is recognized, when on the addition of sodium acetate, in slight excess, a white precipitate is formed, which is insoluble in acetic acid, and by ignition is converted into calcium carbonate.

Fluorine, which may be present as calcium fluoride, must be tested for with the original substance, and may be recognized by the etching produced upon a glass plate, which is partially covered with wax, and placed over a lead or platinum capsule in which a little of the substance is heated with concentrated sulphuric acid.

(**c**) The portion of the ammonium sulphide precipitate, insoluble in cold dilute hydrochloric acid, may consist, as stated under (**a**), of the sulphides of cobalt and nickel, or simply of sulphur. If the latter alone is present, it may be recognized by its color, as also by its complete volatilization when heated on platinum-foil. The sulphides of cobalt and nickel are black, and may be separated by the following method: The precipitate is dissolved in nitro-hydrochloric acid, the solution evaporated, and the residue taken up with water containing a little acetic acid. To this solution potassium nitrite in considerable quantity is added, and allowed to stand for several hours, when **cobalt** will be completely separated as a yellow, pulverulent double salt, whilst **nickel** remains in solution, and may be precipitated therefrom on the addition of sodium hydrate, as light green colored nickel hydrate.

The metals **thallium** and **indium,** which also belong to this group, are of such rare occurrence that when their presence may be reasonably suspected they must be tested for by means of the spectroscope.

Group IV.

Filtrate No. 3, page 56, is supersaturated with hydrochloric acid, and heated until the odor of hydrogen sulphide has entirely disappeared; when cold, it is filtered, slightly supersaturated with ammonia water, and ammonium carbonate in slight excess added. If no precipitate is formed on the addition of these reagents, the solution may be further examined as directed under group V. If, however, a precipitate is obtained, it is collected and washed on a filter, and the **filtrate** therefrom, which may be marked **No. 4,** reserved for the examination of bases of group V. The **precipitate,** marked **No. 4,** which may contain barium, calcium, or strontium, is examined as follows: It is dissolved in dilute hydrochloric acid, and to a portion of the solution a saturated solution of calcium sulphate is added. If a precipitate is formed at once, it will indicate the presence of barium; but if the precipitate is only formed after standing for some time, strontium is indicated, whilst if no turbidity is produced, only calcium can be present. In the latter case ammonia water, in slight excess, and ammonium oxalate are added to another portion of the dilute hydrochloric acid solution, when, if calcium is present, a white precipitate of calcium oxalate will be produced. If calcium has thus been found to be present, the dilute hydrochloric acid solution first obtained is exactly neutralized with ammonia water, and solution of neutral potassium chromate added, when barium will be precipitated as yellow **barium** chromate. To the filtrate from the last-named precipitate dilute sulphuric acid is added, and allowed to stand for some time, when strontium will be precipitated as white **strontium** sulphate. The filtrate from the latter, on the addition of ammonia water, in slight excess, and afterward of ammonium oxalate, will yield a white precipitate of **calcium** oxalate.

Group V.

Filtrate No. 4, page 59, may still contain magnesium, sodium, potassium, lithium, and ammonium.

Magnesium is recognized by an ensuing white crystalline precipitate of ammonio-magnesium phosphate on the addition of solution of ammonium phosphate.

The methods employed for testing the filtrate for potassium, sodium, and lithium are subject to some variation in their application, and depend upon the previously determined presence or absence of magnesium. If the solution contains no magnesium, it may be evaporated to dryness, the residue ignited to expel ammonium salts, and the final residue dissolved in a small amount of water. It is then examined on platinum-wire in the non-luminous flame, to which **sodium** imparts a yellow, **potassium** a violet, and **lithium** a carmine-red color; the detection of potassium in the presence of sodium being effected by observing the flame, through blue cobalt glass. For the verification of potassium the remainder of the solution may be tested with a few drops of platinic chloride; a yellow crystalline precipitate of potassio-platinic chloride will be formed, if potassium be present.

For the special detection of lithium, the dry mixture of the chlorides is digested with a mixture of about equal parts of alcohol and ether, filtered, and the filtrate allowed to evaporate spontaneously; the residue from the alcohol-ether solution will contain all the lithium, which may be recognized when examined on platinum-wire in the non-luminous flame.

If, however, magnesium has been found to be present, it has to be first removed before potassium, sodium, and lithium can be tested for. The solution is accordingly evaporated to dryness, ignited to expel ammonium salts, and the residue taken up with water. To the filtered liquid, solution of barium hydrate is added until alkaline to test-paper, again filtered, and the excess of barium in the filtrate removed by solution of ammonium carbonate to which a little ammonia water has been added. The filtrate from the latter precipitate is evaporated to dryness, gently ignited, and the residue tested for potassium, sodium, and lithium as above described. In case lithium is absent, the filtrate from the above-mentioned ammonio-magnesium phosphate precipitate may be directly employed for the ordinary flame tests for potassium and sodium.

Ammonium is always sought for in a separate portion of the original substance or solution, by heating with a concentrated solution of potassium or sodium hydrate; any ammonium compound evolves the characteristic odor of ammonia gas, which changes moistened red litmus-paper to blue, and produces white fumes when a glass rod, moistened with acetic acid, is held over the orifice of the test-tube.

Minute traces of ammonia may be detected by conducting the vapors into a test-tube containing a small quantity of distilled water; if ammonia be present a brown precipitate will then be produced on the addition of a few drops of solution of potassio-mercuric iodide with potassium hydrate (Nessler's reagent).

II. Examination for Acids.

The examination for the bases is followed by that for the acids and for chlorine, iodine, and bromine. The preliminary examination, as well as the nature of the substance and the bases found therein, will give information, in most cases, as to what acids cannot be contained in the substance, and what acids may be present therein, or should especially be looked for. Thus the acids of arsenic, chromic and carbonic acids, and hydrogen sulphide, have already been indicated. With soluble substances containing earthy and metallic bases, the presence of carbonic, phosphoric, boric, and oxalic acids, is excluded; soluble substances, containing silver, lead, and mercurous compounds, exclude chlorine; soluble substances, containing lead, barium, strontium, and mercurous salts, exclude sulphuric acid.

In the examination for acids, a neutral solution is frequently required, and generally ammonia water is used for neutralization; but, as most of the heavy metals, as well as some alkaline earthy salts, are precipitated when their solutions are neutralized by ammonia water, it is often necessary to remove from the solution all metals, except those of the alkalies, before proceeding to search for acids. When this is not necessary, it is frequently requisite, according to the nature of the substance and its chemical relations, to substitute, instead of hydrochloric acid and its salts, nitric acid and the corresponding nitrates.

The general reagents employed in the examination for acids are barium chloride or nitrate, calcium chloride, magnesium sulphate or chloride, ferric chloride, argentic nitrate, and indigo solution. By these reagents the more commonly occurring acids may be divided, analogously to the bases, into certain groups, but, unlike the latter, the perfect separation of the individual acids embraced in the different groups cannot thus be effected.

I. *Acids which are precipitated by barium chloride or nitrate.*

(*a*) *From acidulated solutions: sulphuric* acid as a white precipitate, insoluble in nitric or hydrochloric acids.

(*b*) *From neutral solutions* (the precipitate being soluble in acids): *sulphurous*, *phosphorous*, *phosphoric*, *carbonic*, *silicic*, *boric*, *arsenious*, and *arsenic acids*, as white precipitates, and *chromic* acid as a yellow one, all soluble in hydrochloric acid. Of the organic acids, *oxalic* and *tartaric* also produce white precipitates, but only from more concentrated solutions, and likewise soluble in hydrochloric acid.

II. *Acids which are precipitated by calcium chloride.*

(*a*) *From neutral solutions only: phosphoric*, *arsenic*, and *boric* acids as white precipitates, which are readily soluble in ammonium chloride; *carbonic* and *sulphurous* acids, as white precipitates, but the latter one only in concentrated solutions; *tartaric* acid, as a white precipitate, soluble in ammonium chloride or potassium hydrate, which alkaline solution becomes turbid on heating; *citric* acid gives a white precipitate, upon the subsequent addition of lime water or ammonia water in excess, and heating; *ferrocyanides* produce gradually a yellowish precipitate. All of the above precipitates are readily soluble in acetic acid, with the exception of that of ferrocyanides, which is difficultly soluble.

(*b*) *From neutral or acetic acid solutions: oxalic* acid, as a white precipitate, insoluble in ammonium chloride; this precipitate is also formed with a saturated solution of calcium sulphate; *sulphuric* acid gives a white precipitate, except in very dilute solutions, when it is only produced on the subsequent addition of alcohol; *hydrofluoric acid* produces a white gelatinous precipitate, which has the property of etching a glass plate, placed over a lead or platinum capsule, in which the precipitate is gently heated with concentrated sulphuric acid.

III. *Acids which are precipitated by magnesium sulphate or chloride in the presence of ammonium chloride and ammonia water.*

Phosphoric acid, as a white crystalline precipitate, which is slowly formed in very dilute solutions, and soluble in all acids; *arsenic* acid yields a precipitate which is precisely analogous in its character to that of phosphoric acid, but from its acid solution, on warming, hydrogen sulphide precipitates yellow arsenic sulphide; *tartaric* acid gradually yields a white precipitate in concentrated solutions, which becomes black on drying, and subsequent incineration upon platinum-foil.

IV. *Acids which are detected by ferric chloride.*

(*a*) *Those which are precipitated.*

(From neutral or acetic-acid solutions.)

Ferrocyanides yield a blue precipitate, which is also produced in the presence of free hydrochloric acid; *phosphoric* acid, a yellowish-white one, insoluble in acetic, but soluble in hydrochloric acid; *arsenic* acid gives a precipitate which is analogous in its properties to phosphoric acid, but is also precipitated from its warm acidulated solution by hydrogen sulphide; *tannic* acid, a bluish-black precipitate, and the original solution is precipitated by gelatin.

(From neutral solutions only.)

Boric acid yields a yellowish precipitate; *benzoic* and *succinic* acids, light brown ones; the latter is also precipitated by a mixture of ammonia water, barium chloride, and alcohol.

(*b*) *Those which produce a coloration, but no precipitate.*

(In the presence of free hydrochloric acid.)

Ferricyanides produce a brownish coloration, and with *ferrous salts* a blue precipitate; *sulphocyanides*, an intense blood-red coloration, which disappears on the addition of mercuric chloride.

(In neutral solutions only.)

Acetic acid, a reddish-brown coloration, and, on boiling, a reddish-brown precipitate, whilst the solution becomes decolorized; *formic* acid gives also a reddish-brown coloration, but the original solution reduces silver and mercury from a solution of their salts; *sulphurous* acid, a reddish-brown coloration, which disappears on boiling the solution, without a precipitate being produced; *meconic* acid, a blood-red coloration, remaining unchanged on the addition of solution of auric chloride; *gallic* acid, a black coloration, but the original solution is not precipitated by gelatin; *salicylic* acid produces a deep violet coloration.

V. *Acids which are precipitated by argentic nitrate.*

(*a*) *Only from neutral solutions* (the precipitate being soluble in dilute nitric acid): *phosphoric* acid (ortho) produces a yellow precipitate, and is also precipitable by magnesium mixture; *pyrophosphoric* acid, a white precipitate; *metaphosphoric* acid, likewise a white one, but the free acid also coagulates albumen, which distinguishes it from the preceding; *phosphorus* and *hypophosphorus* acids give white precipitates, which soon change to black; *carbonic* acid, a white precipitate; *arsenic* acid, a reddish-brown one, and is also precipitable by magnesium mixture, and from a warm acidulated solution by hydrogen sulphide; *arsenious* acid, a yellow precipitate, and is also precipitable from an acid solution by hydrogen sulphide; *chromic* acid, a brownish-red one, and the original yellow or red compound is changed by sulphurous acid to green; *boric* acid gives a white precipitate, and, after the addition of sulphuric acid to the compound, the alcohol flame is colored green; *sulphurous* acid, a white precipitate, becoming blackened on heating; *hyposulphurous* acid, a white precipitate, soon changing to black, and soluble in an excess of a solution of the ensuing hyposulphite; *oxalic* acid, a white precipitate, insoluble in acetic acid; *tartaric* acid, a white precipitate, becoming black on heating; *citric* acid, a white precipitate, changing to black by the action of light; *formic* acid, a white precipitate, becoming black on heating; *salicylic* acid, a white precipitate; *gallic* and *pyrogallic* acids produce a separation of metallic silver; *acetates* and *benzoates*, in concentrated solutions, produce white crystalline precipitates, soluble in hot water.

(*b*) *Also from acid solutions* (the precipitate being insoluble in dilute nitric acid): *hydrochloric* acid produces a white curdy precipitate, soluble in ammonia water and sodium hyposulphite; *hydrobromic* acid, a white precipitate, and the original solution imparts a reddish-yellow color to carbon bisulphide, when agitated therewith after the addition of a little chlorine water; *hydriodic* acid, a yellowish precipitate, insoluble in ammonia water, and the original compound imparts a violet color to carbon bisulphide, or a blue color to mucilage of starch, when agitated therewith after the addition of a little chlorine water; *hydrocyanic* acid, a white precipitate, soluble in ammonia water and sodium hyposulphite, and the original compound, on the addition of a solution of potassium hydrate, a ferrous and ferric salt, and of hydrochloric acid in slight excess, produces a precipitate of Prussian blue; *sulphocyanides*, a white precipitate, difficultly soluble in ammonia water, and the original solution produces with ferric chloride a blood-red coloration; *sulphides*, a black precipitate, insoluble in ammonia water, which is also produced in solutions of lead and copper salts; *iodic* acid, a white precipitate, soluble in ammonia water, from which solution sulphurous acid precipitates argentic iodide; *ferrocyanides*, a white precipitate, insoluble in ammonia water, and the original compound gives with ferric salts a precipitate of Prussian blue; *ferricyanides*, a reddish-brown precipitate, and the original solution gives with ferrous salts a deep blue precipitate.

VI. *Acids which decolorize indigo solution.*

Free chlorine and bromine, and their oxygen acids, when free; free nitric acid, if not too dilute, and alkaline sulphides. On the addition of sulphuric or hydrochloric acids, and heating, indigo solution is also decolorized by all chlorates, bromates, iodates, and nitrates, and, on the addition of hydrochloric acid and heating, besides all the foregoing acids, also by chromates, permanganates, and all peroxides.

By the application of these group reagents the identity of many acids can often be determined; but, should this not be the case, the investigation may be further continued according to the following method: The preliminary examination of the substance will have shown whether it be soluble in water, either alone or by the aid of an acid, or whether, in order to effect its solution, the process of fusion with an alkaline carbonate must be resorted to. According to this deportment of the substance towards solvents, the three following divisions may be made, which are also of service in defining the nature of the acid, and render its identification possible. Many of the known acids, and particularly of the organic acids, being of rare occurrence, only those will be taken into consideration which are more commonly met with in analysis, or which are of practical importance.

A. *The substance is wholly or partially soluble in water.*

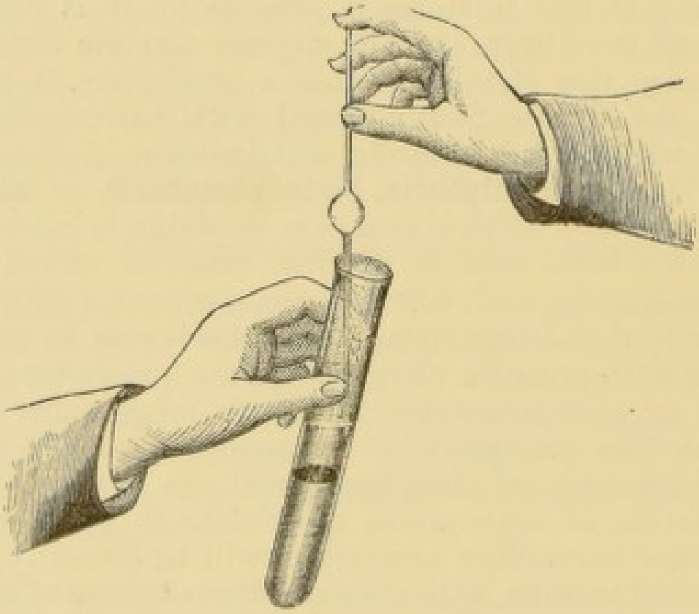
If a portion of the substance, when heated on platinum-foil, becomes blackened, or emits combustible vapors, *organic acids* should be sought for. **Chromic, arsenic,** and **arsenious** acids will already have been found in the examination for bases, groups II. and III. **Carbonates** and **sulphides** will be recognized by the development of gas bubbles when dilute hydrochloric acid is added to a portion of the liquid; the former produces a white precipitate when the gas is led into lime-water, and the latter may be recognized by the odor, as also by the blackening of a strip of paper, previously moistened with a solution of lead acetate, and placed in contact with the gas. **Tannic, gallic, benzoic, succinic,** and **acetic** acids, and **ferrocyanides,** may be detected by the addition of a little neutral ferric chloride to the solution, and discriminated from each other as indicated on pages 62 and 63.

(*a*) A portion of the original solution is acidulated with hydrochloric acid; if this produces a precipitate, it is separated by filtration, and the filtrate is made slightly alkaline with ammonia-water; in case this should produce a precipitate, it is again filtered, and the filtrate finally tested with barium chloride. A precipitate with barium chloride will indicate, in the absence of organic acids, either **sulphuric, boric, phosphoric,** or **silicic** acids; the precipitate with sulphuric acid is insoluble in nitric or hydrochloric acids; boric acid in the free state, or mixed with concentrated sulphuric acid when in the form of a salt, imparts a green color to the alcohol flame; phosphoric acid, in neutral solutions, gives with argentic nitrate a yellow precipitate, soluble in nitric acid or ammonia-water, and with magnesium mixture, a white crystalline precipitate of ammonio-magnesium phosphate; very small amounts of phosphoric acid are detected by heating with a solution of ammonium molybdate in dilute nitric acid, when a yellow crystalline precipitate will be instantly produced; silicic acid and its salts, with the exception of those of the alkalies, are insoluble in water, and may be detected by evaporating a portion of the solution to dryness, and taking up the residue with water containing a little hydrochloric acid, when the silica will remain behind as an insoluble powder. If organic acids are present in the original solution, the precipitate produced by barium chloride may also indicate **oxalic, tartaric,** and **citric** acids, and these, in neutral solutions, likewise produce white precipitates with argentic nitrate, which are soluble in ammonia-water and in nitric acid. They may be distinguished as follows: oxalic acid, upon the addition of lime-water in excess, yields at once a precipitate, insoluble in acetic acid; tartaric acid yields a precipitate, soluble in acetic acid; citric acid affords no precipitate until the liquid is boiled, and the precipitate is soluble in acetic acid. Beside the acids already mentioned as producing precipitates with a neutral solution of barium chloride (*a*), page 65, may be added chromic, carbonic, arsenious, and arsenic acids; but, as previously stated, these acids would also be found in the examination for bases, and may thus be readily identified.

(*b*) A portion of the original solution is acidulated with nitric acid, and solution of argentic nitrate added, when a precipitate, insoluble in dilute nitric acid, will indicate **hydrochloric, hydriodic, hydrobromic,** and **hydrocyanic** acids, as also **ferrocyanides, ferricyanides, sulphocyanides,** and **sulphides,** all of which may be distinguished from each other by the reactions given on page 64, V. (*b*).

(*c*) A portion of the original solution is tinted faintly blue with indigo solution, and a little concentrated sulphuric acid added and heated. Ensuing decolorization will indicate **nitric, chloric,** or **hypochlorous** acids, as also **free chlorine.** Nitric acid may be readily detected by adding to the solution to be tested, contained in a test-tube, concentrated sulphuric acid, cooling the mixture, and then carefully pouring upon the surface of the liquid a solution of ferrous sulphate, so as to form two distinct layers (Fig. 34); a brown or violet coloration of the liquid, or a brownish colored zone at the point of contact of the two liquids will then be produced; chloric acid, besides being indicated, together with nitrates,

FIG. 34.



in the preliminary examination, page 47, is also recognized in its salts by strongly heating, when it is reduced to chloride, and may then be tested by argentic nitrate.

Of the more commonly occurring acids, only **acetic, sulphurous,** and **hydrofluoric** acids still remain; these have already been mentioned, and may be recognized by the distinctive tests of the preceding group reagents, as described on pages 61, 62, and 63.

B. *The substance is insoluble in water, but soluble in acids.*

A portion of it is heated on platinum-foil, to ascertain the presence or absence of organic acids.

(*a*) The powdered substance is treated with nitric acid, and heated; **carbonic** acid may be recognized by effervescence, and by the formation of a white precipitate when the evolved gas is led into lime-water; violet or brown vapors will indicate **iodine** and **bromine,** which may be recognized by a purple or yellowish coloration of chloroform or carbon bisulphide, when shaken with a small part of the dilute nitric acid solution.

(*b*) To a portion of the nitric acid solution, solution of argentic nitrate is added, when a white precipitate, insoluble in nitric acid but soluble in ammonia-water, will indicate **hydrochloric** acid.

(*c*) A portion of the substance is boiled with a solution of potassium carbonate, and filtered; a few drops of a solution of a ferrous and ferric salt are then added, and subsequently hydrochloric acid in slight excess, when a blue precipitate will indicate **hydrocyanic** acid.

(*d*) A portion of the substance is dissolved in hydrochloric acid, and solution of barium chloride added; a white precipitate, insoluble in water, or in an excess of hydrochloric or nitric acids, will indicate **sulphuric** acid.

(*e*) **Boric, silicic,** and **hydrofluoric** acids may be recognized in the preliminary examination, and by previous mentioned tests (pages 61, 62, and 65); **phosphoric** and **oxalic** acids, if in combination with alkaline earths, would have been found in the examination for bases, page 58; if combined with metallic oxides, they should be tested for in the liquid from which the bases precipitable by hydrogen sulphide and ammonium sulphide have been previously removed.

(*f*) A portion of the substance is dissolved in hydrochloric acid, ammonia-water in slight excess added, and, in case a precipitate is produced, filtered therefrom. Solution of calcium chloride is then added to the filtrate, when a precipitate, soluble in acetic acid or potassium hydrate, will indicate **tartaric** acid; if the precipitate is formed only after boiling the solution, then **citric** acid is present; if the precipitate produced in the *cold* solution is insoluble in acetic acid, and also produced in the ammoniacal solution by the addition of solution of calcium oxalate, then **oxalic** acid is present.

C. *The substance is insoluble, or only partially soluble in acids.*

The substance, or portion of the substance, insoluble in acids, may be best brought into a condition suitable for further examination by mixing it intimately with four parts of dry sodium carbonate, and fusing at a red heat. The fused mass, when cold, is boiled with water, and the solution filtered from the insoluble residue. To the solution nitric acid is added in slight excess; **sulphides** will be recognized by the odor of the developed gas, and by imparting a black stain to paper moistened with lead acetate. If a precipitate is produced by the addition of nitric acid, it may consist of **silicic** acid, and is collected upon a filter for further examination; in the latter case the solution may also contain some silica, and a portion of it is evaporated to dryness with strong hydrochloric acid, and the residue taken up with water acidulated with a little hydrochloric acid, when silica will remain behind as an insoluble powder. To a portion of the original solution, acidulated with nitric acid, solution of argentic nitrate is added, when a white precipitate, insoluble in excess of nitric acid, and soluble in ammonia-water, will indicate **hydrochloric** acid; the formation of a white precipitate on the addition of barium chloride to the acidulated liquid will indicate **sulphuric** acid. **Boric** and **hydrofluoric** acids may be recognized by previously indicated tests, pages 61 and 62; **phosphoric** acid is recognized on the addition of ammonium molybdate to the nitric acid solution, and gently heating, by the production of a yellow crystalline precipitate, insoluble in nitric acid, and soluble in ammonia-water; or by the yellow precipitate produced in the carefully neutralized solution on the addition of argentic nitrate, as also by a white crystalline precipitate on the addition of magnesium mixture. It should, however, be remembered that arsenic acid produces with ammonium molybdate, and magnesium sulphate in ammoniacal solution, precipitates precisely analogous to those of phosphoric acid; the arsenic acid may be readily recognized by its reaction with argentic nitrate, or by saturating the warm solution with hydrogen sulphide, when arsenious sulphide and sulphur will be precipitated.

If the solution, as above obtained, by boiling the fused mass with water, shall have been found to contain nothing more than the excess of the applied sodium carbonate, then the entire fused mass may be treated with dilute nitric acid, and the solution thus obtained examined for the above-mentioned acids, in the manner already indicated.

This outline of a systematic course of analysis, although necessarily open to modification in some of its details, such as may frequently be indicated by the results of the preliminary examination, and of that for bases, will, it is believed, for those possessing ordinary chemical knowledge, be found a reliable and trustworthy guide, whenever recourse has to be taken to such a method in the examination and identification of medicinal chemicals, and the more commonly occurring chemicals used in medicine, and in the arts and trades.

TABLE

OF THE DEPORTMENT OF THE COMPOUNDS OF THE PRINCIPAL METALS WITH SOME OF THE GENERAL REAGENTS.

Precipitable by Hydrogen Sulphide

From Acid Solutions:	*From Alkaline Solutions:*	
as Sulphides:	*as Sulphides:*	*as Hydrates:*
As Sb Sn Mo Au Pt Pd Bi Ag Cu Pb Cd.	Fe Mn Co Ni Zn Ur Tl In.	Al Cr Ce.

Sulphides soluble in

Nitric Acid:	*Nitro-hydrochloric Acid:*	*Ammonium Sulphide:*
Pb Bi Cu Ag Cd Fe Mn Zn Ur Tl In.	Hg Co Ni.	As Sb Sn Mo Au Pt.

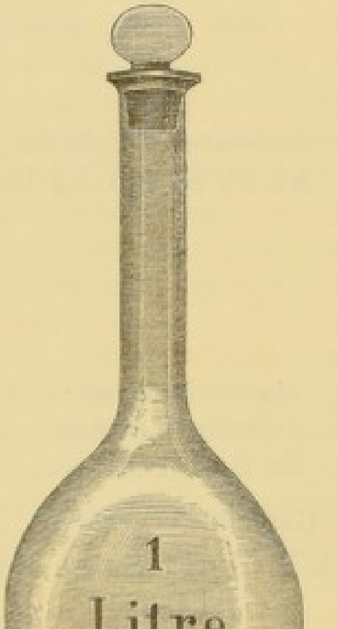
Precipitable by

Hydrochloric Acid:	*Sulphuric Acid:*	*Ammonia-Water:*
Pb Ag Hg_2O.	Pb Hg Sb Sn Ba Ca Sr.	(soluble in excess) Zn Cu Cd Ni Co (insoluble in excess) Pb Bi Hg Fe Sn Sb Mn Al Cr.
Ammonium Carbonate: (in the presence of ammonium chloride)	*Water:*	*Potassium Hydrate:* (insoluble in excess)
Ba Sr Ca.	Bi Hg_2O Sn Sb.	Cu Cd Ni Co Bi Hg Fe Mn (soluble in excess) Pb Sn Sb Zn Al Cr (re-precipitated by boiling) Zn Cr.

VOLUMETRIC ANALYSIS.

THE quantitative estimation of a number of medicinal chemicals and their preparations has been much simplified in practice by the volumetric method of chemical examination, which is based upon the fact that chemical substances combine in definite and equivalent proportions, and consists in noting the volume of a test-solution of known strength, required to produce by chemical reaction a certain visible effect when added to a known quantity of the substance under examination. On obtaining this effect, the quantity of the reagent being ascertained, and that of the substance being already known, an accurate estimate may readily be made by equation and simple calculation.

FIG. 35.



By the aid of this simple and rapid mode of examination, the proportion of the constituents of many chemical compounds and their preparations may be at once quantitatively estimated. In the following part of this volume, in treating of all those chemicals and preparations in which a quantitative determination of the principal constituents is required, and to which the volumetric mode of examination is best suited, either alone or as a confirmatory test, reference has frequently been made to these pages in explanation of the processes involved; and in connection with which, for many substances, is also stated the quantity of the volumetric test solution requisite to produce, with a definite weight of the substance under examination, in direct relation or corresponding to its molecular weight, the exact reaction indicative of its officinal strength. In treating of the various chemicals in the following pages of this volume, where special volumetric methods of analysis are indicated for their examination, or when for those methods here given a more detailed description of the process may be considered necessary or desirable, the method of procedure will in all cases be fully explained.

The apparatus required for volumetric analysis consists, besides the common utensils, as beakers, funnels, porcelain-capsules, crucibles, stirring-rods, balances, etc., of one or several liter-flasks for the preparation of the test-solutions (Fig. 35); these, when filled to a mark on the neck, have mostly a capacity of 1000 cubic centimeters (1 liter) of distilled water at the temperature of 15° C. (59° F.); some cylindrical graduated liter-jars (Figs. 36 and 37), divided into 100 or 1000 centimeter-parts, and used for the preparation of test-solutions as well as for the admixture of parts of a liter; and one or several graduated tubes for the delivery and measurement of the test-solutions; pipettes and burettes. The pipettes (Figs. 38, 39, and 40) are provided either with a

FIG. 36.

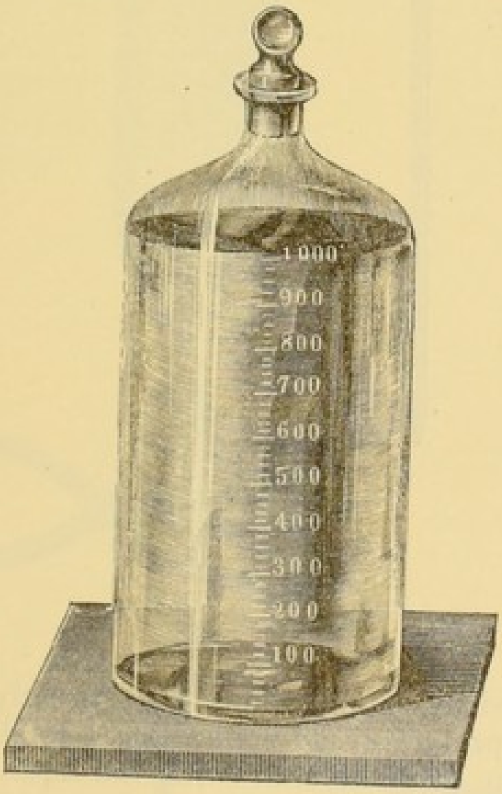
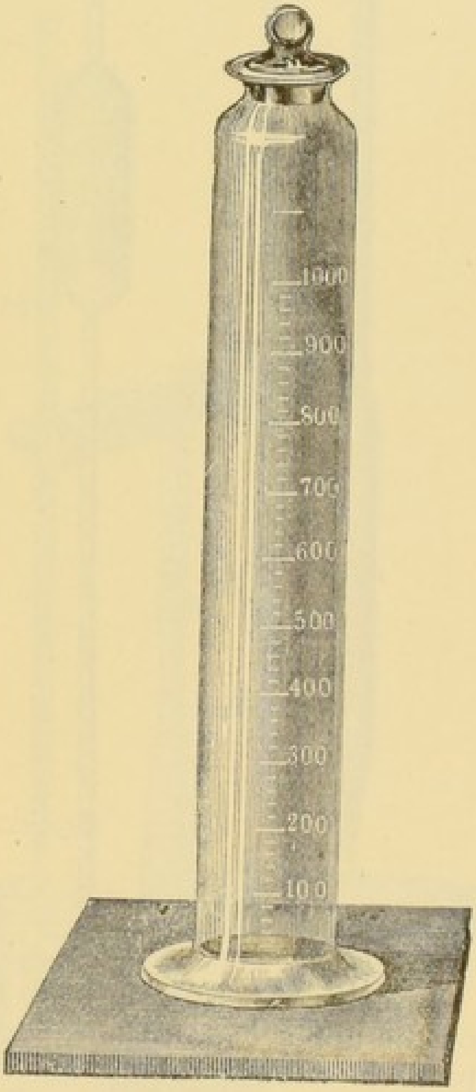


FIG. 37.

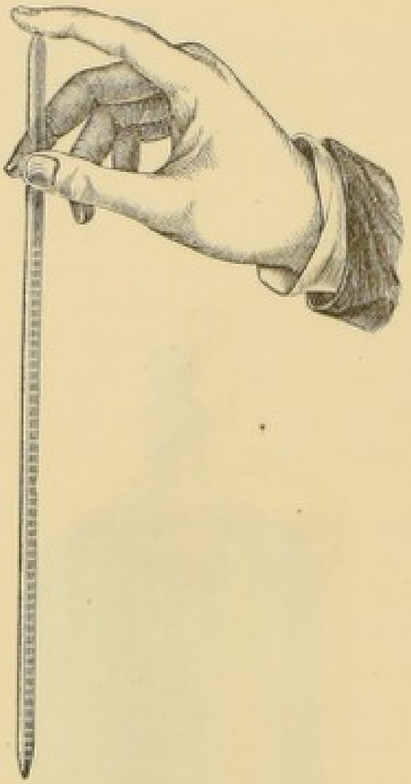


single mark upon the narrow neck, or are graduated into a number of cubic centimeters, or parts thereof, and have a capacity varying from 1 to 50, 100, or more cubic centimeters.

Fig. 38.

Fig. 39.

Fig. 40.

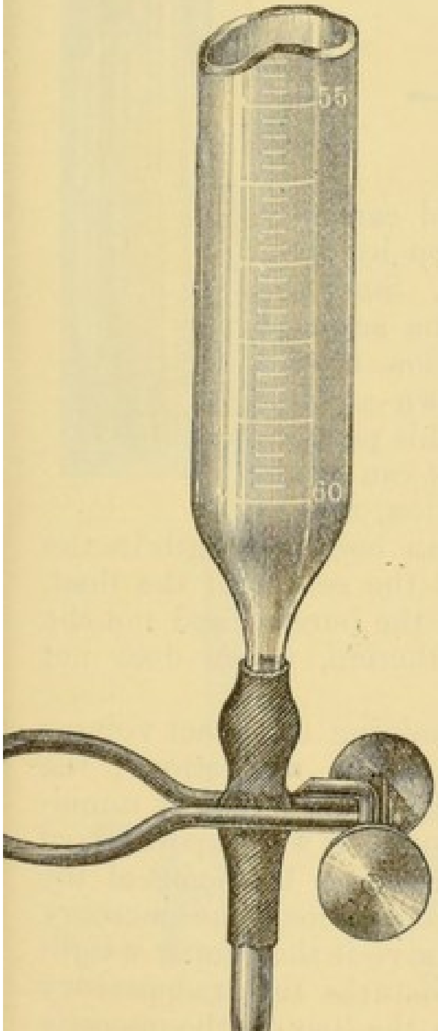


In using pipettes, they are filled by placing the mouth directly on the upper end of the tube, or preferably by connecting a small piece of rubber tubing, and then by suction drawing the liquid into the tube until it rises slightly above the mark on the neck; it is then closed above by the forefinger of the right hand (Fig. 40), or by compression of the rubber tubing, and the liquid allowed to flow out until its surface exactly coincides with the mark on the neck of the tube; by a more or less gentle displacement of the finger, the whole or a portion of the contents of the pipette may then be delivered.

Burettes are preferable for delivery and measurement, and are now quite universally employed; they hold to a certain mark 100 or less cubic centimeters, and are divided by graduation into a corresponding number of equal parts. There are three kinds of burettes in use, which differ mainly in their construction for delivery: Mohr's burette, Gay Lussac's burette, and Geissler's burette.

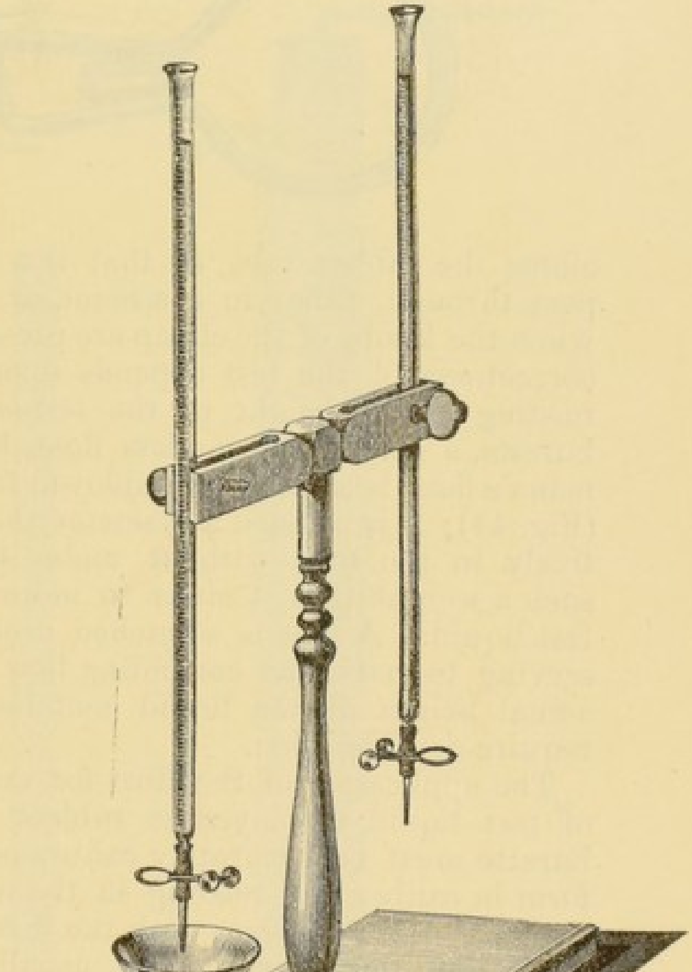
Of these, Mohr's burette (Figs. 41 and 42), on account of its cheapness, simplicity, and convenience, is now in general use for the more common purposes, but its application is excluded in the employment of such solutions as would be affected by contact with rubber tubing, as in the case of potassium permanganate, silver, or iodine solutions. It consists of a graduated glass tube,

Fig. 41.



Mohr's burette.

Fig. 42.



Mohr's burette.

of about 12 millimeters (half an inch) internal diameter, and 50 centimeters (twenty inches) in length; to its contracted lower extremity is fitted a small piece of rubber tubing, into the lower end of which a small piece of glass tubing, about 25 millimeters (one inch) in length, and drawn out at the lower orifice to quite a fine point, is tightly inserted. A strong wire clamp (Fig. 43) closes the rubber tube, so that the fluid can only pass through, either in a stream, or drop by drop, when the knobs of the clamp are pressed. Since the correctness of the test depends upon the accurate reading of the height of the test-solution in the burette, a small hollow glass float, known as Erdmann's float, is sometimes employed for this purpose (Fig. 44); it is of such a diameter that it can move freely in the tube without undue friction, and of such a weight that it sinks to more than half its length in the test liquid. A line is scratched around the centre of the float, serving to mark the coinciding line on the burette, and not the actual height of the liquid contained therein, which does not require consideration.

FIG. 43.

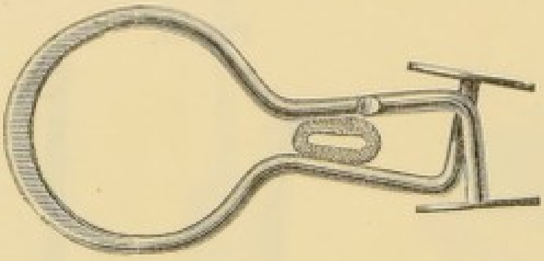
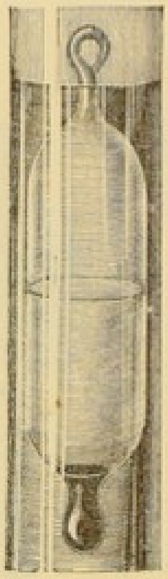


FIG. 44.



The application of the float for determining the exact volume of test liquid employed is subject to certain restrictions; the burette must be accurately calibrated, for, if in the least ununiform in caliber, the reading in the narrow and wider portions of the tube will not agree with the direct reading by means of the marks on the burette. As usually constructed, the mercury contained in the lower end in order to give it the proper weight is also liable to oxidation, which then disturbs the transparency of the interior of the bulb, and renders the line on the opposite side either invisible or indistinct; also in the case of highly colored solutions, as potassium permanganate, iodine, etc., the fine line on the float is seen with difficulty, or not at all. For these reasons the float is not very generally employed, and the readings may usually be attained with sufficient accuracy, and with but slight error, by observing, in the case of colorless liquids, simply the mark on the burette coinciding with the lower line of the concave meniscus of the liquid when held towards the light; with colored liquids the lower line produced by the concave surface of the liquid is not so distinctly seen, and in this case it is therefore better to observe the mark on the burette coinciding with the upper line of the concave surface when held from the light, or against a dark object, by which means readings proportionately accurate may readily be obtained.

Other forms of Mohr's burette are provided with a glass stop-cock (Figs. 45 and 46), so as to be suitable for all liquids, including those which are affected by organic matter; they are, however, more expensive than the one above described, and in the hands

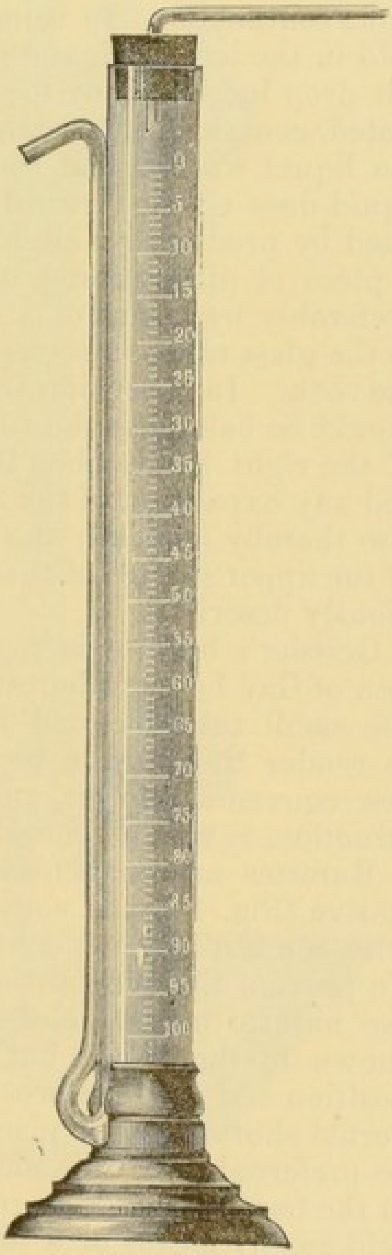
Fig. 45.

Mohr's burette, with glass stop-cock.

Fig. 46.

Mohr's burette, with glass stop-cock.

Fig. 47.



Gay Lussac's burette.

of the inexperienced are less convenient, as also not permitting an equally ready control over the flow of liquid.

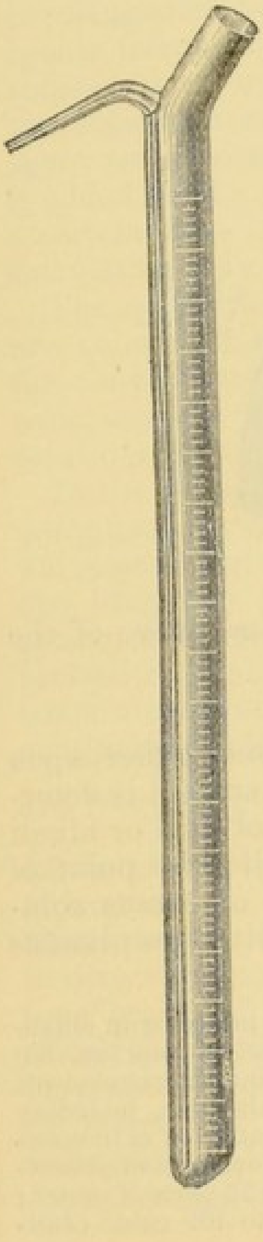
Gay Lussac's burette is represented in Fig. 47. This is one of the oldest forms of burette, and is still in quite frequent use, as being composed entirely of glass it may be used for estimations with any of the volumetric test-solutions, and is thus not open to the objections of the simple form of Mohr's burette. The burette is graduated from a point somewhat below the point of delivery downward, and has usually a capacity of 50 cubic centimeters to the lowest point of graduation, subdivided into tenths of a cubic centimeter. In using the burette it is most conveniently held in the left hand, and so inclined as to allow the test-liquid to fall drop by drop into the solution of the substance to be estimated, contained in a beaker or other vessel, meanwhile stirring the liquid with a glass rod held in the right hand. When the liquid does not flow readily from the exit tube, it may be facilitated by producing a slight pressure with the mouth by means of a piece of glass tubing inserted in the cork of the burette, or preferably by means of a small piece of rubber tubing attached to the glass tube; in no case should the liquid come in contact with the cork. In observing the height of the liquid in the burette it should be held near the top by means of the thumb and forefinger of the right hand, when it assumes a perfectly vertical position, and any expansion of the liquid caused by the heat of the hand is also thereby avoided; the same rules in relation to the concavity of the upper surface of the liquid being observed, as have been previously described.

Geissler's burette is represented in Fig. 48. It is a modification of Gay Lussac's burette, but differs from the latter by having the small tube inclosed within the larger one, thereby tending to render the burette less fragile; this is, however, one of the less convenient forms, and being also difficult of accurate construction, is not in general use.

Burettes are conveniently kept for ready use on a revolving stative (Fig. 49), and should be properly labelled in accordance with the test-solution contained therein, in order to avoid error. To prevent the evaporation of the test-solution and exclude dust, the burette may be closed at the top by means of a marble, as shown in the figure, but as these are liable to fall from their position and produce breakage of other apparatus beneath, an inverted short test-tube placed over the top of the burette is much to be preferred; alkaline solutions, when kept for any length of time in the burette, should be protected from the absorption of carbonic acid gas by means of a tube filled with fragments of fused potassium hydrate, and inserted in the cork of the burette, as shown in the figure.

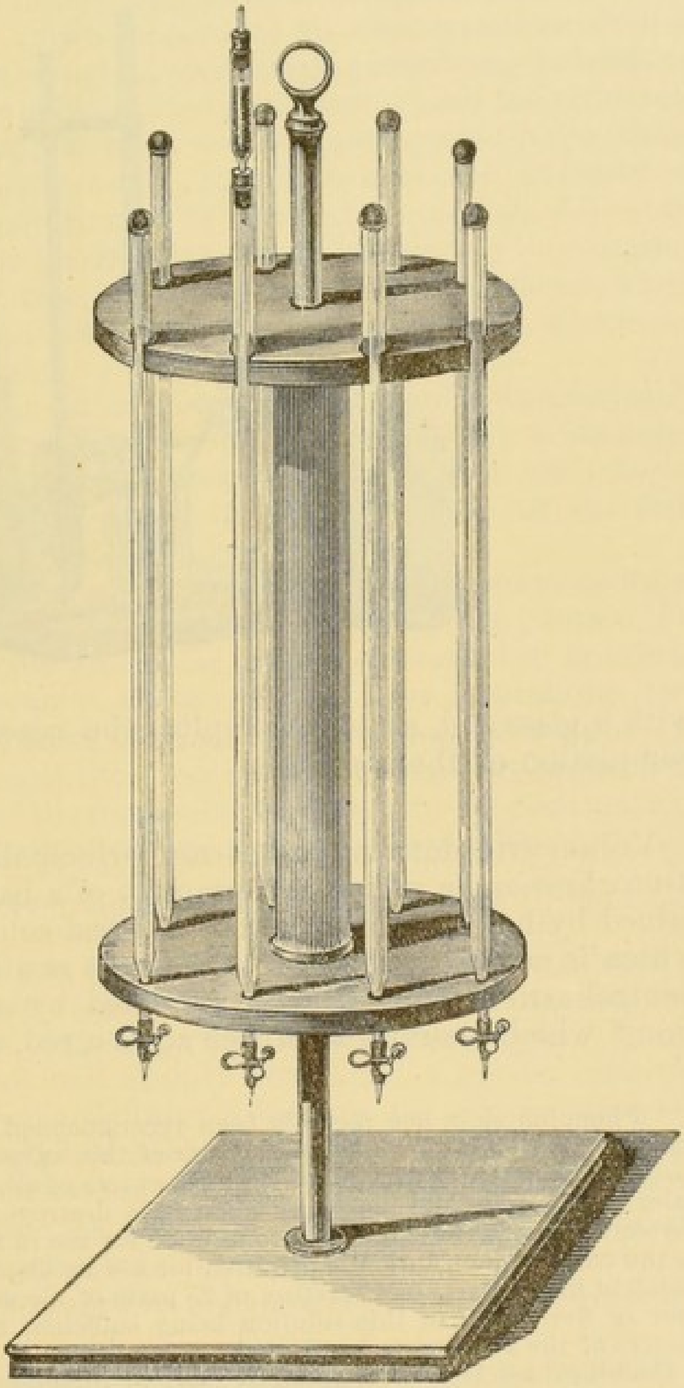
The tests are made by first filling the burette with the test-solu tion to exactly such a height that the mark on the float is coincident with the 0 on the scale of the tube, or, if the float is not

Fig. 48.



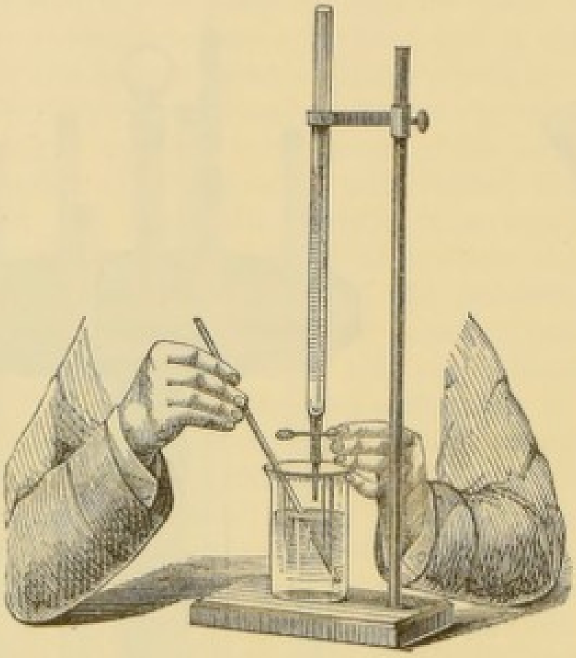
Geissler's burette.

Fig. 49.



employed, the mark on the burette coinciding with the surface of the liquid contained therein should be accurately observed. The solution or mixture to be tested is placed in a beaker under the burette (Fig. 50), and then so much of the test-solution is gradually and carefully delivered into the beaker, with gentle stirring with a glass rod, as to accomplish the reaction indicative of the completion of the operation.

FIG. 50.



Volumetric determinations are principally based, either upon *neutralization*, in which the quantity of a base or an acid is determined by noting the volume of the test-solution of acid or alkali which is necessary to convert it into a neutral salt; the point of neutralization being usually indicated by means of litmus solution,* which assumes with free acids a red, and with free alkalies

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* Phenolphtaleïn has recently been recommended as an indicator in alkalimetry; the neutral and acid solutions of this substance being colorless, but assuming in the presence of the slightest excess of alkali an intense carmine-red color. The color developed by alkalies is destroyed by all acids, including carbonic; hence, like litmus, it is unfitted for use in the titration of carbonates in the cold. The solution is prepared for use by dissolving one part of phenolphtaleïn in 100 parts of a mixture of 25 parts of alcohol and 75 parts of water; four or five drops of this solution being sufficient for 50 to 100 cubic centimeters of the solution to be titrated.

Cochineal solution is occasionally used in preference to litmus, particularly with solutions of the alkaline earths, such as calcium and barium hydrates, and possesses the additional advantage that it is much less modified in color by the presence of carbonic acid. The solution is prepared by digesting 3 grams of powdered cochineal in a mixture of 40 cubic centimeters of alcohol and 160 cubic centimeters of water. Its color is yellowish-red, which is changed to violet by alkalies, mineral acids restoring the original color; but it is not so sensibly a blue coloration; or, upon *oxidation* and *reduction*, in which the quantity of the substance to be determined is found by noting the volume of the test-solution of the oxidizing or reducing agent to which it is equivalent, or which is required to produce a certain reaction; the changes indicating the final completion of the process varying in their nature according to circumstances or the process employed; the principal oxidizing agents being potassium permanganate, potassium bichromate, and iodine, and the reducing agents, ferrous and stannous salts, and sodium hyposulphite (thiosulphate); or, upon *precipitation*, in which case the quantity of the substance to be determined is derived from that of the reagent required to cause its complete precipitation, or, the reagent is added until a precipitate begins to make its appearance, when a certain stage in the process is thereby indicated, from which the calculation may be made.

The quantities of the substances to be assayed volumetrically are submitted to examination by weight, which are sometimes for convenience in calculation made coincident with their molecular weights, and are expressed in grams;[*] those of the test-solutions by measure in cubic centimeters.[†]

In the preparation of solutions for volumetric estimations those designated as *normal* are, as a general rule, such as contain, for univalent substances, the molecular weight expressed in grams in one liter, and for bivalent substances, or salts containing two atoms of a univalent base, one-half of the molecular weight expressed in grams in each liter; solutions of trivalent substances containing one-third of the molecular weight, etc. Decinormal and centinormal solutions are, therefore, one-tenth of this strength, and are frequently for convenience briefly designated as $\frac{N}{10}$ and $\frac{N}{100}$ solutions. Solutions are, however, sometimes made of such a strength as to be only *empirically* normal, and are so prepared that a certain volume of the liquid (100 cubic centimeters) stands in direct relation to, or will exactly neutralize, a known quantity (one gram) of some one definite substance in a pure state, by which means the number of cubic centimeters of the test-solution employed for the same amount by weight of the substance to be estimated, will indicate at once the percentage strength of the substance under examination. Such solutions, although sometimes conveniently employed in the analysis of technical products,

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affected by the weaker organic acids as litmus, and for these the latter is, therefore, to be preferred.

[*] One gram is equal to 15.434 grains of Troy weight.

[†] A cubic centimeter (Fig. 51) is the volume occupied by one gram of distilled water at its point of greatest density, 4° C.; metric measurements, however, are uniformly taken at 15° C. (59° F.).

FIG. 51.

are limited in their application to the estimation of one single substance, requiring for each acid and alkali a special liquid, whereas with virtually normal solutions but one acid is required for all bases, and one alkali for all acids.

Solutions are sometimes designated as normal which bear no definite relation to the molecular weight of the substance contained therein, or to its neutralizing power, but, as in the processes of oxidation and reduction, refer to a particular reaction involved in the process to which the solution is applied; thus a normal solution of potassium permanganate ($K_2Mn_2O_8$) is made to contain one-tenth of the molecular weight expressed in grams in a liter, with reference when used as an oxidizing agent to the amount of available oxygen:

$$2K_2Mn_2O_8 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2.$$

A normal solution of stannous chloride, although tin is a quadrivalent metal, will thus likewise, when used as a reducing agent, contain one-half, and not the fourth of its molecular weight expressed in grams in a liter, as is shown by the expression of its reaction with ferric chloride: $Fe_2Cl_6 + SnCl_2 = 2FeCl_2 + SnCl_4$.

ANALYSIS BY NEUTRALIZATION.

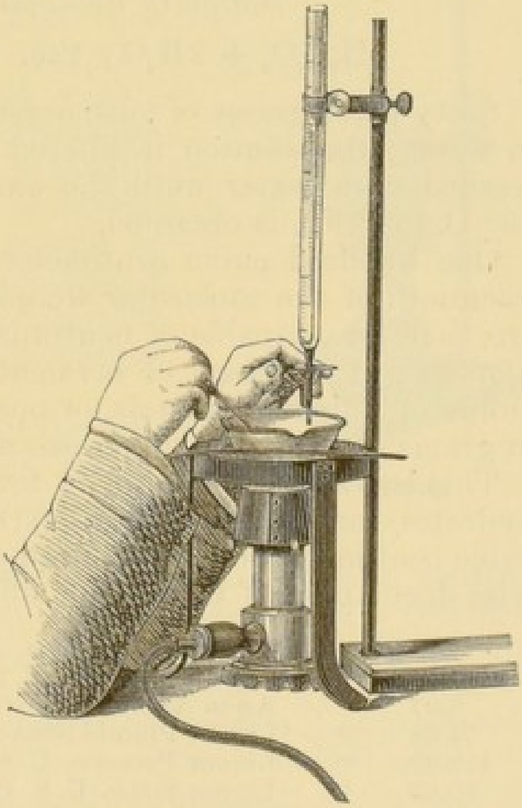
ESTIMATION OF ALKALIES (ALKALIMETRY).

The operations of analysis by neutralization are based upon the fundamental and simple principle, that the proportions in which chemical substances unite with each other in forming new compounds are definite and invariable, and that these proportions are represented by the molecular weights. In the formation of solutions, therefore, for volumetric estimations by neutralization, a simple equation, and the molecular weights deducted therefrom, will at once indicate the amount of solid substance necessary for the production of a normal solution, which then bears a direct and simple relation to all other substances with which it may be employed for neutralization, and which is expressed by the molecular weight of the substance, or a corresponding fraction deducted therefrom.

The standard test-solutions employed for the estimation of alkalies are either oxalic or sulphuric acids; the oxalic acid solution is the more commonly employed, and is generally preferred on account of the convenience of preparation, but as the amount of water of crystallization which the acid contains (two molecules) has to be considered in the preparation of the solution, it is necessary that it should be neither moist, nor that it should have lost a part of the water of crystallization by exposure—conditions which would materially influence the correctness of the strength of the solution, and consequently the results of all the estimations obtained therewith. Its action upon litmus is moreover not quite as decisive or as distinct as that of sulphuric acid, for which reason, and that above mentioned, sulphuric acid is considered in careful research to furnish more accurate results.

For the preparation of a standard sulphuric acid, 49 grams (corresponding to one-half the molecular weight) of concentrated sulphuric acid are diluted with water to the measure of one liter. This affords a solution which is approximately normal, and the exact strength of which is afterwards determined. A burette being filled with the acid solution, a certain number of cubic centimeters are allowed to flow into a beaker, a few drops of litmus solution added, and from another burette containing a solution of potassium or sodium hydrate of empirical or unknown strength, but which should be stronger than the acid solution, a sufficient amount is added until the indications of the point of neutralization are obtained, or until the last drop of the alkaline solution which is added produces a decided blue coloration. From the number of cubic centimeters of the alkaline solution required, as determined by two or three experiments with concordant results, a simple calculation will show to what extent the alkaline solution has to be diluted in order that equal volumes of the acid and alkali shall precisely neutralize each other, and which must again be confirmed by experiment after the dilution of the alkaline solution. This having been attained, two or three portions of pure, freshly ignited sodium carbonate, of about two grams each (readily obtainable by the ignition of portions of pure sodium bicarbonate, of about three grams each, in an open porcelain crucible, and preserved after ignition by filling, while still warm, into tightly corked test-tubes), are accurately weighed. The several portions, dissolved separately, in small amounts of water, in a percelain capsule or beaker, and a few drops of litmus solution added, are then titrated with the acid solution (Fig. 52); the liquid being heated from time to time to insure the complete removal of the disengaged carbonic acid gas, until a slight excess of acid has been added, which is evidenced

FIG. 52.



by the appearance of a bright cherry-red coloration. The excess of acid employed may be then inversely titrated with the alkaline solution until the blue coloration is produced, when the amount required of the latter, deducted from the number of cubic centimeters of acid employed, will give the number of cubic centimeters of acid which were required for the exact neutralization of the amount of carbonate taken. The number of cubic centimeters of acid which would be required if the latter were exactly normal, may be found by dividing the amount of sodium carbonate taken by the decimal 0.053 (the amount of sodium carbonate equivalent to one cubic centimeter of strictly normal sulphuric acid). This number, which will usually be found to be somewhat greater or less than the number of cubic centimeters employed, will, when divided by the latter, give a number slightly greater or less than one, showing that the acid is a little weaker or stronger than normal, and, designated as the correction factor or coefficient, must be used to multiply the number of cubic centimeters of acid or alkali used in each estimation, in order to convert it into its equivalent of normal strength. The exact strength of the acid and alkali and their correction factor having thus been accurately determined, the methods of their application remain the same as will be described for the standard solution of oxalic acid.

Standard Solution of Oxalic Acid.

$H_2C_2O_4 + 2H_2O$; 126. 63 Grams in 1 Liter.

Sixty-three grams of pure crystallized oxalic acid are dissolved in water; the solution is filtered into a liter-flask, and the filter washed with water until the exact volume of 1 liter, at about 15° C. (59° F.), is obtained.

One hundred cubic centimeters of this solution contain one-twentieth of the molecular weight, in grams, of oxalic acid, and are, therefore, capable of neutralizing one-twentieth of the molecular weight in grams of bivalent bases, or salts containing two atoms of univalent metals, or one-tenth of the molecular weight in grams of salts containing one atom of univalent bases.

This test solution is applied for the estimation of the alkaline hydrates, carbonates, acetates, tartrates, citrates, and borates: 100 cubic centimeters of the solution will exactly neutralize, or otherwise decompose, if pure, or of officinal strength:

5.23	grams of	Ammonii Carbonas, $NH_4HCO_3+NH_4NH_2CO_2$.
17.00	"	Aqua Ammoniæ, U. S. P., spec. grav. 0.959.
6.07	"	Aqua Ammoniæ fortior, U. S. P., spec. grav. 0.900.
54.68	"	Liquor Plumbi Subacetatis, U. S. P., spec. grav. 1.228.
112.00	"	Liquor Potassæ, U. S. P., spec. grav. 1.036.
80.00	"	Liquor Sodæ, U. S. P., spec. grav. 1.059.
9.80	"	Potassii Acetas, $KC_2H_3O_2$.*

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* After ignition.

10.01	grams of	Potassii Bicarbonas, $KHCO_3$.
18.80	"	Potassii Bitartras, $KHC_4H_4O_6$.*
8.30	"	Potassii Carbonas, depuratus.
6.91	"	Potassii Carbonas, purus, K_2CO_3.
10.80	"	Potassii Citras, $K_3C_6H_5O_7 + H_2O$,* or 10.20 grams of anhydrous salt.
14.10	"	Potassii et Sodii Tartras, $KNaC_4H_4O_6 + 4H_2O$.*
5.61	"	Potassii Hydras, KHO.
3.14	"	Potassii Permanganas, $K_2Mn_2O_8$.
11.76	"	Potassii Tartras, $2K_2C_4H_4O_6, H_2O$.*
13.60	"	Sodii Acetas, $NaC_2H_3O_2 + 3H_2O$.*
8.40	"	Sodii Bicarbonas, $NaHCO_3$.
8.92	"	Sodii Bicarbonas Venalis
19.10	"	Sodii Boras, $Na_2B_4O_7 + 10H_2O$.
14.30	"	Sodii Carbonas, $Na_2CO_3 + 10H_2O$, or 5.3 grams of anhydrous salt.
4.00	"	Sodii Hydras, NaHO.
17.00	"	Spiritus Ammoniæ, U. S. P., spec. grav. 0.810.

The operation is conducted by weighing the above quantity of the substance, or the preparation to be estimated, placing it in a beaker, and, when required, diluting or dissolving it by the addition of a sufficient quantity of water. The tartrates, citrates, and acetates have first to be completely converted into carbonates by ignition in a platinum or porcelain crucible (Fig. 53), care being taken that no loss of substance is occasioned by the increase of volume on first heating; to avoid this, the crucible should be sufficiently large, and at first very gently heated, after which the heat may be increased until inflammable vapors cease to be evolved, and perfect reduction is effected. As this operation is usually accompanied by the separation of considerable carbon, the fused mass should be extracted with hot water, filtered into a capsule or beaker, and the filter, together with the insoluble residue, well washed with water.

Fig. 53.

When the solution is ready for the test, a few drops of litmus solution are added, so as to impart a distinct bluish tint; the capsule or beaker is then placed under the burette containing the test-solution (Fig. 54), and, with constant gentle stirring with a small glass rod, the test-solution is delivered into the beaker, first in a stream, and, when approaching the point of neutralization, drop by drop, until the blue liquid assumes a cherry-red hue. In the estimation of carbonates it is preferable, as stated on page 81, to add an excess of the standard acid solution above that required for the neutralization of the alkali, the

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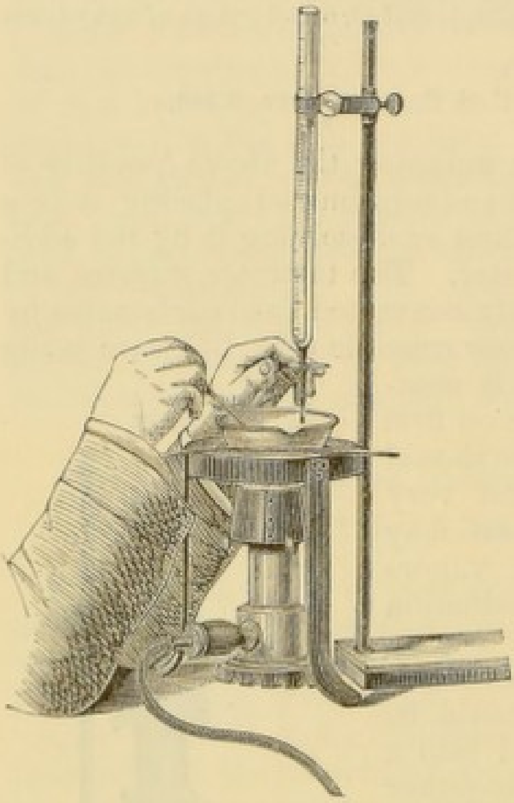
* After ignition.

solution being heated to expel completely the liberated carbonic acid gas, which, by its action upon litmus, imparts a violet or wine-red coloration to the liquid, as distinguished from the light cherry-red coloration which is produced by the acid test-solution. The excess of acid employed may then be inversely titrated or neutralized by a corresponding standard alkali solution, the preparation of which has already been mentioned (page 81), and will be further described under the estimation of acids; the difference between the amounts of the two solutions employed, both being equal in volumetric strength, will give the exact amount of acid solution required for the neutralization of the alkali or alkaline carbonate. This method of procedure has the additional advantage that the change of color of the litmus solution from red to blue is much more prominent than from blue to red, thus insuring a more accurate determination of the exact point of neutralization.

Fig. 54.



These operations require care and skill in every point, so as to avoid the slightest loss of either of the liquids, and a consequent error in the final result.

When neutralization is indicated by the light, cherry-red coloration in the one case, or, in the above described method of inverse titration, by the appearance of the blue coloration in the other, the process is completed, and the volume of the acid test-solution employed is observed. The number of cubic centimeters employed, less than 100, indicates at once the percentage of impurities, or of deficiency of strength in the substance estimated.

On the other hand, each cubic centimeter of the test-solution of oxalic acid employed corresponds to one milligram molecule of alkaline hydrate, one-half milligram molecule of alkaline carbonate, or the proportionate amount of other salts, *i. e.:*

1 cubic centimeter corresponds to 0.017 gram Ammonia gas, NH_3.
1 " " " " 0.05233 " Ammonium Carbonate, $NH_4HCO_3.NH_4NH_2CO_2$.
1 " " " " 0.18925 " Lead Acetate, crystallized, $Pb(C_2H_3O_2)_2+3H_2O$.

1	cubic	centimeter	corresponds	to	0.13675	gram	Lead Subacetate, as $Pb_2O(C_2H_3O_2)_2$.
1	“	“	“	“	0.0980	“	Potassium Acetate, $KC_2H_3O_2$.*
1	“	“	“	“	0.1000	“	Potassium Bicarbonate, $KHCO_3$.
1	“	“	“	“	0.1880	“	Potassium Bitartrate, $KHC_4H_4O_6$.*
1	“	“	“	“	0.0690	“	Potassium Carbonate, anhydrous, K_2CO_3.
1	“	“	“	“	0.1020	“	Potassium Citrate, anhydrous, $K_3C_6H_5O_7$.*
1	“	“	“	“	0.0560	“	Potassium Hydrate, KOH.
1	“	“	“	“	0.0314	“	Potassium Permanganate, $K_2Mn_2O_8$.
1	“	“	“	“	0.1410	“	Potassium Sodium Tartrate, $KNaC_4H_4O_6+4H_2O$.*
1	“	“	“	“	0.1175	“	Potassium Tartrate, $2K_2C_4H_4O_6.H_2O$.*
1	“	“	“	“	0.1360	“	Sodium Acetate, $NaC_2H_3O_2+2H_2O$.*
1	“	“	“	“	0.0840	“	Sodium Bicarbonate, $NaHCO_3$.
1	“	“	“	“	0.1910	“	Sodium Borate, $Na_2B_4O_7+10H_2O$.
1	“	“	“	“	0.1430	“	Sodium Carbonate, crystallized, $Na_2CO_3+10H_2O$.
1	“	“	“	“	0.0530	“	Sodium Carbonate, anhydrous, Na_2CO_3.
1	“	“	“	“	0.0400	“	Sodium Hydrate, NaOH.

A simple equation will give the amount of alkaline hydrate, carbonate, or other salt present. By operating on 100 times the half-milligram molecule, *i. e.*, 6.9 grams of potassium carbonate, or 5.3 grams of anhydrous sodium carbonate, all calculation is dispensed with; for, as this amount, if present, would require 100 cubic centimeters of standard oxalic acid solution for its neutralization, the number of cubic centimeters actually required, at once indicate the percentage of alkaline carbonate.

On the other hand, it is sometimes preferable, instead of weighing a certain definite quantity of a salt, or of a solution, to take any convenient quantity, and then ascertain its exact weight. This is especially the case with liquids like ammonia-water, which, by exposure during the time of weighing, would suffer considerable loss by the volatilization of the gas, or, in the case of concentrated acids, a certain loss by evaporation or absorption of moisture would be experienced. In the latter case, whatever the number of cubic centimeters of standard acid or alkali solution employed may be, a reference to the molecular weight of the substance and a simple equation will give the amount of pure alkali or acid in the substance under examination.

When, in estimating alkaline carbonates, the amount of carbonic acid, namely, the percentage of real carbonate, has to be determined, the following method is simple and accurate: Two small light flasks with twice-perforated rubber corks, are con-

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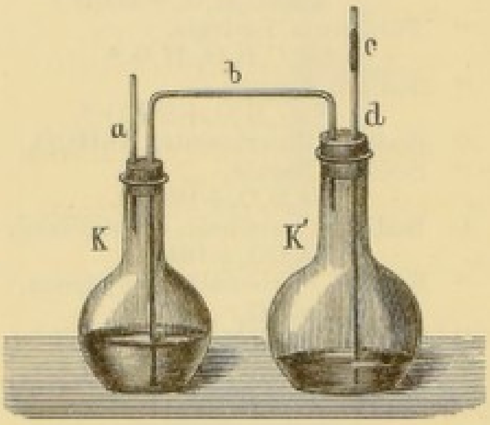
* After ignition.

nected with a twice-bent tube b (Fig. 55); the flask K' is provided with the tube d, reaching to the bottom of the flask, and closed at its outer end with a globule of soft wax, or by means of a small piece of rubber tubing, the outer end of which is closed with a small piece of tightly fitting glass rod c; that of K is provided with the short tube a. Two grams of the carbonate under examination are weighed, and introduced into the flask K', together with a little water; the flask K is half filled with concentrated sulphuric acid; the apparatus is then tightly fitted, and weighed. A small quantity of air is now by suction drawn out of flask K by means of the tube a, whereby the air in K' is likewise rarefied. On allowing the air to return, a quantity of sulphuric acid ascends in the tube b, and flows over into flask K', causing a disengagement of carbonic acid gas, which escapes through the tube a, after having been dried by passing through the acid in K. This operation is repeated until the whole of the carbonate is decomposed, and the process is terminated by opening the wax stopper, or removing the rubber tubing, and drawing some air through the apparatus by means of a piece of rubber tubing attached to tube a, and suction, or by connecting the latter with an aspirator. Should the amount of heat liberated by the admixture of the sulphuric acid with the water be considered insufficient for the complete decomposition of the carbonate, the flask K' may be gently heated, and, after cooling, air again drawn through the apparatus. The apparatus is then re-weighed, and the difference between the first and final weighings will express the amount of carbonic acid in the 2 grams of carbonate under examination.

FIG. 55.



ESTIMATION OF ACIDS (ACIDIMETRY).

The volumetric estimation of acids is the reverse operation of the estimation of alkalies, and the methods involved are founded upon precisely the same principle as has been explained under alkalimetry. Nothing more is therefore needed than a normal or standard test-solution of potassium or sodium hydrate, of such a strength that one cubic centimeter exactly neutralizes one cubic centimeter of a normal solution of oxalic or sulphuric acid. A solution of potassium hydrate having less tendency to attack the glass vessels in which it is contained than a similar solution of sodium hydrate, it is preferred for the preparation of the normal alkali solution. The preparation of such a solution for use with sulphuric acid, and the method of determining its exact strength has been explained on page 81; the preparation of a normal alkali solution, corresponding in strength to that of the normal oxalic acid, is accomplished as follows:

Standard Solution of Potassium Hydrate.

KOH; 56. 56 Grams in 1 Liter.

A convenient amount (20 or 30 cubic centimeters) of the normal oxalic acid solution is allowed to flow from a burette into a beaker, a few drops of litmus solution added, and, from another burette, containing a moderately strong solution of potassium hydrate, a sufficient amount is added to the oxalic acid solution, stirring gently with a glass rod until exact neutralization is effected, or until the last drop of the alkaline solution added, produces a distinct blue coloration of the liquid. The number of cubic centimeters of alkali solution required, which should be less than the number of cubic centimeters of acid taken, is then noted, and, from two determinations with concordant results, a simple calculation will show to what extent the alkali solution must be diluted in order that equal volumes of the two liquids shall exactly neutralize each other; thus, if 20 cubic centimeters of the normal acid solution have required but 18 cubic centimeters of the alkali solution for exact neutralization, it then follows that to every 18 cubic centimeters of the alkali solution 2 cubic centimeters of water must be added, or, 900 cubic centimeters of the alkali solution diluted with water to the measure of a liter, for the attainment of volumetric equivalence. Simple proportion will show to what extent any other quantity is to be diluted.

One hundred cubic centimeters of this normal test-solution of potassium hydrate contain one-tenth of the molecular weight (=5.6) of potassium hydrate, expressed in grams, and will neutralize an equivalent quantity of an acid.

This test-solution is employed for the estimation of the following medicinal acids:

One hundred cubic centimeters of the solution will neutralize, if of officinal strength:

16.66	grams of	Acidum Aceticum, U. S. P., spec. grav. 1.048.
100.00	"	Acidum Aceticum Dilutum, U. S. P., spec. grav. 1.0083.
6.00	"	Acidum Aceticum Glaciale, spec. grav. 1.058.
7.00	"	Acidum Citricum.
81.00	"	Acidum Hydrobromicum Dilutum, U. S. P., spec. grav. 1.077.
11.41	"	Acidum Hydrochloricum, U. S. P., spec. grav. 1.16.
36.40	"	Acidum Hydrochloricum Dilutum, U. S. P., spec. grav. 1.049.
12.00	"	Acidum Lacticum, U. S. P., spec. grav. 1.212.
9.08	"	Acidum Nitricum, U. S. P., spec. grav. 1.42.
63.45	"	Acidum Nitricum Dilutum, U. S. P., spec. grav. 1.059.
6.30	"	Acidum Oxalicum.
4.90	"	Acidum Sulphuricum, U. S. P., spec. grav. 1.84.
27.22	"	Acidum Sulphuricum Aromaticum, U. S. P., spec. grav. 0.955.
49.00	"	Acidum Sulphuricum Dilutum, U. S. P., spec grav. 1.067.
7.50	"	Acidum Tartaricum.

The concentrated liquid acids are to be diluted with four or five times their volume of water, and the solid ones to be dissolved in about eight times their weight of water before being tested. To determine the point of neutralization, and the consequent completion of the process, litmus solution is employed, and the same rules observed for the details of the manipulation as have been previously described on page 83. The number of cubic centimeters of the normal alkaline solution employed, less than 100, indicates at once the percentage of impurities, or of deficiency of strength in the substance estimated.

Instead of employing the quantities of acid given in the above table, it is sometimes preferable, for the reasons stated on page 85, to take any convenient quantity of the substance to be tested, and then to ascertain its exact weight; the weighings being conducted in a glass-stoppered bottle, the weight of which has been previously determined. For such estimations, where the quantity of substance taken for analysis is different from the amount expressed in the preceding table, the relation of the normal potassium hydrate solution to the officinal acids with which it may be employed, is represented as follows:

1	cubic	centimeter	corresponds	to	0.0600	gram	Acetic Acid.
1	"	"	"	"	0.0700	"	Citric Acid, crystallized, $C_6H_8O_7+H_2O$.
1	"	"	"	"	0.0808	"	Hydrobromic Acid, HBr.
1	"	"	"	"	0.0364	"	Hydrochloric Acid, HCl.
1	"	"	"	"	0.1276	"	Hydriodic Acid, HI.
1	"	"	"	"	0.0900	"	Lactic Acid, $C_3H_6O_3$.
1	"	"	"	"	0.0630	"	Nitric Acid, HNO_3.
1	"	"	"	"	0.0630	"	Oxalic Acid, crystallized, $C_2H_2O_4+2H_2O$.
1	"	"	"	"	0.0490	"	Sulphuric Acid, H_2SO_4.
1	"	"	"	"	0.0750	"	Tartaric Acid, crystallized, $C_4H_6O_6$.

ANALYSIS BY OXIDATION AND REDUCTION.

The principles involved in the process of analysis by oxidation or reduction have been briefly alluded to on page 79; the methods of estimation being based upon the determination of the volume of the solution of an oxidizing agent of known composition requisite for the complete oxidation of the substance under examination, or, in the process of reduction, a definite amount of the solution of the reducing agent in slight excess of the amount actually required is first added, the excess being afterwards determined by the addition of the proper quantity of the oxidizing agent of known and definite strength.

The number of substances which may be estimated by these methods is very large, embracing, in addition to many medicinal chemicals and preparations, a large number of technical products which receive no direct application in pharmacy, whilst the results attained are usually characterized by a remarkable accuracy, combined with rapidity and convenience of determination. Indicators to designate the completion of the process are usually the permanent pink coloration imparted by potassium permanganate solution, the deep blue color produced by the reaction of ferrous salts with potassium ferricyanide, or of free iodine with mucilage of starch, all of which are so delicate that a little experience on the part of the operator will insure precision and uniformity of result.

Standard Solution of Potassium Permanganate.

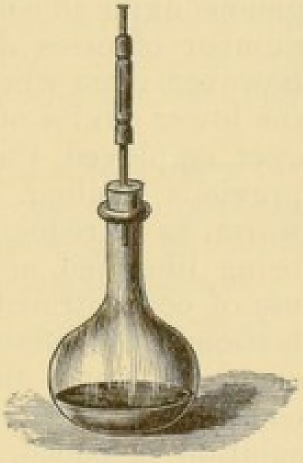
$K_2Mn_2O_8$; 314. 3.14 Grams in 1 Liter.

This solution is prepared, with reference to the amount of available oxygen, of a decinormal strength, by dissolving 3.14 grams of pure crystallized potassium permanganate in distilled water, and diluting to the measure of one liter. The solution should not be filtered, but separated by decantation from any residual insoluble matter which may be formed upon standing, and carefully preserved for use in a glass-stoppered bottle; the solution being decomposed by contact with organic matter, the use of Mohr's burette with rubber tubing is not admissible, but the one provided with a glass stop-cock or the Gay Lussac burette has to be employed.

To determine the exact strength of the solution, about 0.2 gram of pure iron wire, free from rust and very accurately weighed, is dissolved in about 20 cubic centimeters of dilute sulphuric acid, in a flask arranged as represented in Fig. 56.

This is made by inserting a piece of glass tubing through the tightly fitting cork of the flask, attaching thereto a piece of rubber tubing in which a vertical slit is made by means of a sharp knife, and securely closed at the upper end with a small piece of glass rod. This arrangement, while permitting the escape of the gas or steam generated by heating, affords the best protection against the oxidizing influence of the air during the solution of the iron; the opening in the rubber tubing, in consequence of diminished internal pressure, being drawn together when the heat is removed, and the solution allowed to cool.

FIG. 56.



When all the iron is dissolved, by the aid of a gentle heat, the solution is quickly cooled and poured into a beaker, and the flask several times rinsed with small portions of distilled water, which are added to the solution contained in the beaker, and the liquid finally diluted to about 100 cubic centimeters.

The solution of potassium permanganate contained in the burette should now be added until the pink coloration of the liquid remains permanent, or, until at least it does not directly disappear, indicating that the entire amount of iron contained in the solution has been oxidized from the ferrous to the ferric state. The coloration is most distinctly seen when the beaker is placed upon a sheet of white paper, and the reaction may be expressed by the following equation:

$$10Fe''SO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2'''(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

The number of cubic centimeters of permanganate solution employed is now noted, and the amount of iron taken being known, a simple calculation will determine the amount of metallic iron equivalent to one cubic centimeter of permanganate solution. Were the permanganate solution exactly decinormal, one cubic centimeter would correspond to 0.0056 gram of metallic iron, but being usually a little deficient in strength, the number obtained, which should be established by at least two experiments with closely agreeing results, is accepted as the factor of the solution.

When the standard permanganate solution has been standing for any considerable length of time, even when well protected from dust, in a glass-stoppered bottle, a slight decomposition takes place, and the proper factor has then to be ascertained anew in the manner above described. It should also be remembered that in volumetric examinations with permanganate, the solution should be slightly acidulous, in order to hold the resulting manganous oxide in solution, and prevent precipitation. In the larger number of cases dilute sulphuric acid is employed; nitric acid, however, even when very dilute, if it contains the least trace of the lower oxides of nitrogen, decomposes the solution, and, whenever employed, these must, therefore, be carefully removed by previous boiling. Hydrochloric acid, when concentrated or warm, has a reducing action on the permanganate, free chlorine being liberated, and consequently in such operations where the use of concentrated hydrochloric acid is required, as in the estimation of potassium nitrate, the solution, after being heated sufficiently to expel the last traces of nitric oxide, must be quickly cooled, and largely diluted with water before the permanganate solution is added. The factor obtained for the permanganate solution by the solution of metallic iron in dilute sulphuric acid, usually differs slightly from that obtained by its solution in hydrochloric acid, and consequently in exact experiments should be determined for the latter acid when this is required to be used for acidulation or for effecting solution.

The officinal substances which may be conveniently estimated by permanganate are the iron salts, chlorine water, chlorinated lime, manganese dioxide, potassium nitrate, alcoholic solution of ethyl nitrite, and oxalic acid. The ferrous salts require no previous preparation for their estimation, whereas the ferric salts must first be reduced to the ferrous state by means of nascent hydrogen, as evolved by the action of dilute sulphuric acid upon zinc; as commercial zinc usually contains a small percentage of iron, this must be separately estimated and considered, if in sufficient amount to influence the result of the estimation.

Standard Solution of Potassium Bichromate.

$K_2Cr_2O_7$; 294.8. 14.74 Grams in 1 Liter.

This solution receives a similar application in the processes of volumetric estimation to that of potassium permanganate, and is sometimes preferred to the latter from the fact of being less subject to decomposition through the influence of light and air, or in contact with organic matter; it possesses, however, the disadvantage of not permitting the observation of the completion of the process by the change in the appearance of the solution itself, and requiring the employment of an external indicator.

The principle of its application depends upon the fact that potassium bichromate, in the presence of an excess of acid, yields four atoms of oxygen to the hydrogen of the acid, leaving three atoms available either for direct oxidation or for combination with the hydrogen of more acid, whilst an equivalent proportion of acidulous radical is liberated. When employed as a volumetric reagent, however, the bichromate always yields the whole of its oxygen to the hydrogen of the accompanying acid, with the liberation of an equivalent quantity of acidulous radical; four-sevenths of this radical then immediately combining with the potassium and chromium of the bichromate, whilst three-sevenths become available.

As one atom of the liberated acidulous radical will convert two molecules of ferrous into one of ferric salt, one molecule of potassium bichromate is capable of converting six molecules of ferrous into three of ferric salt, as shown by the following equations:

$$K_2CrO_4,CrO_3 + 7H_2SO_4 + 6FeSO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3.$$

$$K_2CrO_4.CrO_3 + 14HCl + 6FeCl_2 = 2KCl + Cr_2Cl_6 + 7H_2O + 3Fe_2Cl_6.$$

The standard solution of potassium bichromate is prepared by dissolving 14.74 grams of the pure crystallized salt in water, and diluting the resulting solution to the measure of one liter. In its application for the estimation of iron, in ferrous combinations, a weighed amount of the salt is dissolved in a small quantity of water, the solution acidulated with dilute sulphuric acid, and the solution of bichromate subsequently allowed to flow into the liquid from a burette until, after well stirring, a drop of the liquid, removed by a glass rod, and placed in contact with a drop of solution of potassium ferricyanide, on a white plate, ceases to produce a blue color.

As 100 cubic centimeters of the bichromate solution contain $\frac{1}{200}$ of the molecular weight of the salt in grams, the same amount will effect the conversion of $\frac{1}{200}$ of the weight of 6 atoms of iron, expressed in grams, or an equivalent amount of the lower salts of iron, from the ferrous to the ferric state. Each cubic centimeter of the test-solution thus corresponds to 0.01474 gram of pure crystallized potassium bichromate, or an equivalent amount of metallic iron and the following officinal salts with which it is employed, *i. e.*:

1 cubic centimeter corresponds to	0.01677	gram of	Metallic Iron, Fe.
1 " " " "	0.03477	"	Ferrous Carbonate, $FeCO_3$.
1 " " " "	0.08337	"	Ferrous Sulphate, crystallized, $FeSO_4+7H_2O$.
1 " " " "	0.05097	"	Ferrous Sulphate, dried, $FeSO_4+H_2O$.

The following named articles are officially directed to be tested with this solution, and, if perfectly pure or of officinal strength, at least 50 cubic centimeters of the test solution should be required to effect the conversion of the stated weights of substance from the ferrous to the ferric state.

Ferri Carbonas Saccharatus	12.12 grams,	indicating	15 per cent. of Ferrous Carbonate.
Ferri Sulphas	4.167 "	"	100 per cent. of the salt.
Ferri Sulphas Præcipitatus	4.167 "	"	100 " " "

Standard Solution of Iodine and Sodium Hyposulphite (*thiosulphate*).

The fundamental principle upon which the method of estimation with these solutions is based, depends upon the indirect oxidizing action of iodine in the presence of water with the formation of hydriodic acid, and the liberation of oxygen in an active state, which then combines with the oxidizable substance, as, *e. g.*, in the case of arsenious acid:

$$As_2O_3 + 2H_2O + 4I = As_2O_5 + 4HI,$$

or sometimes, as in the case of hydrogen sulphide, by the direct abstraction of hydrogen:

$$H_2S + 2I = 2HI + S.$$

These solutions may be employed for the estimation of bodies capable of absorbing oxygen and decolorizing the iodine solution, such as sulphurous acid, sulphites, hydrogen sulphide, alkaline hyposulphites, arsenites, etc., as also for bodies which contain available oxygen, free chlorine, or from which chlorine may be liberated when treated with concentrated hydrochloric acid, such as the chromates, manganates, and all metallic peroxides. Free chlorine, however, cannot be estimated by direct titration with sodium hyposulphite solution as in the case of iodine, for instead of tetrathionic acid being produced, as with the latter, sulphuric acid is formed, as may be confirmed by testing with barium chloride; the chlorine must, therefore, in such cases be passed into, or added to, an excess of solution of potassium iodide, by which means the liberation of an equivalent amount of free iodine is effected, and the latter can then be directly estimated with sodium hyposulphite solution.

The completion of the reaction or process is in all cases indicated by means of mucilage of starch, which assumes in the presence of the slightest excess of free iodine a beautiful deep blue color.

Standard Solution of Iodine.

I; 126.6. 12.66 Grams in 1 Liter.

This solution is prepared of decinormal strength, and therefore contains one-tenth of the atomic weight of iodine, expressed in grams, in one liter.

12.66 grams of pure iodine,* and 18 grams of pure potassium iodide are placed in a liter flask, about 200 cubic centimeters of distilled water are then added, and, as soon as the solution of the iodine is effected, the liquid is diluted to the exact measure of one liter.

Each cubic centimeter of this solution contains 0.01266 gram of iodine, and bears a simple relation to the following substances with which it may be employed, *i. e.:*

1 cubic centimeter corresponds to 0.0072 gram of Antimonious Oxide, Sb_2O_3.
1 " " " " 0.0167 " Antimony Potassium Tartrate, crystallized, $K(SbO)C_4H_4O_6+\frac{1}{2}H_2O$, or 0.0162 gram of anhydrous salt.
1 " " " " 0.004945 gram of Arsenious Acid (anhydride), As_2O_3.
1 " " " " 0.0097 " Potassium Sulphite, crystallized, $K_2SO_4+2H_2O$.
1 " " " " 0.0052 " Sodium Bisulphite, $NaHSO_3$.
1 " " " " 0.0248 " Sodium Hyposulphite, crystallized, $Na_2S_2O_3+5H_2O$.
1 " " " " 0.0126 " Sodium Sulphite, crystallized, $Na_2SO_3+7H_2O$.
1 " " " " 0.0032 " Sulphurous Acid (anhydride), SO_2.

The following named articles are officially directed to be tested with this solution, and, by the employment of the stated weights

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* In weighing the iodine, it should be brought into a perfectly dry test-tube, which is afterward tightly corked, in order to protect the balance from the corrosive action of the vapors.

of substance, at least 50 cubic centimeters of the standard test-solution should be required, corresponding to the purity or percentage strength below indicated.

Acidum Arseniosum	0.2546	gram,	indicating	97	per cent.	of the	anhydride.
Acidum Sulphurosum	4.571	grams,	"	3.5	"	"	dry gas.
Liquor Acidi Arseniosi	25.464	"	"	0.97	"	"	anhydride.
Liquor Potassii Arsenitis	25.464	"	"	0.97	"	"	"
Potassii Sulphis	0.538	"	"	90	"	"	crystallized salt.
Sodii Bisulphis	0.288	"	"	90	"	"	salt.
Sodii Sulphis	0.700	"	"	90	"	"	crystallized salt.

Standard Solution of Sodium Hyposulphite (*thiosulphate*).

$Na_2S_2O_3 + 5H_2O$; 248. 24.8 Grams in 1 Liter.

This solution, being likewise of decinormal strength, is prepared by dissolving 24.8 grams of pure crystallized sodium hyposulphite in water, and diluting the solution to the exact measure of one liter.

Each cubic centimeter of the solution contains 0.0248 gram of crystallized sodium hyposulphite, and bears a simple relation to the following substances which may be estimated therewith, *i. e.:*

1 cubic centimeter corresponds to	0.00798	gram of	Bromine,	Br.
1 " " " "	0.00354	"	Chlorine,	Cl.
1 " " " "	0.01266	"	Iodine,	I.

The following named articles are officially directed to be tested with this solution, and, by the employment of the stated weights of substance, at least 50 cubic centimeters of the standard test-solution should be required, corresponding to the purity or percentage strength below indicated:

Aqua Chlori	44.25	grams,	indicating	0.4	per cent.	of the	dry gas.
Calx Chlorata	0.71	gram,	"	25	"	"	chlorine.
Iodum	0.633	"	"	100	"	"	iodine.
Liquor Iodi Compositus	12.66	grams,	"	5	"	"	iodine.
Liquor Sodæ Chloratæ	8.88	"	"	2	"	"	chlorine.
Tinctura Iodi	7.71	"	"	8	"	"	iodine.

The solutions of iodine and sodium hyposulphite, if accurately prepared from pure materials, will be volumetrically equal, and this is rendered necessary in consequence of their frequent inverse application in the methods of volumetric estimation. In order to ascertain this fact, one burette is filled with the iodine solution (only the form of burette provided with a glass stop-cock or the Gay Lussac burette should be used for this solution), and another one with the solution of sodium hyposulphite; a certain number of cubic centimeters of the latter solution are then allowed to flow into a beaker, placed upon a sheet of white paper, a little mucilage of starch added, and subsequently the solution of iodine, stirring constantly with a glass rod, until the last drop produces a permanent blue coloration of the liquid. The reaction which thus takes place, resulting in the formation of sodium iodide and tetrathionate, is expressed by the following equation; the permanent blue coloration only appearing in the presence of a slight excess of free iodine:

$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6.$$

The number of cubic centimeters of each solution employed is now noted, and should the one solution be found to be slightly weaker or stronger than the other, the stronger solution must by calculation be diluted with so much water, that an exactly equal number of cubic centimeters or volume of the two solutions shall be required to produce the above-mentioned effect.

As the test-solutions, however, even when carefully prepared, are seldom of precisely the correct strength, their standard must be fixed with relation to perfectly pure and dry iodine, and the proper factor thus determined. This is accomplished by reducing about one gram of pure iodine to a fine powder, drying it on a watch-glass over sulphuric acid, and then dividing it into two nearly equal portions, which should be separately weighed in small glass tubes, and the weight of which, when empty, has been previously determined. The vials, with their contents, are then placed in a small flask, each containing about 10 cubic centimeters of a ten per cent. solution of potassium iodide, and, as soon as the iodine has become perfectly dissolved, the sodium hyposulphite solution added from a burette until complete decolorization takes place, and a slight excess of the latter solution has been employed; a little mucilage of starch is now added, and the solution inversely titrated with the iodine solution until the blue coloration is produced. The amount of iodine solution, deducted from the amount of sodium hyposulphite solution employed, will give the number of cubic centimeters of sodium hyposulphite solution equivalent to the amount of iodine taken, and from which a simple calculation will show the amount of pure iodine corresponding to one cubic centimeter of either of the test-solutions. The factor thus obtained, which will usually be found somewhat less than that theoretically required, will receive application in all subsequent estimations for which the test-solutions may be employed.

The further details relating to the mode of procedure for the estimation of individual substances with these volumetric test-solutions will, in order to avoid repetition and to retain the proper systematic arrangement of the special chemicals, be more fully described in the second part of this volume, in the appropriate place.

VOLUMETRIC ESTIMATION OF SUGARS.

The most convenient method for the volumetric estimation of sugars is by a process of reduction, and is based upon the fact that the copper from an alkaline solution of cupric tartrate may be completely precipitated in the form of red cuprous oxide by boiling with a solution of grape- or milk-sugar; one molecule of pure grape-sugar being capable of reducing exactly five molecules of cupric oxide to the cuprous state, and, from which relation, the amount of copper reduced from a solution of known strength will bear a direct and simple proportion to the amount of sugar contained in a definite volume of the solution under examination.

The estimations by this method require but little time, and are capable of yielding sufficiently accurate results.

The method of preparation of the test-solution of alkaline cupric tartrate, or "Fehling's solution," has been described under the head of reagents, page 32; it should have been well preserved in a glass-stoppered bottle, and should give no precipitate on boiling. In performing the tests, ten cubic centimeters of the copper solution are measured off by means of a pipette, brought into a glass flask of about 100 cubic centimeters capacity, and diluted with water to about fifty cubic centimeters. The solution is then heated nearly to the boiling-point, and the solution of sugar, contained in a burette, gradually added, allowing the liquid to boil for a few minutes after each addition, and the precipitate thereby formed to subside until, after carefully repeating the operation, the blue color of the liquid entirely disappears. The point at which exactly the proper amount of sugar solution has been added is difficult to observe by the simple loss of color of the solution, and, in order to determine this more exactly, as soon as the blue color of the liquid is no longer distinctly visible, a few drops should be removed by means of a pipette, brought upon a porcelain plate, and, after acidulating with acetic or hydrochloric acid, tested with a drop of solution of potassium ferrocyanide, when, if copper still be present in the solution, a distinct, brown coloration will occur; this manner of testing should be frequently repeated towards the close of the operation to insure the perfect reduction of the copper, care being taken, on the other hand, that an excess of the sugar solution be not added.

Grape-sugar and milk-sugar require no previous preparation for their estimation when in the form of solution, whereas cane-sugar requires to be first boiled with a dilute acid, by which process it is converted, through the assumption of a molecule of water, into grape-sugar, or dextrose, and fruit-sugar or lævulose, both of which exercise the same reducing action on the alkaline copper solution.

$$\underbrace{C_{12}H_{22}O_{11}}_{\text{Cane-sugar.}} + H_2O = \underbrace{C_6H_{12}O_6}_{\text{Grape-sugar.}} + \underbrace{C_6H_{12}O_6}_{\text{Lævulose.}}$$

The alkaline copper solution, if properly and accurately prepared, bears the following relation to the different varieties of sugar, and is capable of being exactly reduced in the proportion of the amounts here indicated.

10 cubic centimeters correspond to 0.05 gram of grape-sugar.
10 " " " " 0.067 " milk-sugar.
10 " " " " 0.0475 " cane-sugar.

The number of cubic centimeters of a sugar solution necessary to effect the complete reduction of 10 cubic centimeters of the copper solution will therefore contain, according to the variety, the amount of pure anhydrous sugar stated above, from which data the percentage strength of the solution may be readily calculated.

The estimation of sugar is attended with more accurate results when in dilute than in concentrated solution; solutions containing not more than one-half, or one per cent., being best adapted for the purpose, and, if found by a preliminary estimation to be considerably more concentrated, they should be diluted with a definite quantity of water to the proper extent, and again estimated, when the result of the second estimation, if found to vary from that of the first, may be accepted as the more accurate.

The test-solution of alkaline cupric tartrate is subject to slight changes by keeping; for this reason, or even when freshly prepared, it is preferable in all cases to verify its strength, and to determine its proper factor with relation to the different varieties of sugar to be estimated. This determination of the factor for grape-, milk-, and cane-sugar may be readily accomplished as follows:

I. *Grape-sugar, dextrose, or glucose*, $C_6H_{12}O_6.H_2O$.—A few grams of pure crystallized grape-sugar should be thoroughly dried in a desiccator, over sulphuric acid, by which means the hygroscopic moisture is removed, but not the water of hydration, which cannot be eliminated without the decomposition of the sugar, and is accordingly to be considered in the calculation. One gram of the sugar, accurately weighed, is then dissolved in water, and the solution diluted to the measure of 200 cubic centimeters, forming a one-half per cent. solution. This solution is then brought into a burette, and the test performed as explained on page 96; the percentage strength of the solution, and the number of cubic centimeters required for the reduction of 10 cubic centimeters of the copper solution being known, the amount of pure, anhydrous grape-sugar equivalent thereto may be readily calculated.

II. *Milk-sugar, or lactose*, $C_{12}H_{22}O_{11} + H_2O$.—A few grams of pure milk-sugar should be thoroughly dried at the temperature of the water-bath until of constant weight; the hygroscopic moisture being perfectly removed at this temperature without causing any decomposition of the sugar. A solution containing exactly one-half per cent. of the dry sugar should now be prepared, and, having been brought into the burette, the process of titration and the method of calculation are the same as has been described for grape-sugar.

III. *Cane sugar, or saccharose*, $C_{12}H_{22}O_{11}$.—Pure cane-sugar, possessing of itself no reducing action, must first be converted by the action of an acid into grape- and fruit-sugars, a process which is commonly designated by the expression inversion. One gram of the sugar, which has been previously dried at 100° C. (212° F.) until of constant weight, is dissolved, in a graduated flask, in about 100 cubic centimeters of water, ten drops of hydrochloric acid are then added, and the liquid heated on the water-bath for half an hour. After cooling, the solution is diluted with water to the measure of 200 cubic centimeters; the process of titration and the calculation of the amount of pure cane-sugar, equivalent to ten cubic centimeters of the copper solution, being afterwards conducted precisely as described for grape- and milk-sugar. The factors obtained by these means may now be employed for the estimation of the three varieties of sugar in solutions of unknown strength, and with accurate results.

For the estimation of the amount of milk-sugar contained in milk, the casein and albumin should first be removed from the latter before being brought into the burette, and the operation of titration then conducted as with a solution of pure sugar. For the quantitative estimation of the amount of sugar contained in diabetic urine, it is usually advisable to first dilute the urine with nine times its volume of water, forming thus a ten per cent. mixture; the latter is then brought into a burette, titrated as previously described, and the calculation made in accordance with the corresponding decimal for grape-sugar, as stated on page 97, or, with the employment of the proper factor, as derived from previous estimations with a solution of pure grape-sugar.

ANALYSIS BY PRECIPITATION.

ESTIMATION OF ACIDULOUS RADICALS PRECIPITATED BY ARGENTIC NITRATE.

Standard Solution of Argentic Nitrate.

$AgNO_3$; 169.7. 16.97 Grams in 1 Liter.

The principle of the method of analysis by precipitation has been briefly alluded to on page 79, so that but a few explanatory remarks will be required; the application of this solution for the estimation of the officinal chemicals and preparations being quite as extended as the solutions which have already received consideration in the processes of analysis by neutralization, or by oxidation and reduction.

The standard test-solution is made of such a strength that it shall be exactly decinormal. 16.97 grams (one-tenth of the molecular weight) of pure, dry, crystallized argentic nitrate, are dissolved in water, and the solution diluted to the exact measure of one liter.

This solution may be employed for the estimation of most of the officinal chlorides, iodides, bromides, and cyanides, including hydrochloric, hydriodic, hydrobromic, and hydrocyanic acids, and bitter-almond water; insoluble chlorides must first be converted into a soluble form by fusing with sodium hydrate, and dissolving the fused mass in water, or by boiling with a solution of sodium hydrate, and acidulating the solutions thus obtained by nitric acid.

A number of other substances may be estimated indirectly by means of the standard argentic nitrate solution, and, in fact, all compounds which are capable of being converted into neutral chlorides by evaporation to dryness with pure hydrochloric acid, and finally heating to about 120° C. (248° F.), may be estimated in this way with accuracy; such are the alkaline hydrates and carbonates, the alkaline earths and their carbonates, and nitrates and chlorates.

The alkalies and alkaline-earths in combination with organic acids are first ignited in order to convert them into carbonates, and then treated with hydrochloric acid, and evaporated as before; nitrates are converted by evaporation with concentrated hydrochloric acid into chlorides, while chlorates are converted into chlorides by ignition. It is evident that in the above mentioned indirect estimations the chlorine in a combined state is the only substance actually determined, but as the laws of chemical combination are well known and constant, the amount of chlorine present in the compound bears a simple relation to the base with which it is combined, and from which the amount of base to be estimated may be calculated.

Each cubic centimeter of the standard argentic nitrate solution, containing 0.01697 gram of the crystallized salt, bears a simple relation to the following officinal substances for the estimation of which it may be employed, *i. e.:*

1	cubic	centimeter	corresponds	to	0.00978	gram of	Ammonium Bromide, NH_4Br.
1	"	"	"	"	0.00534	"	Ammonium Chloride, NH_4Cl.
1	"	"	"	"	0.0155	"	Ammonium Iodide, NH_4I.
1	"	"	"	"	0.01276	"	Hydriodic Acid, HI.
1	"	"	"	"	0.00808	"	Hydrobromic Acid, HBr.
1	"	"	"	"	0.00364	"	Hydrochloric Acid, HCl.
1	"	"	"	"	0.0054	"	Hydrocyanic Acid, HCN.
1	"	"	"	"	0.01198	"	Potassium Bromide, KBr.
1	"	"	"	"	0.00744	"	Potassium Chloride, KCl.
1	"	"	"	"	0.0130	"	Potassium Cyanide, KCN.
1	"	"	"	"	0.01656	"	Potassium Iodide, KI.
1	"	"	"	"	0.01028	"	Sodium Bromide, $NaBr$.
1	"	"	"	"	0.00584	"	Sodium Chloride, $NaCl$.
1	"	"	"	"	0.01028	"	Sodium Iodide, NaI.

The following named articles are officially directed to be tested with this solution, and, by the employment of the stated weights of substance, at least 50 cubic centimeters of the standard argentic nitrate solution should be required, corresponding to the purity or percentage strength below indicated:

Acidum Hydrocyanicum Dilutum	13.5 grams,	indicating	2	per cent.	of	absolute acid.
Ammonii Bromidum	0.477 gram,	"	97	"	"	bromide.
Potassii Bromidum	0.583 "	"	97	"	"	bromide.
Potassii Cyanidum	0.722 "	"	90	"	"	the salt.
Sodii Bromidum	0.503 "	"	97	"	"	bromide.

The operation of analysis with the argentic nitrate solution may be performed in the case of chlorides, bromides, and iodides, by dissolving a convenient and accurately weighed quantity of the salt in water, or by diluting a weighed quantity of the respective acids with a small amount of water in a bottle with closely fitting glass stopper, and allowing the standard test-solution to gradually flow into the liquid from a burette (preferably the Gay Lussac burette, or the form provided with a glass stop-cock) until, after actively shaking the liquid, and allowing the precipitate to subside, a drop of the test-solution ceases to produce in the clear liquid any further precipitation. The number of cubic centimeters of argentic nitrate solution employed represents an equivalent amount of the substance under examination, as deduced from the molecular weight.

In the estimation of the neutral chlorides, iodides, and bromides, it is more convenient to dissolve the salt in a small amount of water, in a flask or beaker, and then to add a few drops of a neutral solution of potassium chromate before titrating with the argentic nitrate solution. By this method, the potassium chromate serving as an indicator, the silver solution is simply added, with constant stirring, until the permanent red coloration of argentic chromate is produced, which does not occur until the entire amount of the chloride, iodide, or bromide present has been converted into the corresponding silver salt.

In the estimation of hydrocyanic acid, or simple cyanides, a slight deviation from the above described process is made, in consequence of the fact of argentic cyanide forming with potassium cyanide an easily soluble double salt. The solution of hydrocyanic acid, or potassium cyanide, is first made slightly alkaline by the addition of the requisite quantity of a solution of potassium or sodium hydrate, a few drops of a saturated solution of sodium chloride are then added, in order to increase the sensibility of the reaction, and the solution of argentic nitrate finally added, with constant stirring, until a permanent cloudiness is produced in the liquid; this marks the completion of the process, and indicates the point when the argentic cyanide or chloride begins to be precipitated; the argentic chloride not being precipitated until after the complete conversion of the cyanide into the soluble double cyanide of potassium and silver. The reaction upon which the method of estimation of cyanides is based will become more clearly understood when expressed by the following equations; the argentic oxide being produced in the liquid from the nitrate, through the agency of the alkali:

$$4KCN + Ag_2O + H_2O = 2AgK(CN)_2 + 2KHO$$
$$2AgK(CN)_2 + Ag_2O + H_2O = 4AgCN + 2KHO.$$

It is obvious that by this method the number of cubic centimeters of the standard argentic nitrate solution employed to produce the reaction above described, will indicate exactly one-half of the equivalent amount of cyanide present in the solution; the soluble double salt still containing one-half of the original amount of undecomposed cyanide. In the calculation of such an analysis, therefore, the number of cubic centimeters of the silver solution employed must be doubled before multiplying with the molecular decimal of hydrocyanic acid or potassium cyanide, or, as has been done in the table on page 99, the decimal may be doubled, and directly multiplied by the number of cubic centimeters of solution used, which result will show in either case the exact amount of true hydrocyanic acid, or pure cyanide in the substance under consideration.

The amounts of the individual substances which are most conveniently employed for estimation with the argentic nitrate solution, and the salts with which its employment is most applicable, will receive further mention in the second part of this volume.

ALKALOIDS.

THE GENERAL CHARACTERS, AND METHOD FOR THE SYSTEMATIC SEPARATION AND RECOGNITION OF SOME OF THE PRINCIPAL ALKALOIDS AND ALLIED PRINCIPLES.

THE alkaloids constitute an important, large, and constantly increasing group of widely distributed organic bases, which are either solid, and then mostly crystalline, or liquid and volatile; and usually represent the active principle of the plant from which they are obtained.

They all contain carbon, hydrogen, and nitrogen as essential constituents, most of them containing also oxygen, which, however, is wanting in some of the liquid alkaloids. They generally possess a distinct alkaline character, neutralizing acids with the formation of salts, which, as a rule, are capable of crystallization, but, analogously to ammonia, their formation is by direct combination, and not attended with the formation of water.

The liquid alkaloids, with the proper precautions and regulation of temperature, may be distilled unchanged, whereas those which are solid at ordinary temperatures, upon heating, usually first melt, and then with increase of temperature become decomposed. They often possess a powerful physiological or toxic action, even when administered in exceedingly small amounts, a fact which renders their separation and recognition of much importance in toxicological chemistry and forensic investigations.

When heated with soda-lime they all develop ammonia, and, by treatment with alkaline hydrates or with acids, they are frequently resolved into other bases, either volatile or permanent, often of a complex nature, and generally accompanied by various other products of decomposition. By the action of concentrated acids and other chemical agents, the products of oxidation or decomposition which are formed are often of a characteristic color, and are frequently employed as a means for their identification.

The alkaloids, with a few exceptions, are very sparingly soluble in cold water, but dissolve much more readily in alcohol and amylic alcohol, as also to a greater or less extent in ether, chloroform, carbon bisulphide, benzol, petroleum benzin, and the volatile and fatty oils. Although no general rule can be established regarding their solubility, the difference of behavior towards the simple solvents affords a means of separating many of the alkaloids from other bodies, and from each other, in a form which will admit of, or aid in, their subsequent identification.

The salts of the alkaloids are for the most part readily soluble in water, and those which are sparingly soluble are dissolved by dilute acids with the formation of acid salts. The larger number of the alkaloids, as also of their respective salts, possess the property of circular polarization; the deviation of the plane of polarization being in most instances to the left, although this deviation is influenced in character as well as in extent by the solvent employed and the concentration of the solution, thus restricting the practical application of this property for their estimation to certain conditions and limits.

With many reagents the alkaloids afford special reactions in common, depending upon their precipitation from their solutions in a form which, although presenting no sharply discriminating individual characters, very frequently serves to determine the presence of a body of this class, or for its obtainment in a form better adapted for its purification, estimation, or further chemical examination. Thus the alkaline hydrates and carbonates precipitate the alkaloids from the aqueous solution of their salts; the precipitates, however, in some cases being readily re-dissolved by an excess of the precipitant. To these may be added the following list of the more important and commonly employed reagents, which, in most cases, produce in aqueous solutions of the alkaloids, or their salts, precipitates possessing general, definite characters.

Tannic acid produces white or yellowish tannates of the alkaloids, many of which are soluble in hydrochloric acid, and in some instances, as in the case of morphine, are readily re-dissolved by a slight excess of the precipitant.

In this connection the fact should, however, be borne in mind that tannic acid also precipitates many non-alkaloidal or neutral bodies, and particularly the large class of so-called bitter principles.

Iodine in potassium iodide solution (Wagner), page 39, produces yellowish, brown, or reddish-brown precipitates, which are insoluble in water, alcohol, and dilute acids.

Potassio-mercuric iodide (Planta and Delffs), page 40, produces white or yellowish-white precipitates, in which the alkaloid takes the place of the potassium of the reagent, and which are either amorphous or crystalline, insoluble in acids, but soluble in alcohol.

Potassio-cadmic iodide[1] (Marmé, Dragendorff) produces, in solu-

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[1] Cadmium iodide is dissolved in a hot, concentrated, aqueous solution of potassium iodide, and this solution is mixed with as much concentrated solu-

tions slightly acidulated with sulphuric acid, white, amorphous precipitates, which, after some time, become yellowish and crystalline, and are readily soluble in alcohol or an excess of the reagent.

Potassio-bismuthic iodide[1] (Dragendorff) produces, in solutions slightly acidulated with sulphuric acid, orange-red, amorphous precipitates.

Phospho-molybdic acid[2] (De Vrij, Sonnenschein).—This reagent, applied in the form of an acid solution of the sodium salt, produces yellow or brownish-yellow, amorphous, flocculent precipitates, which are insoluble in alcohol and dilute mineral acids, but are dissolved by the concentrated mineral acids, and by several of the organic acids.

Mercuric chloride, page 39, produces white, crystalline precipitates, which are soluble in hydrochloric acid.

Platinic chloride, page 39, and *auric chloride*, page 31, form with most of the alkaloids double salts, analogous in composition to those of the inorganic alkalies, which are usually of a bright yellow color, either crystalline, or gradually becoming so upon standing, or amorphous and flocculent, and generally sparingly soluble in water, but soluble in warm hydrochloric acid.

Picric acid (Hager) precipitates most of the alkaloids, even from very dilute solutions, in a yellow, crystalline, or amorphous form; the precipitates are insoluble in an excess of the precipitant, or in dilute sulphuric acid, but are soluble in hydrochloric acid.

In addition to the large class of alkaloids derived from the vegetable kingdom, science has been enriched, and at the same time the labors of the chemical expert rendered more arduous, by the comparatively recent discovery and development of a class of bodies produced by the putrefaction of animal substances, which closely resemble some of the vegetable alkaloids in their physical and chemical properties, and which have been designated as *ptomaines* (cadaver poisons).

From the time of their discovery by Selmi and Gauthier, in 1873, much valuable knowledge has been contributed respecting their physiological action and chemical behavior, by the labors

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tion of potassium iodide as will be sufficient to retain the cadmium iodide in solution when cold.

[1] Prepared from bismuth iodide as potassio-cadmic iodide is prepared from cadmium iodide.

[2] An aqueous solution of ammonium molybdate, acidulated with nitric acid, is added to an aqueous solution of sodium phosphate, acidulated with nitric acid; the resulting precipitate, after standing for some time, is filtered off, well washed with water, and dissolved in a solution of sodium carbonate. The solution is then evaporated to dryness, and the residue gently ignited until ammonia ceases to be given off. The cooled product is finally dissolved in water, and so much nitric acid added as may be required to dissolve the precipitate which is first formed.

and observations of a number of investigators, but which is not yet sufficiently complete to admit of their classification. The ptomaines appear to exist in several distinct forms, although Hager has designated the alkaloidal product of the decomposition of animal matter as *septicin*, with reference to one special body, which, in explanation of the difference in physical, chemical, and physiological properties, he believes to be capable of assuming different modifications, or of undergoing further decomposition with the production of other bodies of an alkaloidal nature, according to the extent of putrefaction.

The ptomaines are mostly volatile, and in this form appear to bear some resemblance to coniine, possessing in addition to the general characters of alkaloids a narcotic odor, as also being precipitated by chlorine-water, but, unlike coniine, not becoming turbid on gently warming; while others present a more permanent character, with some analogies to atropine, hyoscyamine, veratrine, etc. They all possess strongly reducing properties, and when added to a solution of potassium ferricyanide convert the latter into ferrocyanide, which, on the addition of ferric chloride, yields a precipitate of Prussian blue. These bodies, although in some instances inert, have been found to possess, in the majority of cases, powerful toxic properties; their distinction from the vegetable alkaloids may, therefore, be destined to become an important factor in the problems of toxicological chemistry and forensic research.

The isolation and identification of the alkaloids and allied principles, and especially those of a toxic character, is a subject of such importance, and of necessity so extended in its details, that it is properly confined to the departments of toxicological chemistry. With this consideration it is the aim to present here simply a brief outline of the generally adopted process of separation, together with the more important and characteristic tests for their recognition.

Although the physical and chemical properties of the alkaloids, as has been indicated, present a marked variation among themselves, yet they are nevertheless capable of being divided into certain groups with respect to their behavior towards solvents, which, although by no means so sharply defined as in the case of the inorganic bases, still suffices for their separation in a form sufficiently pure for their identification, or for further experiment.

For the separation of the alkaloids and allied principles from other extraneous, organic, coloring, or extractive matters, the method of Stas, as modified by Otto, will here be briefly described. This method, which consists in treating the acid and alkaline solutions successively with ether, and finally with amylic alcohol, recommends itself by its simplicity, and is often adopted in preference to the more complicated method of Dragendorff, which consists in the successive treatment of both the acid and the alkaline solution with benzin, benzol, chloroform, and amylic alcohol, or to the other variously modified processes.

The organic material to be examined, if not already in a fluid condition, should first be mixed with, or dissolved in, water, and then tested with litmus-paper, in order to ascertain its possible acid or alkaline character. If it be perfectly neutral, it should be slightly acidulated with tartaric acid, or, if acid, it is first to be neutralized with sodium hydrate, and then, as in the case of an originally neutral reaction, slightly acidulated with tartaric acid; if, however, it possess an alkaline reaction, in which case the volatile alkaloids coniine and nicotine would be indicated by their odor, tartaric acid is likewise added until a perceptibly acid reaction is obtained. If the substance in its acidulated solution, as above obtained, forms a perfectly clear liquid, it may be treated at once with ether, but in the case of articles of food, the contents of a stomach, vomited matter, etc., the direct treatment with ether is precluded, in consequence of the presence of fatty matter or other impurities, which would likewise become dissolved, and disguise the characteristic reaction of the subsequently applied tests. The substance in this case, after the previously described treatment, should first be evaporated upon the water-bath to a semi-solid consistence, then transferred to a flask, about twice its weight of strong alcohol added, and digested upon the water-bath for about half an hour. The clear liquid is then poured off, and the residue digested twice or thrice successively in the same manner with alcohol. The entire amount of mixed alcoholic liquid is then filtered into a capsule, and evaporated upon the water-bath to the consistence of a soft extract; this is again treated with strong alcohol, and the alcoholic solution filtered and evaporated as before.

This latter residue is now treated with a small amount of cold water, and the slightly acid solution thus obtained filtered into a flask or other suitable glass vessel, and successively shaken with two or three times its volume of pure ether. The ethereal solutions, which have been separated as completely as possible from the aqueous liquid by means of a glass separating funnel, are then allowed to evaporate spontaneously.

I. *From the acid solution are hereby absorbed by ether:*

COLCHICINE.
DIGITALIN.
PICROTOXIN.
CANTHARIDIN.

(Also traces of *atropine* and *veratrine*, which, however, if present, will be subsequently extracted much more completely from the alkaline solution.)

The residue left by the evaporation of the ether from the acid solution, as previously described, is to be dissolved in a small amount of hot water, the solution filtered, and further examined for the above-named substances.

In order to avoid repetition, the description of all the more important alkaloids, together with the allied neutral principles and glucosides, will be reserved for the second part of this volume, where their physical properties and chemical characteristics will be fully detailed, and to which in searching for the above-named substances, reference should always be made. For this reason, but a limited number ot the more important individual reactions of these bodies will here be stated, when, if such be found to correspond with any one of the substances mentioned, and in order to exclude any possibility of error, its identity should be invariably confirmed by the other known tests.

Colchicine, if present, will be indicated by the yellow color of the solution; it is, moreover, precipitated by tannic acid and iodine solution, but by potassio-mercuric iodide only after being previously acidulated with a mineral acid. Chlorine-water produces a yellow precipitate, soluble in ammonia-water with an orange-yellow color. Concentrated nitric acid colors its solution violet, changing to red; if the nitric acid solution be diluted and made alkaline with sodium hydrate, an orange-red color is produced.

Digitalin, not properly an alkaloid but closely related by its properties, is precipitated by tannin only from a concentrated solution. When it is dissolved, in a capsule, with concentrated sulphuric acid, and a trace of bromine water is brought into the liquid, a violet-red color is produced. If a trace of digitalin, together with a little purified ox-gall, be dissolved in a little water, in a capsule, a small amount of concentrated sulphuric acid added, and warmed at from 60 to 80° C. (140 to 176° F.), the solution gradually assumes a fine red color.

Picrotoxin is not precipitated by tannin, nor by the other alkaloidal reagents. It may be readily obtained in a crystalline form from its solution in hot water or in alcohol. Its aqueous solution possesses an intensely bitter taste, and, when made alkaline with a few drops of sodium hydrate solution, reduces an alkaline solution of cupric oxide on heating.

Cantharidin does not afford the general reactions of alkaloids, and may be obtained in a crystalline form from its solution in ether or hot alcohol. It is very sparingly soluble in water, and, for want of characteristic chemical tests, may be extracted from the ethereal residue by fatty oils, and recognized by its vesicating properties.

The original acidulated, aqueous liquid, which has been subjected to the above treatment with ether, is subsequently gently warmed in order to expel the small amount of ether which remains dissolved therein, and solution of sodium hydrate in slight excess then added until, upon testing with litmus or turmeric-paper, a distinct alkaline reaction is obtained; the alkaloids are thus liberated from their combination, and are precipitated, or, as in the case of morphine, become re-dissolved by the excess of alkali. The alkaline liquid is then agitated twice or thrice successively with pure ether, allowing an interval of about half an hour to elapse before the separation of each portion of ether from the aqueous liquid, and finally the mixed ethereal liquids are allowed to evaporate spontaneously.

II. *From the alkaline solution are hereby absorbed by ether:*

(*a*) LIQUID AND VOLATILE.

NICOTINE.
CONIINE.

(*b*) SOLID AND PERMANENT.

STRYCHNINE,
BRUCINE.
VERATRINE.
ATROPINE,
ACONITINE,
DELPHININE,
NARCOTINE,
THEBAINE,
CODEINE,
PAPAVERINE,
HYOSCYAMINE,
PHYSOSTIGMINE,
EMETINE.

(Also, possibly, traces of *colchicine* and *digitalin*, which are difficult to abstract perfectly from the acid solution by means of ether.)

Before proceeding to apply the individual tests for the identification of the alkaloids, it is preferable first to test the residue which may be left by the evaporation of the ether, in order primarily to establish or confirm the presence or absence of such a body. This may be conveniently accomplished without loss of material, by placing a very small portion of the residue upon a watch-glass, together with a few drops of water, and then, by means of a glass rod, adding a trace of hydrochloric acid, in order to form a solution of the salt. A few drops of this solution may then be tested upon a glass or porcelain plate, with some of the general alkaloidal reagents, *e. g.*, potassio-mercuric iodide, iodine solution, tannic acid, platinic chloride, etc., adding a drop of the reagent by means of a glass rod, and, for better observing the formation of such precipitates with the reagents as are of a light color, the glass plate should be placed upon a piece of dark paper or other suitable object. With the attainment of a negative result by the use of these reagents no further examination need be made of the substance in question for an alkaloid, and much time and labor will, therefore, be saved.

If, however, the above general tests have revealed the presence of an alkaloid, small portions may then be taken for applying the most characteristic individual tests, commencing the search by testing for the more commonly occurring alkaloids of the list, and finally, in case of an affirmative reaction, confirming the result by the application of as many of the other well-known tests for the substance as may seem necessary to establish its identity, or as the usually limited supply of the substance may admit.

Nicotine, in case of the obtainment of a liquid residue by the evaporation of the ether, will be indicated by its strong narcotic odor. It is not precipitated by chlorine-water, and its aqueous solution does not become turbid on warming. When mixed with hydrochloric acid, and cautiously warmed, a reddish-brown mixture ensues, which, by further evaporation and cooling, gives upon the addition of nitric acid a violet color, gradually changing to orange.

Coniïne will be indicated by the strong, peculiar, and unpleasant odor of the obtained liquid residue. It is precipitated by chlorine-water, and its aqueous solution becomes turbid on gently warming. Dry hydrochloric acid gas produces first a purplish-red, and finally an indigo-blue color.

Strychnine dissolves in concentrated sulphuric acid, forming a colorless solution, which, upon the addition of a trace of potassium bichromate, assumes a bluish-violet color, changing to cherry-red, and rapidly fading. (Curarine produces a reaction somewhat similar to strychnine, but it is not absorbed by ether, either from an acid or an alkaline solution, and is further distinguished by other tests, which will be described under group III.)

Brucine produces with concentrated nitric acid an intense blood-red color, which soon changes to yellowish-red, and, upon gently warming, becomes yellow. If to this solution water then be added, it assumes, upon the addition of stannous chloride or ammonium sulphide (preferably freshly prepared), a beautiful violet color.

Veratrine dissolves in concentrated sulphuric acid with a yellow color, which, upon warming, changes to blood-red. It dissolves in concentrated hydrochloric acid, forming a colorless solution, which, upon warming, assumes a fine, permanent, dark-red hue.

Atropine, when heated with concentrated sulphuric acid and potassium bichromate or ammonium molybdate, develops the odor of bitter almond oil. When applied to the eye, it powerfully dilates the pupil.

Aconitine produces with concentrated phosphoric acid, upon warming, or slowly with concentrated sulphuric acid at ordinary temperatures, a violet color. (*Delphinine* produces a similar reaction with phosphoric acid, but gives also the digitalin reaction with sulphuric acid and bromine-water.)

Narcotine dissolves without color in concentrated sulphuric acid, but the solution soon becomes yellow, and, upon the addition of a trace of nitric acid, blood-red. Concentrated sulphuric acid, which contains a trace of sodium molybdate, produces a green color, but if the solution of molybdate be applied more concentrated, the green soon changes to a fine cherry-red. A freshly prepared solution of narcotine in dilute sulphuric acid (1 part of concentrated acid to 5 parts of water), when evaporated very gradually in a small porcelain capsule, produces a successive change of colors, becoming first orange-red, then on the edges bluish-violet, and finally, at the temperature at which the sulphuric acid begins to volatilize, intensely reddish-violet. Chlorine-water colors solutions of salts of narcotine greenish-yellow, which, upon the addition of a very little ammonia-water, changes to a transient cherry-red color.

Thebaine assumes with concentrated sulphuric acid a fine, deep blood-red color, which gradually changes to yellowish-red; with ammonium molybdate in concentrated sulphuric acid the same coloration is produced. Its solution in chlorine-water assumes upon the addition of ammonia-water an intense reddish-brown hue.

Codeine assumes with concentrated sulphuric acid which contains a trace of ferric oxide in solution, gradually at ordinary temperatures, or immediately upon warming, a beautiful indigo-blue color. When dissolved in concentrated sulphuric acid, one or two drops of a concentrated cane-sugar solution added, and gently warmed, a fine purplish-red color is produced.

Papaverine dissolves in cold concentrated sulphuric acid with a slight yellowish color, which, upon warming, changes to violet. The solution in chlorine-water is colored deep reddish-brown upon the addition of ammonia-water, after some time becoming almost blackish-brown. With concentrated sulphuric acid, containing a little ammonium molybdate in solution, it assumes a green color, which, upon warming, rapidly changes to blue, and finally becomes of a fine cherry-red.

Hyoscyamine, for want of any specially characteristic chemical reactions, may be best recognized by the physiological property, which it shares with atropine, of producing dilation of the pupil when applied to the eye. It is distinguished from atropine in being precipitated from its solutions by platinic chloride, if not applied in excess, whereas atropine is precipitated by this reagent only from relatively very concentrated solutions.

Physostigmine is characterized by its physiological property of producing contraction of the pupil when applied to the eye. Its aqueous solution assumes a reddish color upon the addition of a small amount of a solution of chlorinated lime, which, upon the further addition of the latter, becomes discharged.

Emetine is particularly characterized by its strongly emetic properties, which may be confirmed by experiments upon small animals, by the subcutaneous injection of its aqueous solution. Its nitrate is a very sparingly soluble salt. An aqueous solution of emetine assumes with a few drops of a freshly prepared, saturated solution of chlorinated lime, and the subsequent addition of one or two drops of hydrochloric or acetic acid, an orange or lemon-yellow color. Concentrated sulphuric acid dissolves emetine with the production of a green color, which soon changes to yellow.

It should be observed that veratrine also possesses violent emetic properties, but this alkaloid is so characterized by other special tests that it cannot be mistaken for emetine.

III. *Alkaloids remaining dissolved in the alkaline solution:*

MORPHINE,
NARCEINE,
CURARINE.

The alkaline liquid remaining after the extraction by ether for the obtainment of the alkaloids of group II. should first be gently warmed in order to expel the small amount of dissolved ether, then acidulated with hydrochloric acid, and subsequently made slightly alkaline with ammonia-water. The ammonical liquid is then treated at least twice successively with warm amylic alcohol, separating the latter liquid carefully from the aqueous solution, and allowing it to evaporate, either spontaneously, or by means of a gentle heat. The amylic alcohol will have thus abstracted the entire amount of morphine, and the larger portion of the narceine from the solution, whilst the remainder of the narceine and the entire amount of curarine still remain dissolved in the ammoniacal liquid. The residue left by the evaporation of the amylic alcohol should first be tested by the general reagents in order to ascertain the presence of an alkaloid, when, in case of an affirmative result, the special tests may be subsequently applied.

Morphine reduces iodine from a solution of iodic acid, which dissolves in carbon bisulphide or chloroform with a violet color. A neutral solution of morphine or its salts assumes with a small amount of a dilute neutral solution of ferric chloride a deep blue color. When dissolved in concentrated sulphuric acid, the solution gently warmed, allowed to cool, and then a trace of dilute nitric acid added, a deep blood-red color is produced.

Narceine assumes upon the addition of iodine-water an intense blue color. Its solution in concentrated sulphuric acid is of a grayish-brown color, which, upon warming, changes to blood-red. A solution of narceine in chlorine-water assumes also upon the addition of ammonia-water a blood-red color. (Narceine may be readily separated from morphine by its much greater solubility in hot water.)

For the separation of the remainder of the narceine (in case its presence should have been determined by the previous extraction with amylic alcohol), as also of the curarine, the alkaline liquid should be evaporated in a porcelain capsule upon the water-bath to dryness, the residue then reduced to powder, transferred to a flask, and digested for some hours with strong alcohol, with the aid of a gentle heat and frequent agitation. The liquid is then saturated with dry carbonic acid gas, in order to convert the free alkali into carbonate, afterwards brought upon a filter, the insoluble residue well washed with strong alcohol, and the alcoholic liquid finally evaporated. If this residue is found to be still too impure for the application of the tests, it should be treated with warm water, the aqueous solution filtered, and evaporated upon the water-bath, this residue again taken up with alcohol by the aid of a gentle heat, the solution filtered, and evaporated as before. In the alcoholic residue the narceine may be recognized by the previously-described tests, whilst the curarine may be readily abstracted therefrom by means of cold water, in which it is freely soluble.

Curarine, as previously stated, page 109, produces with sulphuric acid and potassium bichromate a reaction somewhat similar to strychnine, but the coloration is more of a bluish tint, and much more permanent. It dissolves in concentrated sulphuric acid with a pale violet color, which gradually changes to a dirty red, and, after some hours, assumes a rose-red color. With potassium bichromate it forms a quite sparingly soluble salt, analogous to the strychnine chromate, differing, however, from the latter by its amorphous character.

It is of particular importance in testing for alkaloids, especially when contained in complex organic mixtures, to obtain them in the purest possible state, as slight impurities may, according to their nature, either altogether conceal, or materially influence the characteristic reactions upon which the recognition of the substance depends.

In order to effect the purification of the alkaloids when contaminated with adhering coloring matter, etc., as also for the separation of the individual alkaloids from each other, recourse must be had to the distinctions in their physical and chemical properties, such as behavior towards the simple solvents, or the production of sparingly soluble simple salts, etc., from which the pure alkaloid, if desired, can again be obtained.

It should also be made a rule in the application of the tests to employ the smallest possible quantity of substance, as the reactions from their delicacy are usually quite as well obtained as with larger quantities, even should the amount of material at disposition be considerable, which, however, in forensic research is rarely, if ever, the case; and the amount of the reagent added should always be proportionate to the amount of the substance to be tested. For the observance of such reactions as depend upon the production or change of color, a small porcelain plate or capsule will be found the most serviceable, applying the reagent, when required in but small quantity, by means of a glass rod or small pipette (Fig. 57).

FIG. 57.

In the preceding briefly described course for the systematic separation of the alkaloids, it will be evident that only the more commonly occurring bodies of this class, and such as possess toxic properties, have been considered, whilst such as are non-poisonous in their character, as, *e. g.*, caffeine, the cinchona alkaloids, etc., have been intentionally omitted, as not properly included within the province of forensic chemistry. Should the presence of such a body, however, be presumed or suspected in the substance under examination, a consideration of its deportment towards ether or other solvents, in acid or alkaline solution, will at once indicate the method to be adopted for its isolation, after the accomplishment of which, the proper tests for its identification may be applied.

For the separation of the alkaloids when associated with other organic or inorganic poisons, such as hydrocyanic acid, phosphorus, arsenic, metallic salts, etc., which may likewise be the object of search, special methods of manipulation and precautions are required to be observed, in order that none of the substances shall undergo decomposition, or escape detection in the process of extraction, or that the correctness of the result may be thereby impaired.

Investigations of this character, therefore, should only be entrusted to the experienced expert, possessing special knowledge of the properties and deportment of the bodies in question, which from their importance are too extended in their scope to admit of a more detailed consideration in this place, although the characteristic and most reliable tests for the recognition of the above mentioned, and the more commonly occurring organic and inorganic poisons, will receive further attention in their appropriate places in the second part of this volume, and the methods indicated whereby their isolation may be effected.

PART II.

THE MEDICINAL CHEMICALS

AND

THEIR PREPARATIONS,

THEIR

PHYSICAL AND CHEMICAL CHARACTERISTICS,

WITH DIRECTIONS FOR THE

EXAMINATION OF THEIR QUALITY AND PURITY, AND FOR
THEIR QUANTITATIVE ESTIMATION.

THE

MEDICINAL CHEMICALS

AND THEIR PREPARATIONS.

ACETUM.

Vinegar.

Ger. Essig; Fr. Vinaigre; Sp. Vinagre.

VINEGAR, as obtained by the acetic fermentation of dilute alcoholic liquids, presents considerable variation in its physical characters, such as color, odor, taste, etc., imparting properties which in most instances are unobjectionable, and are frequently desired in its employment for domestic purposes, while they do not always render it inadmissible for pharmaceutical applications. It must, however, form a perfectly transparent liquid, possessing a true acetic odor, free from empyreuma, and should contain no metallic impurities or acrid vegetable substance, as also no free inorganic or other foreign acids, with which it is not unfrequently adulterated for the purpose of increasing its strength.

Vinegar contains, on an average, from 4.5 to 6 per cent. of true acetic acid. The British Pharmacopœia requires a spec. grav. of 1.017 to 1.019, corresponding to 4.6 per cent. of absolute acetic acid. The Pharmacopœia Germanica requires that 10 cubic centimeters of vinegar neutralize 10 cubic centimeters of normal solution of potassium hydrate, corresponding to 6 per cent. of absolute acetic acid.

Examination:

Free mineral acids are readily detected by adding to 20 cubic centimeters of the vinegar, about 4 or 5 cubic centimeters of strong ammonia-water, and evaporating in a shallow glass capsule on the water-bath. If the vinegar is pure, a slight yellow or brownish residue will remain, whereas in the presence of free mineral acids, or with tartaric and citric acids, a crystalline mass is obtained. As the ammonium salts are readily volatilized on heating, and the tartrate and citrate become thereby carbonized, the presence of fixed impurities may at the same time be determined.

The presence of mineral acids may be also readily detected as follows: A solution of ferric acetate is diluted with water to such an extent as to appear slightly yellowish, and a small amount of ammonium or potassium sulphocyanide dissolved therein, when no red coloration will be produced, even upon the addition of acetic acid; the smallest trace of free sulphuric, nitric, or hydrochloric acids, however, produces an intense red coloration, which may be rendered still more evident by shaking the liquid with ether, when the latter will absorb the red ferric sulphocyanide.

Another method consists in mixing a freshly prepared solution of pure ferrous sulphate, free from oxide, with a solution of gallic acid in cold water, which has been previously well boiled; to the colorless liquid thus obtained a little sodium acetate is added, and subsequently a small portion of the vinegar to be tested. The violet coloration produced by sodium acetate is destroyed by the presence of mere traces of free mineral acid, but is not affected by acetic acid.

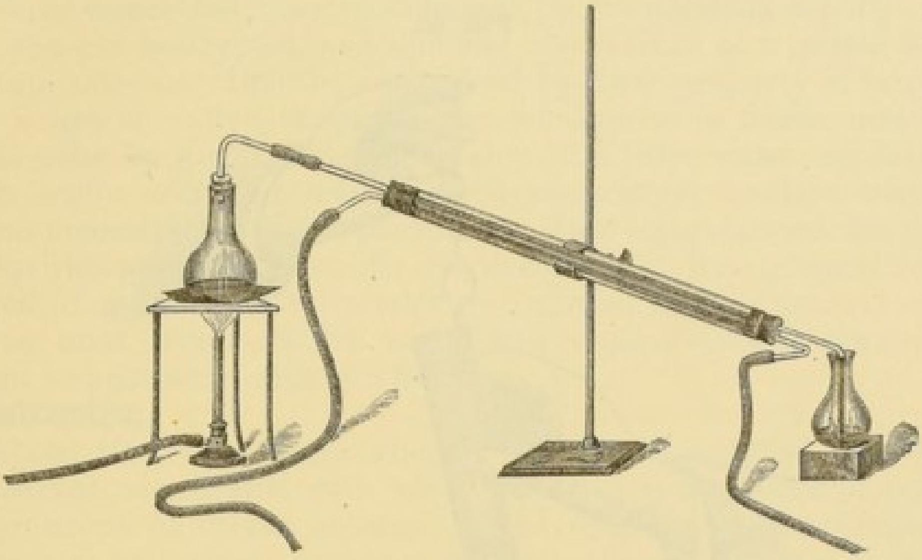
Sulphuric and Hydrochloric Acids.—A crude mode of detecting the presence of sulphuric acid in vinegar consists in the addition of a little cane-sugar to a small portion of it, and evaporating the solution, at a gentle heat, in a porcelain capsule, to the consistence of a thick syrup; this will become almost black if free sulphuric acid be present.

Since the water and the materials used for the preparation of vinegar generally contain traces of sulphates and chlorides, most vinegar yields a slight turbidity with barium and argentic nitrates. An undue proportion of sulphuric or hydrochloric acid may, however, be readily detected by adding to 20 grams of the vinegar 0.5 cubic centimeter of solution of barium nitrate and 1 cubic centimeter of decinormal solution of argentic nitrate, and filtering; the filtrate should afford no turbidity upon the subsequent addition of either barium or argentic nitrates.

The presence of sulphuric acid may also be detected, or verified, by adding to a portion of vinegar, contained in a test-tube, a saturated solution of calcium chloride, and subsequently heating to boiling; if, upon cooling, a cloudiness or a precipitate of calcium sulphate is produced, the presence of free sulphuric acid will be verified. Oxalic acid would also yield a white precipitate, but may be distinguished by affording a precipitate with a solution of calcium sulphate.

The presence of hydrochloric acid, in the free state, will be detected or verified by submitting a portion of the vinegar to distillation (Fig. 58), changing the receiver when about one-fourth of the liquid has distilled over, and reserving this portion for examination for aldehyde, and afterward continuing the distillation until nearly the entire amount of liquid has passed over; the second portion of the distillate is then acidulated with nitric acid, and tested with argentic nitrate, when a white, curdy precipitate, insoluble in nitric acid, but soluble in ammonia-water, will prove the presence of hydrochloric acid.

FIG. 58.

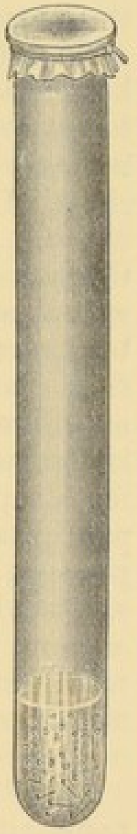


Aldehyde, if present, will be indicated in the first or reserved portion of the distillate by its peculiar and unpleasant odor, and may be recognized by its property of reducing metallic silver from a solution of the nitrate; by the formation of a crystalline compound when shaken with an alkaline bisulphite; and by a yellow or brown coloration, or formation of resinous bodies, when mixed with a strong solution of a caustic alkali, and gently heated.

Sulphurous acid and *sulphites* may be detected by adding a portion of the vinegar to a few fragments of zinc and a little dilute sulphuric acid, contained in a test-tube, and placing over the orifice of the tube a small cap of white, bibulous paper, moistened with a drop of solution of plumbic acetate (Fig. 59); if sulphurous acid be present, hydrogen sulphide will be evolved, and cause the production of a black stain upon the paper.

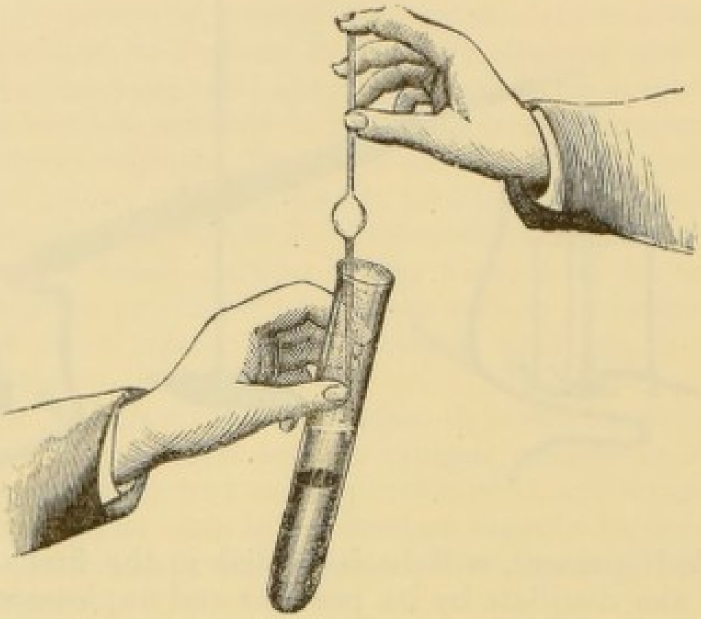
Nitric acid may be detected by adding a drop of indigo solution to a small portion of the vinegar, contained in a test-tube, and heating, when decoloration of the liquid will indicate free nitric acid; if, upon heating, the original tint of the liquid remains permanent, a few drops of concentrated sulphuric acid should be added, and the liquid again heated, when decoloration of the liquid after this addition will indicate the presence of nitrates. The test may also be made by mixing carefully, in a test-tube, 2 volumes of the vine-

FIG. 59.



gar with 1 volume of concentrated sulphuric acid, and subsequently adding 1 volume of a concentrated solution of ferrous sulphate, so as to form two layers (Fig. 60); a brown or violet colored zone at the line of contact of the two liquids will reveal the presence of nitric acid or nitrates.

FIG. 60.



Metallic impurities are detected by saturating the vinegar with hydrogen sulphide, and allowing the liquid to stand for a few hours in a closed vessel; if a white turbidity is produced, it will indicate zinc or sulphurous acid, the latter giving rise to the deposition of sulphur, whereas a brown or black precipitate may indicate tin, lead, or copper. The precipitate may be examined for the latter metals by collecting it on a filter, washing with a little water, and digesting with ammonium sulphide; sulphide of *tin* will become thereby dissolved, and, after filtration, may be precipitated from its solution on the addition of an excess of hydrochloric acid as yellow stannic sulphide. The portion of the precipitate insoluble in ammonium sulphide is dissolved in a little nitric acid, and a few drops of dilute sulphuric acid added, when an ensuing white precipitate will indicate *lead;* after the removal of the latter, if present, by filtration, ammonia-water is added, in slight excess, when a blue coloration of the liquid will reveal the presence of *copper*. Other metallic impurities than those here mentioned, which may accidentally be present, may be sought for or determined according to the systematic method of analysis, as described on pages 51 to 61.

Acrid vegetable substances may be recognized by their odor and taste, either in the residue obtained by the direct evaporation of a portion of the vinegar, or by previously neutralizing the latter with magnesium or sodium carbonate, filtering, and subsequently evaporating the filtrate, at a gentle heat, to about one-third of its volume.

Fixed impurities may be detected by evaporating a portion of the vinegar to dryness, and igniting the residue at a gentle heat; sodium salts may then be recognized by their property of imparting a bright yellow color to the non-luminous flame, and calcium salts by dissolving the residue in a little water, acidulated with acetic acid, and testing with ammonium oxalate, when a white precipitate will be produced. This examination for fixed impurities may also serve for the detection of free mineral acids, which, if present, would render the ignited residue neutral in its action upon litmus, whilst with pure vinegar it will always be found to possess an alkaline reaction.

Estimation:

About 10 grams of the vinegar, accurately weighed in a flask or beaker, are diluted with about 50 cubic centimeters of water, a few drops of litmus solution added, and a normal solution of potassium or sodium hydrate, page 87, allowed to flow into the liquid from a burette, until a slight excess above that required for the perfect neutralization of the liquid has been employed, and the liquid assumes a distinct bluish tint; the excess of alkali is then inversely titrated with normal nitric acid until a permanent red coloration is produced. From the difference between the number of cubic centimeters of alkali and acid employed, the number of cubic centimeters of normal alkali required for the perfect neutralization of the liquid is given, and from this the acetic strength of the vinegar may be calculated; one cubic centimeter of normal alkali corresponding to 0.06 gram of absolute acetic acid.

As vinegar is frequently more or less colored, the transition of color of the litmus from blue to red is not always clearly perceptible, and in this case it is better to omit the litmus entirely, titrating the excess of alkali first added by means of normal nitric acid as before, until a drop of the liquid, removed by means of a glass rod, after repeated testing, no longer produces a brown zone upon turmeric paper, which thus proves the perfect neutralization of the free alkali.

Should free sulphuric or hydrochloric acid be present in the vinegar, these must be separately estimated by precipitating small portions of the vinegar with barium chloride or argentic nitrate; from the amount of barium sulphate or argentic chloride thus obtained, the equivalent amount of free sulphuric or hydrochloric acid may be determined, and the result of the calculation of the acetic estimation correspondingly corrected.

ACIDUM ACETICUM.

Acetic Acid.

Ger. Essigsäure; Fr. Acide acétique; Sp. Acido acético.

$$C_2H_4O_2 = CH_3\text{-}CO\text{-}OH;\ 60.$$

Acetic acid, when free from water, forms at or below 15° C. (59° F.) large, colorless, transparent, tabular crystals of the rhombic system (Glacial Acetic Acid), which melt at 17° C. (62.6° F.), to a colorless, limpid liquid, of a pungent odor, and strongly acid reaction. The acid containing much water does not crystallize even at 0° C. (32° F.). The specific gravity of the pure liquid acid is 1.056 to 1.058, at 15° C. (59° F.); it boils at 118° C. (244.4° F.), emitting very pungent and acid, inflammable vapors, which burn with a blue flame.

Acetic acid is miscible in all proportions with water, alcohol, and ether, and dissolves albumen, fibrin, camphor, and many resins, gum-resins, and essential oils; diluted with water, it forms the commercial and medicinal acetic acids, which maintain the character of acetic acid as long as the admixture of water does not exceed 18 to 19 per cent., beyond which dilution the acid loses more or less the character of a strong acid, and its solvent properties for the above mentioned substances.

In addition to the glacial acid (Acidum Aceticum Glaciale), two strengths of acetic acid are officinal: Acidum Aceticum of the spec. grav. of 1.048 (1.044 British Pharmac., 1.064 Pharm. German.), and Acidum Aceticum Dilutum of the spec. grav. of 1.0083 (1.006 British Pharmac., 1.041 Pharmac. German.). The strong acid of 1.048 spec. grav. contains 36 per cent. of absolute acetic acid, or 30.6 per cent. of acetic anhydride, and 6 grams of it require for neutralization 36 cubic centimeters of volumetric solution of potassium or sodium hydrate, or 100 parts are neutralized by 60 parts of crystallized potassium bicarbonate; the diluted acid of 1.0083 spec. grav. contains 6 per cent. of absolute acetic acid, corresponding to 5.10 per cent. of acetic anhydride, and 24 grams of it require for neutralization 24 cubic centimeters of volumetric solution of potassium or sodium hydrate, or 100 parts are neutralized by 10 parts of crystallized potassium bicarbonate.

Acetic acid is recognized in its soluble salts, or in the free state, after previous neutralization with an alkali, by the production of a deep-red color on the addition of a few drops of solution of ferric chloride; this coloration is discharged on strongly acidulating the solution with sulphuric acid, or by boiling, in the latter case the iron being completely precipitated as a basic salt. The acid may also be recognized, when not too dilute, by the odor of acetic ether, when heated with a mixture of equal parts of alcohol and concentrated sulphuric acid.

Examination:

Glacial acetic acid may be tested for water by mixing 10 parts of it with 1 part of fresh or unaltered lemon oil, when a perfectly clear solution should be formed. A much better method, however, for the determination of the presence of small quantities of water consists in mixing equal parts of the acid and carbon bisulphide in a small dry test-tube, which is inclosed in the hand; when maintained at this temperature for a few moments, a perfectly clear mixture should result, whilst the smallest amount of water will produce a cloudiness in the liquid. The other tests of purity are the same as those applied for the examination of the diluted acids, as follows:

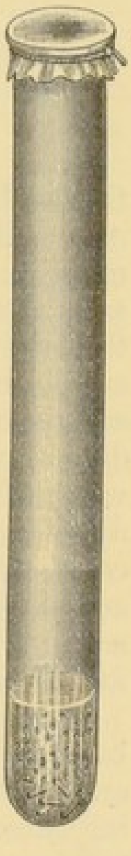
Empyreumatic substances will be rendered evident by their odor, and, when present in but small amount, may be also recognized by neutralizing a little of the acid with solution of potassium hydrate, and subsequently tingeing the solution faintly with potassium permanganate; the color should not be sensibly changed by standing five minutes at the ordinary temperature.

Organic impurities may be recognized by an ensuing dark coloration, when the acid is mixed with an equal volume of concentrated sulphuric acid, and subsequently heated to boiling.

Sulphuric and *hydrochloric acids* may be detected by an ensuing white precipitate, when the diluted acid is tested, in separate portions, with barium nitrate or chloride, and with argentic nitrate.

Sulphurous acid is indicated by a greenish coloration, when a little of the acid is heated with a few drops of solution of potassium bichromate; it may also be recognized by adding a portion of the acid to a few fragments of zinc and a little dilute sulphuric acid, contained in a test-tube, and placing over the orifice of the tube a small cap of white, bibulous paper, moistened with a drop of solution of plumbic acetate (Fig. 61); if sulphurous acid be present, hydrogen sulphide will be evolved, and cause the production of a black stain upon the paper.

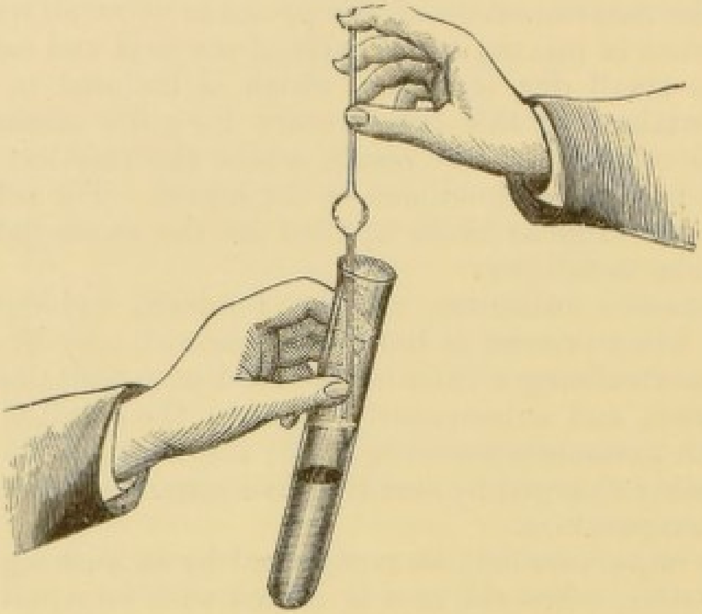
Fig. 61.



Nitric acid may be detected by the decoloration of the liquid, when the acid is tinged slightly blue with indigo solution, and heated; or by mixing the acid with an equal volume of concentrated sulphuric acid, and subsequently carefully adding to the cooled mixture a concentrated solution of ferrous sulphate, so as to form two layers (Fig. 62); a brown or reddish-brown zone at the line of contact of the two liquids will reveal the presence of nitric acid.

Metallic impurities are recognized by a turbidity or precipitate upon saturating the acid with hydrogen sulphide, or upon subsequent supersaturation with ammonia-water. If a brown or black precipitate is produced by hydrogen sulphide, it may indicate tin, lead, or copper, and may be further examined by collecting it on a filter, washing with a little water, and digesting with ammonium sulphide; sulphide of *tin* will become thereby dissolved, and, after filtration, may be reprecipitated from its solution by the addition of an excess of hydrochloric acid as yellow stannic sulphide. The portion of the precipitate insoluble in ammonium sulphide is dissolved in a little nitric acid, and a few drops of dilute sulphuric acid added, when an ensuing white precipitate will indicate *lead;* after the removal of the latter, if present, by filtration, ammonia-water is added in slight excess, when a blue coloration of the liquid will reveal the presence of *copper*. If the acid, after saturation with hydrogen sulphide, and filtering, yields a black precipitate upon subsequent supersaturation with ammonia-water, the presence of *iron* is indicated.

FIG. 62.



Pure acetic acid should leave no residue upon evaporation; a brownish-colored residue would indicate foreign organic matters, and, upon subsequent ignition, a permanent white residue will indicate salts of the inorganic bases, sodium, calcium, etc. If the residue, when heated on a platinum wire, imparts a bright-yellow color to the non-luminous flame, *sodium* salts will be indicated, and, when subsequently dissolved in water, the solution acidulated with a few drops of acetic acid, and tested with ammonium oxalate, an ensuing white precipitate will indicate *calcium* salts.

Estimation:

In consequence of the existing anomaly between the specific gravity of acetic acid and its strength, the hydrometer does not always give a correct indication of the latter; the specific gravity being increased to a certain extent upon the dilution of the acid, in consequence of contraction, as will be seen by reference to the subjoined table.

Thus an acid containing from 77 to 80 per cent. of absolute acetic acid has the highest specific gravity, 1.0748 at 15° C. (59° F.), above which strength it again decreases similarly as upon dilution, so that the anhydrous acid and an acid containing 43 per cent. of absolute acid have the same specific gravity at 15° C. (59° F.), viz., 1.055. It will be seen, however, that a specific gravity below 1.0552 can only apply to an acid containing less than 43 per cent. of absolute acetic acid.

The strength of acetic acid may be determined by observing the exact quantity of crystallized potassium bicarbonate required to saturate a known weight of the acid, and by subsequent equation, see page 122; or by the following process of volumetric analysis:

Five grams of the acid, accurately weighed in a flask or beaker, are diluted with about 10 times its volume of water, a few drops of litmus solution added, and a normal solution of potassium or sodium hydrate (page 87) allowed to flow into the liquid from a burette until, with constant stirring, the liquid assumes a distinct bluish tint. From the number of cubic centimeters of alkali solution required for the exact neutralization of the liquid, the percentage strength of the acid may be readily calculated: 1 cubic centimeter of normal alkali corresponding to 0.06 gram of absolute acetic acid.

Instead of the employment of a normal solution of potassium or sodium hydrate, as above described, very accurate results may also be obtained by the addition of so much of a measured volume of baryta-water of known strength to a weighed quantity of acid, as to be slightly in excess of that required for its exact neutralization, and subsequently determining the excess employed by means of a normal acid; the point of exact neutralization being determined by means of turmeric paper, which, by the delicacy of its reaction with baryta-water, will indicate the slightest excess of the latter by the production of a brown coloration. From the amount of baryta-water, of previously ascertained strength, required to neutralize a definite amount of acid, the percentage strength of the acid may be readily calculated: 1 part of barium hydrate, $Ba(OH)_2$, corresponding to 0.7017 part of absolute acetic acid, $C_2H_4O_2$.

TABLE *of the quantity by weight of absolute Acetic Acid contained in* 100 *parts by weight of aqueous Acetic Acid of different specific gravities* (*Oudemans*).

Temperature at 15° C. (59° F.).

Specific gravity.	Per cent. of acetic acid.	Specific gravity.	Per cent. of acetic acid.	Specific gravity.	Per cent. of acetic acid.	Specific gravity.	Per cent. of acetic acid.
1.0007	1	1.0363	26	1.0623	51	1.0747	76
1.0022	2	1.0375	27	1.0631	52	1.0748	77
1.0037	3	1.0388	28	1.0638	53	1.0748	78
1.0052	4	1.0400	29	1.0646	54	1.0748	79
1.0067	5	1.0412	30	1.0653	55	1.0748	80
1.0083	6	1.0424	31	1.0660	56	1.0747	81
1.0098	7	1.0436	32	1.0666	57	1.0746	82
1.0113	8	1.0447	33	1.0673	58	1.0744	83
1.0127	9	1.0459	34	1.0679	59	1.0742	84
1.0142	10	1.0470	35	1.0685	60	1.0739	85
1.0157	11	1.0481	36	1.0691	61	1.0736	86
1.0171	12	1.0492	37	1.0697	62	1.0731	87
1.0185	13	1.0502	38	1.0702	63	1.0726	88
1.0200	14	1.0513	39	1.0707	64	1.0720	89
1.0214	15	1.0523	40	1.0712	65	1.0713	90
1.0228	16	1 0533	41	1.0717	66	1.0705	91
1.0242	17	1.0543	42	1.0721	67	1 0696	92
1.0256	18	1.0552	43	1.0725	68	1.0686	93
1.0270	19	1.0562	44	1.0729	69	1.0674	94
1.0284	20	1.0571	45	1.0733	70	1.0660	95
1.0298	21	1.0580	46	1.0737	71	1.0644	96
1.0311	22	1.0589	47	1.0740	72	1.0625	97
1.0324	23	1.0598	48	1.0742	73	1.0604	98
1.0337	24	1.0607	49	1.0744	74	1.0580	99
1.0350	25	1.0615	50	1.0746	75	1.0553	100

ACIDUM ARSENIOSUM.

ACIDUM ARSENICOSUM. ARSENICUM ALBUM.

Arsenious Acid. White Arsenic. Arsenious Oxide.

Ger. Arsenige Säure ; Fr. Acide arsénieux ; Sp. Acido arsenioso.

As_2O_3;* 197.8.

A heavy, white solid, occurring either in transparent or semi-transparent masses, which usually have a striated appearance, or as a white, crystalline powder. In the crystalline condition it is dimorphous, presenting either the form of octahedra or tetrahedra of the regular system (Fig. 63), which are obtained by the condensation of its vapor under ordinary circumstances, or by crys-

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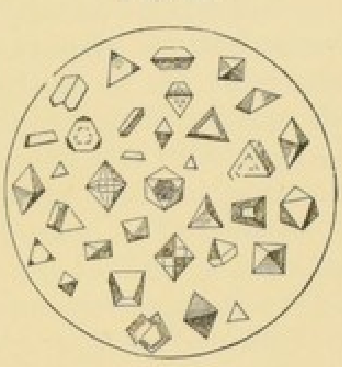
* According to the determinations of the vapor density of arsenious oxide, its molecular composition is more correctly expressed by the formula As_4O_6.

tallization from its solution in water or hydrochloric acid; or the form of rhombic prisms, which are occasionally deposited in the roasting furnaces, and are also obtained when hot saturated solutions of arsenious acid, in solution of potassium hydrate or arsenic acid, are allowed to evaporate slowly.

When freshly prepared by sublimation it forms heavy, transparent, glassy cakes, with a smooth conchoidal fracture, and has a spec. grav. of 3.738; this becomes gradually opaque and porcelain-like by passing into the crystalline state, which change proceeds from the surface toward the interior; at the same time its specific gravity is slightly diminished (3.689), and its solubility in water increased. In consequence of the simultaneous occurrence of the amorphous and the crystalline modifications, and the difference in their solubility, the statements of the solubility of arsenious acid in water are slightly at variance.

FIG. 63.



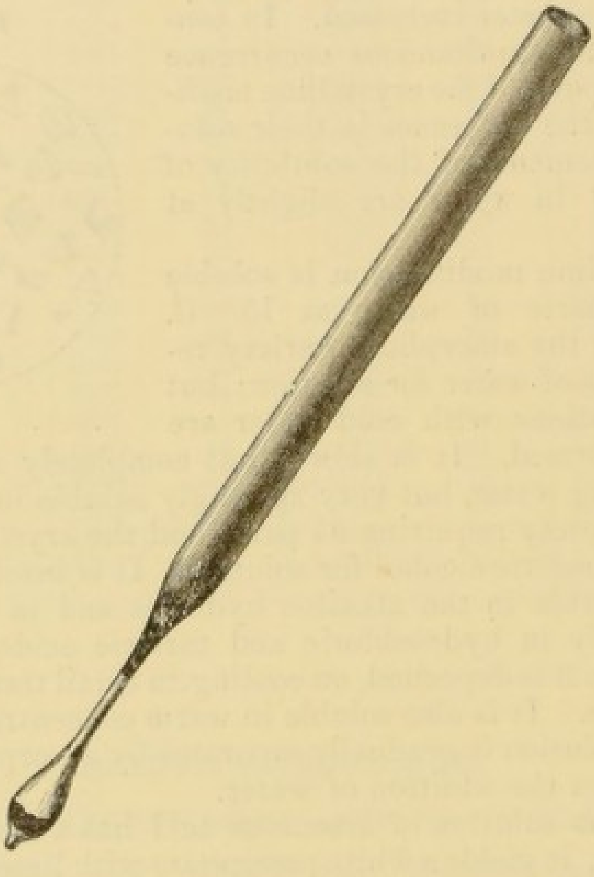
The crystalline modification is soluble in about 9 parts of water at 15° C. (59° F.), while the amorphous variety requires 25 parts of water for solution; but saturated solutions with cold water are very slowly formed. It is slowly but completely soluble in 15 parts of boiling water, but very sparingly soluble in alcohol; the amorphous variety requiring 94 parts, and the crystalline variety 400 parts of absolute alcohol for solution. It is insoluble in ether, but freely soluble in the alkaline hydrates and in warm diluted acids, especially in hydrochloric and tartaric acids, from which latter solutions it is deposited, on cooling, in small transparent octahedral crystals. It is also soluble in warm concentrated glycerin, from which solution it gradually separates by absorption of water, or at once upon the addition of water.

The aqueous solution of arsenious acid has a feeble acid reaction on litmus; it yields a white precipitate with lime-water, which is soluble in ammonium chloride; and, after acidulating with hydrochloric acid, a yellow precipitate with hydrogen sulphide, which is soluble in ammonia-water or in ammonium sulphide, but insoluble in hydrochloric acid. Argentic nitrate and cupric sulphate produce only a turbidity in an aqueous solution of arsenious acid; upon exact neutralization with ammonia-water, however, a yellow precipitate is formed with the former reagent, and a brilliant green one with the latter, both precipitates being soluble in an excess of ammonia-water or of acid.

Arsenious acid, when heated in an open tube, volatilizes at about 218° C. (424.4° F.) without fusion, forming a colorless, inodorous vapor, which condenses, on cooling, in small, transparent, and brilliant, octahedral crystals. When heated in contact with reducing agents, such as a mixture of equal parts of fused sodium carbonate and potassium cyanide, or with carbon, the acid is reduced to metallic arsenic, which, when the reduction is performed in a glass tube, sublimes and is deposited in the form of a bright metallic incrustation, emitting at the same time a peculiar and characteristic odor somewhat similar to garlic.

For the reduction of arsenious acid by means of the previously mentioned mixture of sodium carbonate and potassium cyanide, the form of tube shown in Fig. 64 is the most suitable.

Fig. 64.



The arsenious acid is first brought into the bulb of the tube, and the powdered and perfectly dry mixture of equal parts of sodium carbonate and potassium cyanide then added in such an amount that the bulb of the tube shall be filled to not more than half its capacity. The upper portion of the tube should be made perfectly clean by means of a narrow strip of bibulous paper or a small camel's-hair brush, and the bulb at first gently heated, in order to expel all traces of moisture, which may also be removed by means of bibulous paper, after which the contents of the tube are heated to fusion, when the reduced arsenic will form a bright metallic mirror in the narrow part of the tube.

This method of reduction is also applicable to the arseniates and to the yellow arsenious sulphide.

The reduction of arsenious acid by carbon is best effected in a small tube, drawn out at one end to a narrow point, as shown in Fig. 65.

Fig. 65.

The small particles of arsenious acid are placed in the point of the tube, and above them a splinter of previously ignited wood-charcoal, as shown in the figure. The portion of the tube containing the charcoal is first heated to redness, maintaining the tube in a nearly horizontal position, after which the tube is gradually inclined, and finally brought into a nearly vertical position, so that the point of the tube becomes also heated. The vapor of the arsenious acid in passing over the red-hot carbon is reduced to the metallic state, and deposited above the carbon in the form of a bright metallic mirror. After cooling, the carbon may be removed from the tube, and the metallic arsenic heated for itself, when, if the amount be quite small, it will be oxidized for the most part in the act of volatilization to arsenious oxide, forming a white sublimate of small, shining, octahedral crystals in the upper part of the tube, and readily distinguishable by the aid of a lens.

A solution of arsenious acid in contact with nascent hydrogen, as developed by the action of dilute sulphuric acid on metallic zinc or magnesium, gives rise to the formation of hydrogen arsenide, which, when ignited, burns with a bluish-white flame, and emits, when considerable arsenic is present, dense white clouds of arsenious oxide; when a piece of cold white porcelain is held in the flame, shining brown or black spots of metallic arsenic are deposited (*Marsh's* test). For further details relating to the application of this test, see pages 33 to 36.

When a solution of arsenious acid is mixed with an excess of concentrated hydrochloric acid, and a piece of bright copper-foil or wire immersed in the liquid, and boiled, a dark gray metallic film, consisting of a compound of copper and arsenic, Cu_5As_2, is deposited upon the copper. If the copper-foil or wire be now removed from the liquid, well washed with water, carefully dried, and then strongly heated in a perfectly dry test-tube, the arsenic will become volatilized, and at the same time oxidized to arsenious acid, forming a sublimate of small, brilliant, octahedral crystals in the upper part of the tube (*Reinsch's* test).

When the same test is made as the preceding, with the employment of pure tin-foil, or stannous chloride, instead of copper, the tin becomes likewise coated with arsenic, and at the same time a more or less voluminous brown deposit is formed (*Bettendorf's* test). To insure success, concentrated hydrochloric acid, and a very small quantity of the arsenical solution must be employed, as the presence of much water prevents the reaction.

Examination of Powdered White Arsenic:

When a small portion of the powder is heated in a glass tube, it should be completely volatilized, and form a colorless sublimate, which will prove its freedom from admixture with metallic arsenic or arsenious sulphide; and when dissolved in warm concentrated sulphuric acid, it should form a perfectly colorless solution, which will prove the absence of organic substances.

Earthy admixtures are recognized by a non-volatile residue when a little of the white arsenic is strongly heated on platinum-foil, or by an insoluble residue when heated with a solution of potassium hydrate or hydrochloric acid. When a residue is obtained by either of these tests, it is collected on a filter, washed with a little water, and, after drying, mixed and fused in a porcelain crucible with four times its weight of a mixture of equal parts of exsiccated sodium and potassium carbonates; the obtained fused mass is triturated and boiled with a sufficient quantity of water, and the filtered solution, after acidulation with nitric acid, tested with barium nitrate for sulphates (calcium and barium sulphates). The residue on the filter is washed with water, and treated with warm diluted hydrochloric acid, and the filtrate subsequently tested with sodium sulphate for *barium*, and, in another portion, neutralized with ammonia-water, with ammonium oxalate for *calcium*.

Ammonium salts will be recognized by the development of the odor of ammonia, when a small portion of the arsenious acid is heated, in a test-tube, with an excess of a strong solution of potassium hydrate, and by the formation of white fumes when a glass rod, moistened with acetic acid, is subsequently held over the orifice of the tube.

Chlorides may be detected by treating a portion of the arsenious acid with concentrated nitric acid until complete solution is effected, and red nitrous fumes cease to be evolved, and subsequently adding to the acid solution, slightly diluted with water, a few drops of solution of argentic nitrate, when a white precipitate, soluble in ammonia-water, will prove the presence of chlorides.

Estimation:

I. One gram of arsenious acid, As_2O_3, when dissolved in warm diluted hydrochloric acid, yields, upon complete precipitation with hydrogen sulphide, a precipitate of arsenious sulphide, As_2S_3, which, when collected upon a tared filter, washed, and dried, should weigh 1.24 grams.

II. One gram of arsenious acid, As_2O_3, is dissolved, by the aid of heat, in dilute hydrochloric acid, and potassium chlorate, in small portions, from time to time added, finally continuing the heat until all free chlorine is expelled; the arsenious acid is thus converted into arsenic acid, which, after dilution with water, may be precipitated by test magnesium mixture, as crystalline, ammonio-magnesium arseniate, $NH_4MgAsO_4 + 6H_2O$. The precipitate, after standing for twenty-four hours, is collected upon a tared filter, which has been previously dried at 105° C. (221° F.), washed with a mixture of three parts of water and one part of ammonia-water, and dried first at 100° C. (212° F.), and finally at 105° C. (221° F.), until of constant weight. Its composition is then represented by the formula $NH_4MgAsO_4 + \frac{1}{2}H_2O$, and 100 parts correspond to 39.47 parts of metallic arsenic, or 52.11 parts of arsenious acid, As_2O_3.

III. The estimation of arsenious acid may also be very accurately and quickly accomplished volumetrically by the following process: 0.1 gram of the acid is accurately weighed, and dissolved in 20 cubic centimeters of boiling water, with the addition of about one gram of pure sodium bicarbonate. To the solution, when cold, a little mucilage of starch is added, and a standard decinormal solution of iodine, page 93, allowed to flow into the liquid from a burette until, after well stirring, a permanent blue coloration is produced. The amount of pure iodine equivalent to the number of cubic centimeters employed may then be calculated, and therefrom its equivalent in pure arsenic trioxide; 508 parts of iodine being equivalent to 198 parts of arsenious oxide, as shown by the equation:

$$\underbrace{2I_2}_{508} + \underbrace{As_2O_3}_{198} + 5H_2O = 4HI + 2H_3AsO_4,$$

or as follows:

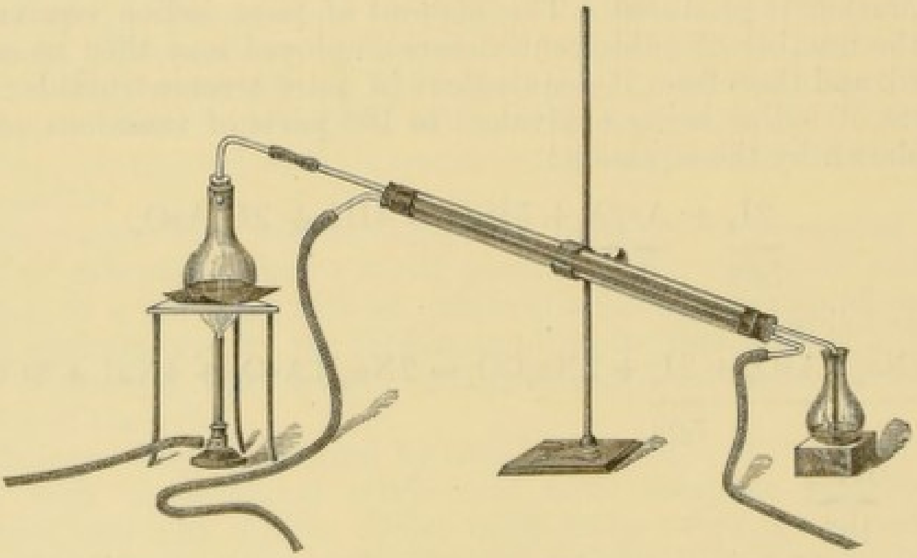
$$\underbrace{2Na_2HAsO_3}_{\substack{\| \\ \underbrace{As_2O_3}_{198}}} + \underbrace{2I_2}_{508} + 2Na_2CO_3 = 2Na_2HAsO_4 + 4NaI + 2CO_2.$$

The calculation may also be made with the consideration that one cubic centimeter of the volumetric solution of iodine, if exactly decinormal, corresponds to 0.00495 gram of pure arsenious oxide, As_2O_3.

The United States Pharmacopœia directs that if 0.247 gram of arsenious acid be dissolved, with 0.5 gram of sodium bicarbonate, in boiling water, the solution should decolorize not less than 48.5 cubic centimeters of the volumetric solution of iodine (corresponding to at least 97 per cent. of pure arsenious acid).

Separation and Detection of Arsenic in Forensic Investigations.—Arsenious acid, from the fact of being one of the more commonly employed and readily obtainable poisons, is sometimes the cause of accidental or intentional poisoning, and therefore becomes not unfrequently the object of search in forensic investigations. In consequence of the sparing solubility of arsenious acid in aqueous liquids, it may frequently, in cases of poisoning, be found adhering to the coatings of the stomach or intestines, or in the vomited matters. In all cases, however, it should be carefully searched for among the folds and in the inflamed portions of the stomach and intestines, when, if thus found, and after purification by washing with a small amount of cold water, it may be at once identified by subjecting it to the several tests already mentioned. Should the direct isolation of the arsenious acid in substance prove unsuccessful, other methods for ascertaining its presence must be then resorted to. The organic matters, as finely divided as possible, are brought into a flask or retort provided with a condenser and well cooled receiver, fused common salt or pure rock salt, and a quantity of pure sulphuric acid not sufficient to decompose the entire amount of the salt, are then added, and the mixture subjected to distillation (Fig. 66). In the presence of arsenic, the very volatile and poisonous arsenic trichloride, $AsCl_3$, is formed, which, in the presence of water, is decomposed into arsenious and hydrochloric acids: $2AsCl_3 + 3H_2O = As_2O_3 + 6HCl$. The distillate thus obtained, which contains the arsenic in quite a pure state, may be at once precipitated by hydrogen sulphide, or employed in part for the application of the previously described tests.

FIG. 66.



The above method for the separation of the arsenic is only applicable, however, when present in the form of arsenious acid or its salts; and in order to ascertain the presence of arsenical compounds in general, which may possibly be accompanied also by other poisonous metallic compounds, the following method may be resorted to.

The substance under examination, in the finest possible state of division, is first deprived as completely as possible of organic matter, an operation which is most effectually and conveniently accomplished by first placing it in a large porcelain dish, and diluting it with sufficient water to form a thin paste. Concentrated hydrochloric acid, equal in amount to the volume of substance, and a few grams of potassium chlorate are then added, and the mixture heated upon the water-bath; the addition of potassium chlorate being from time to time renewed, and the evaporated water or expended acid being also renewed, if necessary, until finally the mixture assumes the form of a thin, homogeneous, yellowish liquid. A small additional quantity of potassium chlorate may now be added, and the mixture again heated until the odor of chlorine entirely disappears. The solution, which should still possess a strong acid reaction, is then filtered into a small flask, and, after heating to about 60–80° C. (140–176° F.), saturated with hydrogen sulphide, the flask loosely stoppered, and allowed to stand in a warm place for about twenty-four hours. If the odor of the gas should have disappeared after standing, the solution must be again warmed, and subsequently again saturated with hydrogen sulphide, until complete precipitation is finally effected. The precipitate thus obtained is collected on a filter, washed with water previously saturated with hydrogen sulphide, and, in consideration of the possible presence of the sulphides of other metals than arsenic, digested with ammonium sulphide. The solution thus obtained is brought upon a filter, and the filtrate, together with the washings, evaporated in a porcelain capsule, by the aid of a gentle heat, to dryness. The residue is then treated with concentrated nitric acid, and the obtained solution evaporated at a gentle heat until the residue no longer shows a dark coloration, but in a moist condition appears of a yellowish hue. A small quantity of pure sodium hydrate, sufficient to neutralize the free acid, is then added, the mixture evaporated to dryness, subsequently mixed with the proper quantity of a mixture of one part of fused sodium carbonate and two parts of sodium nitrate, and brought into a small porcelain crucible, and, with a gradually increased temperature, heated to fusion. The fused mass, which will contain the arsenic in the form of soluble sodium arseniate, is treated with water, the soluble portion filtered off, and the residue washed with water containing a little alcohol, when any antimony present will remain behind as insoluble sodium antimoniate. To the arsenical solution a small quantity of sodium bicarbonate is added, or preferably carbonic acid gas is passed into the solution, in order to separate any traces of tin which may have become dissolved, and the solution filtered. The solution is now strongly acidulated with dilute sulphuric acid, and carefully evaporated, at a gentle heat in a porcelain capsule, until vapors of sulphuric acid begin to appear, in order to effect the removal of the nitric and nitrous acids. The residue in the capsule, which will form a colorless, strongly acid liquid, is to be diluted with water, and is then adapted for the application of the several tests. If a quantitative estimation of the arsenic is desired, it may be either precipitated from the warm solution directly, or, after previous reduction by means of sulphurous acid, as arsenic trisulphide, and weighed as such; or precipitated in the form of the crystalline ammonio-magnesium arseniate by the addition of test magnesium mixture. 100 parts of arsenic trisulphide, As_2S_3, when dried at 100° C. (212° F.), correspond to 80.49 parts of arsenious oxide, As_2O_3, or 61 parts of metallic arsenic; and 100 parts of ammonio-magnesium arseniate, $NH_4MgAsO_4 + \frac{1}{2}H_2O$, dried at 105° C. (221° F.), correspond to 52.11 parts of arsenious oxide, As_2O_3, or 39.47 parts of metallic arsenic.

Detection of Arsenic in Coloring-matters, Wall-paper, Fabrics, etc.—The employment of arsenic in the preparation of some of the aniline colors, and the application of Scheele's Green (cupric arsenite) or Schweinfurth Green (cupric arsenite and acetate) in painting, paper staining, etc., often renders the examination of various materials and products for arsenic necessary or desirable. The following method, which is simple and accurate, will admit of general application:

The material to be examined is finely divided, and, when possible, the coloring-matter separated from the material (wood, paper, cotton, wool, silk, etc.) to which it is attached. It is then brought into a porcelain capsule, concentrated hydrochloric acid and a little potassium chlorate added, and gradually heated upon the water-bath. The organic substances will thereby become completely destroyed and dissolved, or, after the complete oxidation of the coloring-matter, may be mechanically removed from the capsule. A little potassium chlorate is occasionally added to the solution, which is further heated on the water-bath, and finally evaporated to dryness, to effect the complete removal of the free chlorine. The residue is then dissolved in water with the addition of a little dilute sulphuric acid, and finally examined in Marsh's apparatus, as described on pages 33 to 36.

Another method consists in digesting the material to be examined, or the coloring-matter removed therefrom, with hydrochloric acid, spec. grav. 1.12, for about one hour, subsequently warming gently, and finally heating a portion of the liquid thus obtained, in a test-tube, with a concentrated solution of stannous chloride, or a piece of pure tin-foil; if arsenic be present a brown coloration, or a brownish-black precipitate, will be produced. As a confirmative test the precipitate may be collected on a small filter, washed with a little dilute hydrochloric acid, subsequently dissolved in nitric acid, and the filtered solution evaporated at a gentle heat, in a porcelain capsule, to dryness. The residue, dissolved in a little water, is then adapted for further examination by the application of Marsh's test.

If the article under examination is suspected to contain Schweinfurth or Scheele's Green, a small portion may be digested with ammonia-water, which will thereby assume a deep blue color. A portion of the ammoniacal solution, after acidulation with dilute sulphuric acid, may then be tested in Marsh's apparatus for arsenic, and another portion, acidulated with hydrochloric acid, tested with potassium ferrocyanide, when a reddish-brown coloration will reveal the presence of copper.

ACIDUM BENZOICUM.

ACIDUM BENZOICUM SUBLIMATUM. FLORES BENZOES.

Benzoic Acid. Phenyl-formic Acid. Benzol-carbonic Acid.

Ger. Benzoësäure ; Fr. Acide benzoique ; Sp. Ácido benzoico.

$C_7H_6O_2 = C_6H_5\text{-}CO\text{-}OH$; 122.

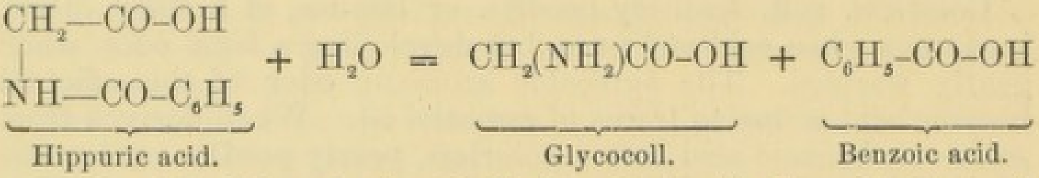
Colorless, soft, feathery needles, or laminæ, of a silky lustre, inodorous when cold and pure, but developing a faint odor when gently warmed. The agreeable aromatic odor of the officinal benzoic acid is due to traces of essential oil. When derived from solutions, benzoic acid forms colorless, pearly needles or laminæ of six-sided prisms. When warmed, the acid begins to volatilize below 100° C. (212° F.), and melts at 121 C. (249.8° F.), forming a colorless liquid, which, on cooling, solidifies to a mass of radiating crystals; at 145° C. (293° F.) it volatilizes freely, and at 249–250° C. (480.2–482° F.) boils, without decomposition, emitting acrid and irritating, inflamable vapors. When heated with water, it is also volatilized to a certain extent with the aqueous vapor; and when heated with an excess of freshly slaked lime, benzol is evolved.

Benzoic acid is soluble in 500 parts of water at 15° C. (59° F.), and in 15 parts of boiling water, the solutions possessing an acid reaction ; it is also soluble in 3 parts of cold, and 1 part of boiling, alcohol, in 3 parts of ether, 7 parts of chloroform, and freely soluble in carbon bisulphide, warm petroleum benzin, glycerin, and many volatile and fatty oils, as also in solutions of the alkaline hydrates. Concentrated sulphuric acid dissolves benzoic acid readily, without decomposition, and without coloration, if pure, the officinal acid producing a slight brownish coloration ; on the addition of water it is precipitated unchanged. A concentrated aqueous solution of benzoic acid, when carefully neutralized by ammonia-water, produces, on the addition of a solution of ferric chloride or sulphate, a reddish-yellow or flesh-colored precipitate of basic ferric benzoate, which dissolves on the addition of a small quantity of warm hydrochloric acid, and, upon cooling, benzoic acid is again separated, re-dissolving on the addition of alcohol or ether.

Pure benzoic acid does not melt under water, but certain impurities, even when present in but small amount, impart to it this property, at the same time rendering it more freely soluble in water, and causing the formation of smaller crystals. These observations formerly led to the incorrect acceptance of the existence of different modifications of the acid, as derived from different sources; a supposition which is not in harmony with the present views of the constitution of benzol derivatives, according to which, but one mono-substitution product of benzol is capable of existence, whilst the error of the conclusion may be also demonstrated by the purification of such an acid, either by distillation with aqueous vapor, treatment with potassium permanganate, or other means, when a product possessing all the physical and chemical properties of the pure acid will be obtained.

Examination:

Hippuric acid, as is well known, is resolved by the action of hydrochloric acid, and other agents, into benzoic acid and glycocoll, and much benzoic acid is obtained from this source.



$$\underbrace{\begin{matrix}CH_2\text{—}CO\text{-}OH\\ |\\ NH\text{—}CO\text{-}C_6H_5\end{matrix}}_{\text{Hippuric acid.}} + H_2O = \underbrace{CH_2(NH_2)CO\text{-}OH}_{\text{Glycocoll.}} + \underbrace{C_6H_5\text{-}CO\text{-}OH}_{\text{Benzoic acid.}}$$

Such acid, although chemically identical with the acid obtained from benzoin or other sources, is usually accompanied by an unpleasant, persistent odor, which renders it objectionable for pharmaceutical or medicinal purposes unless further purified, or the characteristic and agreeable odor of the officinal acid subsequently imparted to it by mixing with a portion of benzoin, and subjecting it to sublimation.

Hippuric acid may be distinguished from, or recognized in, benzoic acid, by heating, in a test-tube, a small portion of the acid with about twice its weight of dry potassium hydrate, and a little water; if hippuric acid is present, it will be indicated by the odor of ammonia, as also by the formation of white vapors, when a glass rod, moistened with acetic acid, is held over the orifice of the tube. It may also be recognized by forming a very dark colored or black solution when warmed with concentrated sulphuric acid; and when heated for itself in a glass tube an odor resembling that of bitter almond oil is produced, accompanied by the final production of a black, carbonaceous, or resinous like residue.

Chloro-benzoic acid may be recognized by mixing a small portion of the acid with a little recently ignited and moistened cupric oxide, and introducing the mixture, contained on the looped end of a platinum-wire, in the non-luminous flame; a green or bluish-green color imparted to the flame would indicate a contamination with chlorinated compounds.

Cinnamic acid may be detected by the development of the odor of bitter-almond oil, when a small portion of the acid is gently heated in a test-tube, with an equal quantity of potassium bichromate and sulphuric acid, and allowed to cool; or when gently heated with about an equal quantity of potassium permanganate and a little water.

Salicylic acid may be detected by the production of a violet coloration upon the addition of a drop of a solution of ferric chloride to the aqueous solution of the acid.

Boric acid may be recognized by the green coloration of the flame of burning alcohol, previously saturated with the acid.

Oxalic acid may be readily detected by its much greater solubility in cold water, and, when subsequently neutralized by ammonia-water, a white precipitate of calcium oxalate will be produced on the addition of a solution of calcium sulphate.

Mineral substances, not readily volatilizable or soluble in alcohol, may at once be detected by a residue left on volatilization, as well as upon solution of the acid in alcohol. If any fixed residue is left, it may be dissolved in warm water acidulated with nitric acid, and tested with barium nitrate for sulphates, and with argentic nitrate for chlorides, and, after neutralization with ammonia-water, with the latter reagent for phosphates.

ACIDUM BORICUM.

Boric Acid. Ortho-boric Acid. Boracic Acid.

Ger. Borsäure; Fr. Acide boracique; Sp. Ácido bórico.

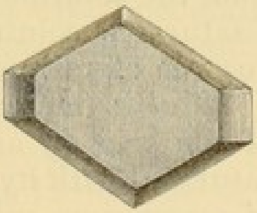
$$H_3BO_3 = B(OH)_3;\ 62.$$

Colorless, translucent, shining, six-sided laminæ (Fig. 67) belonging to the tri-clinic system, permanent in the air, and somewhat unctuous to the touch. Its specific gravity is 1.4347 at 15° C. (59° F.).

Boric acid is soluble in 25 parts of cold, and in 3 parts of boiling, water. The solution has but little taste; it feebly affects blue litmus-paper, but imparts to turmeric-paper a reddish-brown tint, which becomes more distinct after drying.*

The acid is also soluble in 15 parts of cold, and in 5 parts of boiling, alcohol, and the

FIG. 67.



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* A similar coloration is produced by alkalies with turmeric paper, but the color disappears on the addition of hydrochloric acid, whilst that produced by boric acid remains unaltered.

solution burns, when ignited, with a flame tinged with green. The same green tint may be observed when the acid is dissolved in warm concentrated glycerin, the latter heated to boiling, and the vapors then ignited, or when a small portion of the acid, contained on the looped end of a platinum-wire, is brought into the fusion zone of a non-luminous flame. The salts of copper and thallium, as also some organic compounds, impart a green coloration to the flame, but these are usually readily distinguished by other physical or chemical characters.

When boric acid is heated to 100° C. (212° F.), it parts with 1 molecule of water of constitution (not crystallization), and is converted into *meta-boric acid*, $BO(OH)$; if heated for some time at 140° C. (284° F.), *pyro-boric acid*, $B_4O_5(OH)_2$ is formed, which may be considered as produced from 4 molecules of the ordinary or ortho-boric acid, by the abstraction of 5 molecules of water, $4B(OH)_3 - 5H_2O = B_4O_5(OH)_2$. This acid, which is dibasic, forms very stable salts, of which the ordinary borax may be taken as a representative. If boric acid be heated to redness, a further decomposition takes place, by which from 2 molecules of the acid 3 molecules of water are abstracted (corresponding to a loss of 43.55 per cent. in weight), and *boron trioxide*, B_2O_3, is obtained.

$$2B(OH)_3 - 3H_2O = B_2O_3.$$

This forms a glassy, transparent, and very hygroscopic solid, which readily unites with water to form boric acid. It possesses the property of dissolving most metallic oxides at a red heat, which frequently impart characteristic colors to the mass, and thus render it, or the more commonly employed borax, a valuable agent in blow-pipe analysis.

Examination:

A small portion of the crystals of boric acid is added to five times its weight of water in a test-tube, and heated; a clear and complete solution must take place, and, when part of the hot solution is dropped into alcohol, no turbidity or precipitate must ensue; otherwise the presence of admixtures insoluble or less soluble in water or alcohol is indicated.

It should dissolve in warm concentrated sulphuric acid without disengagement of gas bubbles, and without coloration, and, when cold, the solution should afford no coloration upon the addition of a saturated solution of ferrous sulphate, which would prove the absence of nitrates.

Metallic impurities may be recognized in the aqueous solution of the acid by an ensuing dark coloration or a precipitate when saturated with hydrogen sulphide, or upon the subsequent addition of ammonium sulphide.

Calcium and Sodium Salts.—The former may be detected in the aqueous solution of the acid by an ensuing white precipitate when tested with ammonium oxalate, and the latter by heating a fragment of the acid, contained on the looped end of a platinum-wire, in the non-luminous flame; a persistent yellow color imparted to the flame would indicate the presence of sodium salts or borax.

Chlorides and *sulphates* are detected in the aqueous solution, acidulated with nitric acid, by white precipitates, when tested with argentic nitrate and barium nitrate respectively.

Estimation:

The estimation of free boric acid may be accomplished by adding an accurately weighed quantity of pure, fused sodium carbonate (about 2 parts of carbonate to 1 part of acid), evaporating to dryness, after the addition of the carbonate, if the acid should be in the form of solution, finally heating the residue to the point of fusion, and, when cold, determining its weight. The amount of carbonic acid contained in the fused mass is now determined, as described on page 86, and, from the difference in the amount of carbonic acid contained in the weighed quantity of carbonate taken, and that determined after fusion with the acid, the amount of carbonic acid expelled by the boric acid is ascertained, from which the equivalent amount of boric acid may readily be calculated.

ACIDUM CARBOLICUM.

Carbolic Acid, or Phenic Acid. Phenol. Phenylic Alcohol. Hydroxyl-benzol.

Ger. Carbolsäure ; Fr. Acide carbolique ; Sp. Ácido carbólico.

$$C_6H_6O = C_6H_5\text{–}OH; \ 94.$$

Long, colorless, prismatic needles, or crystalline masses, possessing a peculiar distinctive odor, and a sharp, burning taste, and having the specific gravity of 1.065 at 18° C. (64.4° F.). When perfectly pure, as obtained by re-crystallization from warm petroleum benzin or other solvents, it undergoes no change, melts at 44° C. (111.2° F.) to an oily, colorless liquid, and boils at 187° C. (368.6° F.); but, when slightly impure, or through the influence of certain agencies, as, for instance, ammonia-gas, it assumes a more or less pinkish tint, absorbs moisture on exposure to the air, and gradually deliquesces. The commercial acid usually contains a small quantity of cresol, and probably also other homologous phenols, which, however, do not materially modify its essential properties or value; but the melting-point and factor of solubility of the pure acid in water become thereby slightly decreased.

Carbolic acid is soluble in 20 parts of water at 15° C. (59° F.); with about one-tenth of its weight of water it forms a crystallizable hydrate $(C_6H_5\text{–}OH)_2 + H_2O$, which remains liquid at temperatures above 16° C. (60.8° F.), and which is rendered turbid by the further addition of water until 20 parts have been added, when a clear and complete solution is formed. It is freely soluble in alcohol, ether, chloroform, carbon bisulphide, glycerin, acetic acid, solutions of the alkaline hydrates, and the volatile and fatty oils. Its aqueous solution has no action upon test-paper, coagulates albumen and collodion (distinction from creasote), and assumes a permanent violet-blue color upon the addition of a few drops of a dilute neutral solution of ferric chloride; with bromine, in the form of vapor or in aqueous solution, it yields a flocculent, white precipitate of the very sparingly soluble tribrom-phenol, $C_6H_2Br_3$–OH, which, by re-crystallization from alcohol, may be obtained in the form of long, fine, colorless needles.

Carbolic acid is miscible with concentrated sulphuric acid, with slight evolution of heat, and forms therewith two isomeric sulphonic acids of the composition $C_6H_4(SO_3H)OH$; these are distinguished and may be separated from each other by the difference in solubility of their salts (sulpho-carbolates, sulpho-phenates), which usually crystallize with great facility. By the action of an excess of concentrated nitric acid, carbolic acid yields bright yellow, shining, prismatic crystals or laminæ of trinitro-phenol (picric acid), $C\,H_2(NO_2)_3OH$.

The presence of very small amounts of carbolic acid may be recognized or detected by the following characteristic reactions and tests: When an aqueous solution of carbolic acid, to which a small quantity of ammonia-water has been added, is brought in contact with the vapor of bromine, a bright blue coloration is produced. This reaction is so delicate, that if the ammoniacal solution of the acid, contained in a test-tube or small porcelain capsule, be thrown out, a sufficient quantity will still adhere to the sides of the vessel to produce in contact with the vapor of bromine the characteristic blue color.

An aqueous solution of carbolic acid assumes, upon the addition of a little mercurous nitrate and a trace of nitric acid, and heating, an intense red color, with the separation of metallic mercury.

If to one or two cubic centimeters of pure concentrated sulphuric acid, contained in a test-tube, an equal volume of an aqueous solution of carbolic acid (1 : 500) is carefully added, and a small crystal of potassium nitrate subsequently allowed to fall into the liquid, a violet coloration will be produced, which is changed to orange-red upon the addition of water.

Examination:

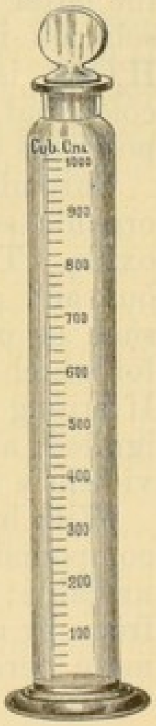
The quality of carbolic acid is sufficiently recognized by the above characteristics, by its odor, and by its appearance; in order to detect admixtures, the liquified acid may be tested by mixing it with twice its volume of solution of potassium hydrate, and warming the mixture by immersing the test-tube in boiling water; a complete solution should be formed, which, when cold, should remain limpid, and not separate any oily liquid upon dilution with three times its bulk of water.

Creasote and *cresylic acid*, or *cresol*, may be likewise detected by adding to the liquefied acid, containing 5 per cent. of water, an equal volume of glycerin; a perfectly clear mixture should be formed, which should not be rendered turbid by the subsequent addition of 3 volumes of water, otherwise an undue amount of the above-mentioned impurities will be indicated.

Estimation:

The estimation of pure carbolic acid in an impure product may be accomplished by dissolving a few grams of it in a porcelain capsule, by the aid of heat, in a solution of potassium or sodium hydrate, evaporating the solution to dryness, heating to a temperature not exceeding 170° C. (338° F.), and dissolving the residue in about ten times its weight of water. To the filtered solution, sufficient dilute hydrochloric or sulphuric acid is added to liberate the combined carbolic acid, which may then be separated by means of a pipette, washed with a saturated solution of common salt, and finally deprived of water by means of fragments of calcium chloride, after which it may be introduced into a dry glass vessel, and weighed; or, after purification, the aqueous solution of the carbolic acid may be precipitated by bromine-water, in the form of the sparingly soluble tribrom-phenol, $C_6H_2Br_3.OH$, the precipitate then collected upon a filter, washed with a very small amount of water, and dried at a temperature not exceeding 90° C. (194° F.). One hundred parts of this compound correspond to 28.40 parts of pure carbolic acid.

Fig. 68.



The estimation of carbolic acid may also be effected with considerable accuracy volumetrically, by a process which likewise depends upon the formation of the sparingly soluble tribrom-phenol. Bromine-water (the strength of which has been previously determined separately by adding an excess of potassium iodide to a measured portion, and estimating the liberated iodine by means of a standard solution of sodium hyposulphite, page 94) is added, in slight excess, to a known amount of an aqueous solution of the carbolic acid; the number of cubic centimeters of bromine-water required are then noted, and, after the separation of the tribrom-phenol by filtration, an excess of potassium iodide is added to the filtrate, and the liberated iodine, which bears a direct proportion to the excess of bromine employed, estimated with standard solution of sodium hyposulphite, as described on page 94. The first reaction is expressed by the equation:

$$\underbrace{C_6H_5\text{-}OH}_{94} + \underbrace{6Br}_{480} = C_6H_2Br_3.OH + 3HBr.$$

As 480 parts of bromine thus correspond to 94 parts of carbolic acid, the amount of pure carbolic acid contained in a weighed quantity of the acid, or in a measured quantity of its aqueous solution, may readily be calculated.

The amount of water contained in solutions of carbolic acid may be determined by agitating it, in a graduated cylinder (Fig. 68), with an equal volume of chloroform, and allowing the mixture to repose until it separates into two layers; the upper layer will consist of the water originally present in the solution.

ACIDUM CHROMICUM.

Chromic Acid. Chromic Anhydride. Chromium Trioxide.

Ger. Chromsäure; Fr. Acide chromique; Sp. Ácido crómico.

CrO_3; 100.4.

Long, scarlet, rhombic prisms, of considerable lustre, or masses of loose, bright red, acicular crystals; very deliquescent, and therefore frequently presenting a moist appearance. Its specific gravity is 2.819 at 20° C. (68° F.). At 193° C. (379.4° F.) it melts to a dark red liquid, which, on cooling, solidifies to a reddish-black, crystalline mass, having a metallic appearance; at temperatures above 250° C. (482° F.) it is decomposed into chromium sesquioxide, Cr_2O_3, and oxygen: $2CrO_3 = Cr_2O_3 + O_3$. Chromic acid dissolves readily and without decomposition in water, cold diluted alcohol, and in pure ether; it also dissolves in glacial acetic acid, and in concentrated sulphuric acid, but not in the latter when containing from 16 to 17 per cent. of water. Its solution in water, in which the presence of true chromic acid, H_2CrO_4, is assumed, is, when concentrated, of a yellowish-brown color, but, on further dilution, it assumes a pure yellow color, and possesses an acid reaction and an acid and astringent taste.

Chromic acid is a powerful oxidizing agent, decomposing most organic substances, and becoming readily reduced to chromic oxide. This reduction is effected by hydrogen sulphide, sulphurous and arsenious acids, as also by various organic substances, such as oxalic acid, sugar, paper, etc., particularly on warming, for which reason its solution cannot be filtered through paper. If strong alcohol be poured upon the acid, the alcohol becomes ignited, and, when dissolved in glycerin, the mixture explodes violently upon agitation.

With hydrogen peroxide, chromic acid forms an intensely blue compound, of not yet ascertained composition, which is very unstable; it is soluble in water, and may be extracted therefrom by agitation with ether. A somewhat similar and much more permanent blue coloration is produced when an alcoholic tincture of guaiacum wood is added to a dilute aqueous solution of chromic acid, and is best observed by allowing the liquids to form two layers, when the coloration will appear at the point of contact. By means of this easily applied reaction exceedingly small amounts of chromic acid may be recognized, although it should be remembered that other oxidizing agents show a similar behavior. An aqueous solution of chromic acid, after the addition of a few drops of hydrochloric acid and a few drops of alcohol, assumes, upon heating, a bright green color, with the evolution of etherial vapors. A similar green coloration is immediately produced by concentrated hydrochloric acid, or by the action of the reducing agents previously mentioned, such as sulphurous acid, hydrogen sulphide, ferrous salts, etc.

Examination:

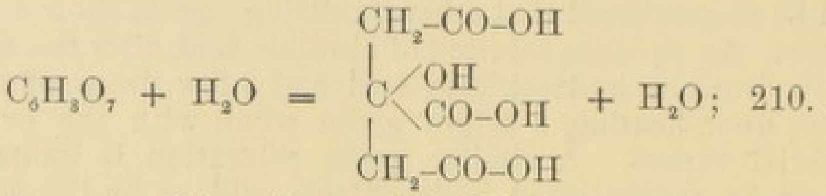
Sulphuric acid may be detected by boiling a diluted solution of the acid, to which a few drops of hydrochloric acid and a little alcohol have been added, until the liquid appears green. It is then tested with barium chloride, when an ensuing white precipitate will indicate the presence of sulphuric acid. Traces of sulphuric acid, from the difficulty of effecting its complete removal, will usually be found, and the following test may serve to establish its limit for pharmaceutical application. One gram of chromic acid is dissolved in 100 cubic centimeters of cold water, and the solution mixed with 10 cubic centimeters of hydrochloric acid; the further addition of 1 cubic centimeter of test-solution of barium chloride should cause not more than a white turbidity.

Potassium bichromate or *sulphate*, which should not be present in any considerable amount, may be detected by igniting a portion of the acid in a platinum crucible, and extracting the residual chromic oxide with boiling water. A portion of the neutral solution is then tested with barium chloride, when a yellow precipitate, insoluble in acetic, but soluble in hydrochloric, acid, will prove the presence of chromate; another portion, previously acidulated with hydrochloric acid, will, with the same reagent, yield a white precipitate, if sulphate be present.

ACIDUM CITRICUM.

Citric Acid.

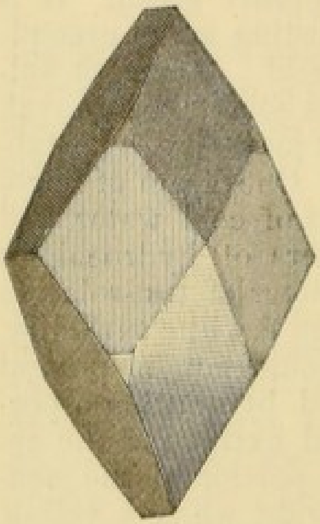
Ger. Citronensäure; Fr. Acide citrique; Sp. Acido cítrico.



$$C_6H_8O_7 + H_2O = \begin{array}{l} CH_2\text{-}CO\text{-}OH \\ \mid \\ C\left\langle\begin{array}{l} OH \\ CO\text{-}OH \end{array}\right. \\ \mid \\ CH_2\text{-}CO\text{-}OH \end{array} + H_2O;\ 210.$$

Colorless, rhombic prisms, with dihedral summits (Fig. 69), containing one molecule (8.6 per cent.) of water of crystallization, and having the specific gravity 1.617. They are permanent in the air, but slightly efflorescent in a dry and warm atmosphere, and becoming moist in a damp one, and possess an agreeable, purely acid taste, and an acid reaction.

Fig. 69.



The acid melts at 100° C. (212° F.) in its water of crystallization, and, when deprived of water, at 153 to 154° C. (307.4 to 309.2° F.). Exposed to a strong heat, the acid first fuses, and afterwards becomes decomposed, with the separation of carbon, and the evolution of carbon monoxide, carbon dioxide, acetone, and empyreumatic acid vapors, finally becoming wholly dissipated. It dissolves in concentrated sulphuric acid on gently warming, at first without coloration, and with the rapid evolution of carbon monoxide and carbon dioxide gases, but afterwards becomes blackened, with the development of sulphurous acid vapors.

Citric acid is soluble in 0.75 part of cold, and in 0.5 part of boiling, water, in 1 part of alcohol at 15° C. (59° F.), and in 0.5 part of boiling alcohol, and in 48 parts of ether; it is nearly insoluble in absolute ether, chloroform, benzol, and benzin. Its aqueous solution possesses a strongly acid taste and reaction, and, when exposed to the air, is subject to gradual and spontaneous change.

When citric acid, with about three times its weight of ammonia-water, contained in a sealed tube, is allowed to repose for some weeks at about 100° C. (212° F.), and the solution then allowed to evaporate slowly in a shallow open vessel, it assumes a beautiful deep blue color.

Citric acid forms no precipitate with potassium salts (except the tartrates), and, when sparingly added to lime-water, so that the alkaline reaction still predominates, it does not render it turbid (distinction from oxalic, tartaric, and racemic acids); when, however, the liquid is warmed and agitated, it becomes turbid, but transparent again upon cooling.

Examination:

In order to obtain an average sample of the crystallized acid for examination, it is advisable to reduce to powder a considerable portion of the crystals, and to make from a small portion of the powder two solutions: an aqueous one, in the proportion of 1 part of the acid to 2 parts of water; and an alcoholic one, in the proportion of 1 part of acid to 4 parts of alcohol. Both the solutions should be complete and clear.

Tartaric acid is detected by the formation of a granular white precipitate, when 2 parts by measure of the above aqueous solution and 1 part by measure of the alcoholic solution are mixed together, and agitated with 1 part by measure of a concentrated solution of potassium acetate. The presence of more than 1 per cent. of tartaric acid may be ascertained by the ensuing darkening of the liquid within five minutes, when one gram of citric acid is dissolved, without heat, in 10 cubic centimeters of a cold, saturated solution of potassium bichromate.

When many samples of the crystallized acid have to be examined, the following method is also applicable:

A large glass pane is placed upon blue or dark-brown paper on a horizontal table or board; a solution of potassium hydrate in diluted alcohol (1 part of dry potassium hydrate in 20 parts of distilled water and 10 parts of strong alcohol) is then spread over the pane as thick as will remain stationary upon it; a number of crystals and fragments of the acid are now placed from one to two inches apart, in this liquid, the crystals of each sample separate. Instead of a glass pane, small plates may be employed. Agitation being carefully avoided, the citric acid crystals, after several minutes' action of the alkaline solution, appear clearer and more transparent; if crystals of tartaric acid be present, they will be recognized by their cloudy and white appearance; after two or three hours, the crystals of citric acid are nearly or quite dissolved, and in their stead is frequently left a small, delicate, dust-like spot (due to traces of calcium salts); if crystals of tartaric acid be present, they will appear whitish, covered with a coat of small transparent acicular crystals, and surrounded by a deposit of small overlapping groups of similar crystals, or a thin, though broad, crystalline film (all crystals of potassium bitartrate).

Metallic impurities may be detected in the aqueous solution by a dark coloration or turbidity with hydrogen sulphide; if it be so considerable as to form a deposit, this is collected and washed upon a filter, and then dissolved in a few drops of warm nitric acid; to the obtained solution a few drops of dilute sulphuric acid are added, when a white precipitate will indicate *lead;* after the removal of the latter by filtration, the liquid, upon supersaturation with ammonia-water, will assume a blue color if *copper* be present.

Sulphates may be detected in the diluted aqueous solution, to which a few drops of diluted nitric acid have been added, by a white precipitate with barium nitrate.

Oxalic acid will be indicated in the aqueous solution by a white precipitate, soluble in hydrochloric acid, upon the addition of a solution of calcium sulphate.

Calcium salts, traces of which are usually present in the commercial acid, will be detected by the production of a white precipitate or an opalescence upon the addition of a solution of ammonium oxalate.

Estimation:

One hundred parts of citric acid neutralize 98.57 parts of dry, anhydrous potassium carbonate, 142.85 parts of potassium bicarbonate, 204.28 parts of crystallized sodium carbonate, 120 parts of sodium bicarbonate, and 68.20 parts of magnesium carbonate.

Citric acid may be estimated volumetrically by means of a standard solution of potassium or sodium hydrate, page 87, one cubic centimeter of which, if exactly normal, corresponds to 0.07 gram of pure crystallized acid; or 3.5 grams of the acid should require for complete neutralization 50 cubic centimeters of the standard alkali solution. The point of neutralization, as determined by litmus, is, however, in the case of citric acid not clearly seen, and only approximately correct results can thus be obtained. It may be more correctly estimated by the following gravimetric process. A weighed quantity of the acid, or its aqueous solution, is carefully neutralized by ammonia-water, a slight excess of a perfectly neutral solution of barium acetate added, and finally a volume of 95 per cent. alcohol, equal to twice the volume of the mixture. The precipitate is then collected on a filter (the weight of the ash of which has been previously determined), washed with 63 per cent. alcohol, and dried at a moderate heat. The barium citrate is then transferred to a porcelain crucible, the burned filter added, and, after the addition of a little concentrated sulphuric acid, it is repeatedly ignited until the carbonaceous matter is removed, and the entire amount of barium citrate has become completely converted into barium sulphate. From the amount of the latter its equivalent in citric acid may be readily determined; 1 part of barium sulphate corresponding to 0.601 part of crystallized citric acid.

TABLE *of the parts by weight of crystallized Citric Acid contained in 100 parts by weight of aqueous solutions of the acid of different specific gravities (Gerlach).*

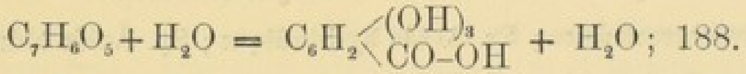
Temperature 15° C. (59° F.).

Specific gravity.	Per cent. of citric acid.	Specific gravity.	Per cent. of citric acid.	Specific gravity.	Per cent. of citric acid.
1.0037	1	1.0930	23	1.1947	45
1.0074	2	1.0972	24	1.1998	46
1.0111	3	1.1014	25	1.2050	47
1.0149	4	1.1060	26	1.2103	48
1.0186	5	1.1106	27	1.2153	49
1.0227	6	1.1152	28	1.22041	50
1.0268	7	1.1198	29	1.2257	51
1.0309	8	1.12439	30	1.2307	52
1.0350	9	1.1288	31	1.2359	53
1.03916	10	1.1333	32	1.2410	54
1.0431	11	1.1378	33	1.2462	55
1.0470	12	1.1422	34	1.2514	56
1.0509	13	1.1467	35	1.2572	57
1.0549	14	1.1515	36	1.2627	58
1.0588	15	1.1564	37	1.2683	59
1.0632	16	1.1612	38	1.27382	60
1.0675	17	1 1661	39	1.2794	61
1.0718	18	1.17093	40	1.2849	62
1.0762	19	1.1756	41	1.2904	63
1.08052	20	1.1814	42	1.2960	64
1.0848	21	1.1851	43	1.3015	65
1.0889	22	1.1899	44	1.3071	66

ACIDUM GALLICUM.

Gallic Acid.

Ger. Gallussäure; Fr. Acide gallique; Sp. Acido gálico.



$$C_7H_6O_5+H_2O = C_6H_2\left\langle\begin{matrix}(OH)_3\\CO\text{-}OH\end{matrix}\right. + H_2O;\ 188.$$

Small acicular prisms or silky needles, or a crystalline powder, nearly colorless, or of a pale fawn color, and containing 1 molecule (9.57 per cent.) of water of crystallization. When heated to about 100° C. (212° F.) the acid loses its water of crystallization, at about 200° C. (392° F.) it melts, and when heated to about 215° C. (419° F.) it is resolved into carbon dioxide and pyrogallol or pyrogallic acid, which latter sublimes in small crystalline plates; when exposed to a strong heat, with free access of air, gallic acid burns away without residue.

Gallic acid is soluble in 100 parts of cold and in 3 parts of boiling water; in 4.5 parts of cold and in 1 part of boiling alcohol; in 40 parts of absolute ether; and is also sparingly soluble in chloroform, benzol, benzin, and glycerin.

The aqueous solution has an acidulous and astringent taste and an acid reaction, and is liable to spontaneous decomposition on exposure to the air; it gives no precipitate with solutions of ferrous salts, if free from ferric salt, but it gives a bluish-black precipitate with solutions of ferric salts, the color of which disappears when the liquid is heated, from the reduction of the ferric to ferrous salt, at the expense of the gallic acid. A solution of gallic acid, when dropped into lime-water, produces a white turbidity, which soon becomes blue, and passes through a greenish or violet tint to a purple color. The solution forms no precipitate with argentic nitrate, but reduces it to metallic silver, gradually at common temperatures, at once when heated.

Solutions of the alkaline hydrates, as well as concentrated sulphuric and nitric acid, when poured upon dry gallic acid, dissolve it, with a deep-red color.

Examination:

Tannic acid may be detected by a white precipitate, when the solution of the acid is added to a dilute solution of gelatin, or by a precipitate occasioned with solutions of alkaloids, albumen, antimony and potassium tartrate with ammonium chloride, and gelatinized starch.

Sugar and *dextrin* remain behind upon solution of the acid in strong alcohol.

Resinous admixtures will remain undissolved, and float upon the surface, when a small portion of the acid is dissolved in boiling water.

ACIDUM HYDRIODICUM.

ACIDUM HYDRIODICUM DILUTUM.

Hydriodic Acid. Diluted Hydriodic Acid.

Ger. Jodwasserstoffsäure; Fr. Acide hydriodique; Sp. Ácido hidroiódico.

A clear, colorless liquid, which, when concentrated, possesses a pungent odor, a strongly acid taste and reaction, and fumes by exposure to the air. The acid, saturated at 0° C. (32° F.), has the specific gravity 1.99. Such an acid, upon warming, develops a large amount of hydrogen iodide, until the temperature of 55° C. (131° F.) is attained, and on further heating, in an atmosphere of hydrogen (to prevent oxidation and liberation of iodine), the temperature rapidly rises to 127° C. (260.6° F.), when an acid of constant composition distils over, having the specific gravity of 1.7, and containing 57.7 per cent. of hydrogen iodide. When a weak acid is subjected to distillation, it loses at first principally water, until at 127° C. (260.6° F.) an acid of constant composition distils over, of the strength above mentioned.

The diluted hydriodic acid has usually a specific gravity of 1.077 at 12 to 14° C. (53.6 to 57.2° F.), corresponding to 10.15 per cent. of true hydriodic acid.

Hydriodic acid in its aqueous solution rapidly undergoes oxidation by exposure to the air, with the liberation of iodine, the originally colorless solution assuming in consequence of the dissolved iodine a brown coloration, and will then impart a blue color to mucilage of starch, and a red or violet one to chloroform or carbon bisulphide when agitated therewith. The dilute solution of the acid assumes upon the addition of a few drops of concentrated nitric acid, or a little chlorine-water, a brown or yellowish-brown coloration, due to the liberated iodine, which may be recognized by its action upon starch, or by agitation with a few drops of chloroform or carbon bisulphide as above described.

Hydriodic acid produces with a solution of argentic nitrate a pale yellow precipitate of argentic iodide, which becomes but slowly discolored by exposure to light, is nearly insoluble in ammonia-water, and quite insoluble in dilute nitric acid; with palladium chloride it yields a black precipitate of palladium iodide, insoluble in nitric acid; and with plumbic acetate a bright yellow precipitate of plumbic iodide, which is insoluble in cold, but soluble in hot water, and in a solution of potassium iodide or sodium hydrate.

Examination:

The acid should be colorless or nearly so, and when a portion is evaporated in a small porcelain capsule, at a gentle heat, it should leave no residue (absence of *phosphoric acid* or *fixed impurities*).

Hydrochloric acid may be detected by completely precipitating a small portion of the acid with argentic nitrate, collecting the precipitate upon a filter, and digesting it with ammonia-water; the ammoniacal solution is then filtered, and supersaturated with nitric acid, when a white precipitate will indicate hydrochloric acid.

Hydrobromic acid may be detected by completely precipitating a small portion of the acid with palladium chloride, filtering the solution from the precipitate of palladium iodide, and adding thereto a little chlorine-water; if hydrobromic acid is present bromine will be liberated, imparting a yellow color to the solution, as well as to a few drops of carbon bisulphide or chloroform, subsequently added and agitated with the same.

Hydrogen sulphide will be recognized by a brown or blackish coloration on the addition of a solution of plumbic acetate.

Estimation:

The strength of aqueous hydriodic acid may be determined by ascertaining its specific gravity, and reference to the subjoined table, or more accurately estimated by the following methods:

I. *Volumetric.*—(1) About 20 grams of the acid are weighed in a beaker, diluted with a small amount of water, a few drops of litmus solution added, and a normal solution of potassium or sodium hydrate (page 87) allowed to flow into the liquid from a burette until a permanent blue coloration is produced. One cubic centimeter of the normal alkali corresponding to 0.128 gram of absolute hydriodic acid, HI, the percentage strength of the acid may be readily calculated.

(2) The acid may be likewise estimated volumetrically by means of a standard decinormal solution of argentic nitrate, page 98; one cubic centimeter of the argentic nitrate solution corresponding to 0.0128 gram of absolute hydriodic acid, HI.

II. *Gravimetric.*—A weighed portion of the acid is completely precipitated by a solution of argentic nitrate, the precipitate collected upon a filter, well washed with water, and, after drying, heated in a weighed porcelain crucible at a temperature just sufficient to fuse the argentic iodide. The crucible and its contents, after cooling, are again weighed, and from the weight of argentic iodide the amount of hydriodic acid is calculated; 100 parts by weight of argentic iodide corresponding to 54.46 parts of absolute hydriodic acid, HI.

TABLE *of the parts by weight of Hydriodic Acid contained in* 100 *parts by weight of aqueous acid of different specific gravities* (*Topsöe*).

Temperature 12 to 14° C. (53.6 to 57.2° F.).

Specific gravity.	Per cent. of HI.	Specific gravity.	Per cent. of HI.	Specific gravity.	Per cent. of HI.
1.017	2.286	1.253	28.41	1.542	49.13
1.052	7.019	1.274	30.20	1.572	50.75
1.077	10.15	1.309	33.07	1.603	52.43
1.095	12.21	1 347	36.07	1.630	53.93
1.102	13.09	1.382	38.68	1.674	56.15
1.126	15.73	1.413	40.45	1.696	57.28
1.164	19.97	1.451	43.39	1.703	57.42
1.191	22.63	1.486	45.71	1.706	57.64
1.225	25.86	1.528	48.22	1.708	57.74

ACIDUM HYDROBROMICUM.

ACIDUM HYDROBROMICUM DILUTUM.

Hydrobromic Acid. Diluted Hydrobromic Acid.

Ger. Bromwasserstoffsäure; Fr. Acide hydrobromique; Sp. Ácido hidrobrómico.

A clear, colorless, and, when concentrated, pungent and strongly acid liquid, which does not readily undergo change by exposure to the air. When saturated at 0° C. (32° F.), it has a specific gravity of 1.78, and contains 81 to 82 per cent. of hydrogen bromide. Such an acid fumes on exposure to the air, and, when subjected to distillation, develops hydrobromic acid gas, until at 125 to 125.5° C. (257 to 257.9° F.) an acid of constant composition distils over, having the specific gravity of 1.49 at 14° C. (57.2° F.), and containing 48 per cent. of hydrogen bromide. When a weak aqueous acid is subjected to distillation, it loses water, until, like hydrochloric acid, at a definite temperature, 125 to 125.5° C. (257 to 257.9° F.), an acid of constant composition distils over, which, however, is subject to variation in strength in accordance with the atmospheric pressure.

The diluted hydrobromic acid (Acidum Hydrobromicum Dilutum, U. S. P.) has the specific gravity of 1.077 at 15° C. (59° F.), corresponding to 10 per cent. of absolute hydrobromic acid. Hydrobromic acid yields with argentic nitrate a yellowish-white precipitate of argentic bromide, which becomes but slowly discolored by exposure to the light, is insoluble in dilute nitric acid, and sparingly soluble in ammonia-water, but dissolves readily in a solution of potassium cyanide; with palladium nitrate (but not with the chloride) it affords a reddish-brown precipitate of palladium bromide; and with solutions of plumbic or mercurous nitrates, white precipitates of plumbic or mercurous bromide, which are sparingly soluble in water. From a dilute solution of hydrobromic acid or a soluble bromide, no bromine is liberated on the addition of a few drops of concentrated nitric acid (distinction from hydriodic acid and iodides); chlorine-water, however, when mixed with the aqueous solution of the acid, liberates bromine, which imparts a reddish-yellow color to the liquid, and, upon subsequent agitation with a few drops of chloroform or carbon bisulphide, it is absorbed by the latter with an orange-yellow color.

Examination:

The acid should be colorless, and, when a portion is evaporated in a small porcelain capsule, at a gentle heat, it should leave no residue (absence *of phosphoric acid* or *fixed impurities*).

Bromine.—The presence of bromine will be indicated by a yellow or reddish-yellow color of the liquid, and, when shaken with a few drops of chloroform, will impart an orange-yellow color to the latter.

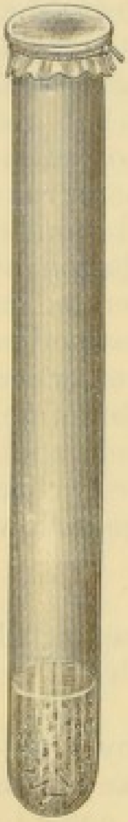
Iodine and *Hydriodic Acid.*—Free iodine may be detected by agitating a small portion of the acid with a few drops of chloroform, when the latter will assume a violet coloration. Hydriodic acid may be detected by the formation of a black precipitate of palladium iodide, on the addition of a solution of palladium chloride; or, by an ensuing turbidity, when 5 drops of the acid are mixed with 5 cubic centimeters of water and an equal volume of stronger ammonia-water, one drop of solution of argentic nitrate added, and the whole well mixed.

Hydrochloric acid may be detected by neutralizing the acid with baryta-water, evaporating the solution to dryness, igniting the residue, and finally extracting with absolute alcohol. The barium bromide will become thereby completely dissolved; should a residue remain, it is dissolved in water, the solution acidulated with nitric acid, and tested with solution of argentic nitrate, when a white precipitate, soluble in ammonia-water, will prove the presence of hydrochloric acid.

Sulphuric acid will be recognized by a white turbidity or precipitate when a dilute solution of the acid is tested with barium chloride or nitrate.

Sulphurous Acid.—A small portion of the acid is added to a few fragments of pure metallic zinc in a test-tube, and a small piece of bibulous paper, moistened with a solution of plumbic acetate, placed over the mouth of the tube (Fig. 70); a discoloration or production of a black stain upon the paper will prove the presence of sulphurous acid.

Fig. 70.



Metallic impurities may be detected by a dark coloration or a precipitate, upon saturating a dilute solution of the acid with hydrogen sulphide, or upon the subsequent addition of ammonium sulphide.

Estimation:

The strength of aqueous hydrobromic acid may be determined by ascertaining its specific gravity, and reference to the subjoined table; or more accurately estimated by the following methods:

I. *Volumetric.*—(1) About 20 grams of the acid are weighed in a beaker, diluted with a small amount of water, a few drops of litmus solution added, and a normal solution of potassium or sodium hydrate (page 87) allowed to flow into the liquid from a burette until a permanent blue coloration is produced. One cubic centimeter of the normal alkali corresponding to 0.081 gram of absolute hydrobromic acid, HBr, the percentage strength of the acid may be readily calculated.

To neutralize 16.2 gram of the officinal acid should require 20 cubic centimeters of normal solution of potassium or sodium hydrate.

(2) The acid may be likewise estimated volumetrically by means of a standard decinormal solution of argentic nitrate, page 98; one cubic centimeter of the argentic nitrate solution corresponding to 0.0081 gram of absolute hydrobromic acid, HBr.

II. *Gravimetric.*—A weighed portion of the acid is completely precipitated by a solution of argentic nitrate, the precipitate collected upon a filter, well washed with water, and, after drying, heated in a weighed porcelain crucible at a temperature just sufficient to fuse the argentic bromide. The crucible and its contents, after cooling, are again weighed, and from the weight of argentic bromide the amount of hydrobromic acid is calculated; 100 parts by weight of argentic bromide corresponding to 43.08 parts of absolute hydrobromic acid, HBr.

TABLE *of the parts by weight of absolute Hydrobromic Acid contained in 100 parts by weight of aqueous acid of different specific gravities* (*Biel*).

Temperature 15° C. (59° F.).

Specific gravity.	Per cent. of HBr.	Specific gravity.	Per cent. of HBr.	Specific gravity.	Per cent. of HBr.
1.0082	1	1.145	18	1.314	35
1.0155	2	1.154	19	1.326	36
1.0230	3	1.163	20	1.338	37
1.0305	4	1.172	21	1.350	38
1.038	5	1.181	22	1.362	39
1.046	6	1.190	23	1.375	40
1.053	7	1.200	24	1.388	41
1.061	8	1.209	25	1.401	42
1.069	9	1.219	26	1.415	43
1.077	10	1.229	27	1.429	44
1.085	11	1.239	28	1.444	45
1.093	12	1.249	29	1.459	46
1.102	13	1.260	30	1.474	47
1.110	14	1.270	31	1 490	48
1.119	15	1.281	32	1.496	49
1.127	16	1.292	33	1.513	50
1.136	17	1.303	34		

ACIDUM HYDROCHLORICUM.

ACIDUM MURIATICUM.

Hydrochloric Acid. Muriatic Acid.

Ger. Salzsäure, Chlorwasserstoffsäure; Fr. Acide hydrochlorique; Sp. Ácido hidroclórico.

Concentrated hydrochloric acid is a colorless fuming liquid, of a pungent and suffocating odor and corrosive acid taste; its specific gravity depends upon the quantity of hydrogen chloride held in solution, and varies in the strong acid between 1.160 and 1.120, corresponding to 32.21 and 24.46 per cent. of absolute hydrochloric acid.

The crude commercial acid has generally a spec. grav. of from 1.160 to 1.180, containing 32.21 to 36.29 per cent. of the gas, together with various impurities, such as sulphuric and sulphurous acids, chlorine, iron, and organic matters (the two latter of which impart a yellowish color to the acid), and also frequently arsenic.

Two strengths of hydrochloric acid are officinal: Acidum Hydrochloricum of the spec. grav. 1.16 (1.16 Brit. Pharm. = 32.21 per cent. HCl, and 1.124 Pharm. Germ. = 25 per cent. HCl), containing 32.21 per cent., and Acidum Hydrochloricum Dilutum of the spec. grav. 1.049 (1.052 Brit. Pharm.=10.6 per cent. HCl, and 1.061 Pharm. Germ.=12.5 per cent. HCl), containing 10.19 per cent. of absolute hydrochloric acid.

Hydrochloric acid may be recognized by the formation of a white, curdy precipitate on the addition of a solution of argentic nitrate; the precipitate is insoluble in nitric acid, but soluble in ammonia-water and in solutions of potassium cyanide and sodium hyposulphite, and assumes a violet or blackish-brown color on exposure to solar light. The acid may also be recognized by the evolution of chlorine gas, when heated in a test-tube with a little manganese dioxide.

Examination:

Fixed impurities are recognized by a residue, upon evaporation of the acid in a watch glass. To determine the nature of such a residue, whether organic or inorganic, or the possible presence of substances of both classes, it should be strongly heated on platinum-foil or in a small porcelain crucible, when organic matters will burn entirely away, while most inorganic substances leave a permanent residue.

Sulphuric acid may be detected in the acid, after dilution with at least five times its volume of water, by the formation of a white precipitate, either immediately or upon standing, on the addition of solution of barium chloride.

Sulphurous acid may be detected in the filtrate of the preceding test, after the sulphuric acid, if such be present, has been completely eliminated, by mixing with it a little chlorine-water; an ensuing white turbidity would indicate sulphurous acid.* This may also be recognized or confirmed when to a little of the hydrochloric acid, diluted with 4 or 5 parts of water, a perfectly clear and saturated solution of hydrogen sulphide in water is added; an ensuing white turbidity or opalescence, due to the separation of sulphur, will, in the absence of ferric salts, likewise indicate sulphurous acid.

Another very reliable test for sulphurous acid, and which will at the same time detect the presence of arsenic, consists in adding to a portion of the acid, diluted with an equal volume of water, in a test-tube, a few fragments of pure granular zinc, and covering the orifice of the tube with a small cap of bibulous paper, moistened with a solution of plumbic acetate (Fig. 71); or, if it is desired at the same time to test for arsenic, a cork provided with two strips of bibulous paper, as shown in the figure, one of which is moistened with a solution of plumbic acetate and the other with a solution of argentic nitrate, is loosely inserted in the mouth of the tube.

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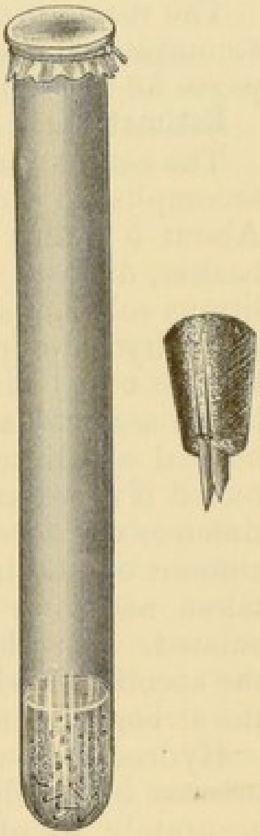
* Chlorine and sulphurous acids, when in contact with water, form hydrochloric and sulphuric acids; therefore the presence of either one of these impurities in hydrochloric acid excludes the other one.

In the presence of sulphurous acid, hydrogen sulphide will be developed, and produce a blackening of both strips of paper, whereas, if arsenic alone be present, only the one moistened with the argentic solution will become discolored.

Chlorine may be detected by the occurrence of a blue coloration, when the acid, diluted with about five times its bulk of water, is mixed with a few drops of solution of potassium iodide (free from iodate) and a little mucilage of starch; or by imparting a violet color to chloroform or carbon bisulphide, when agitated therewith, after the addition of a few drops of solution of potassium iodide.

Fig. 71.



Iodine and Bromine.—About eight volumes of the acid are agitated in a test-tube with one volume of chloroform; after subsidence, the stratum of chloroform will appear red when iodine, and yellowish when bromine, is present. If the chloroform, however, remains colorless, a few drops of chlorine-water are added; when, after agitation and subsequent subsiding, the chloroform still remains colorless, the absence of hydrobromic and of hydriodic acids is also proved.

Metals are detected in the acid, diluted with at least four times its bulk of water, when tested with hydrogen sulphide: a white turbidity would indicate sulphurous acid or ferric chloride, a yellow one, arsenic, and a dark one, copper, lead, or tin. In order to distinguish the latter, the precipitate is collected upon a filter, washed, and then treated with a little warm ammonium sulphide; the sulphides of tin or arsenic would become thereby dissolved, and, after their removal by filtration, may be separated by again precipitating them from their solution by hydrochloric acid, and digesting the resulting precipitate with a concentrated solution of ammonium carbonate, when the *arsenic* is redissolved, and upon the addition of hydrochloric acid in excess is obtained as yellow arsenious sulphide, whilst the *tin* by digestion with the ammonium carbonate solution remains undissolved as yellow stannic sulphide. The portion of the original precipitate insoluble in ammonium sulphide is washed with water upon the filter, and dissolved in a small quantity of warm nitric acid. To this solution a few drops of dilute sulphuric acid are added, when a white precipitate will indicate *lead;* after the removal of the latter by filtration, if present, ammonia-water in slight excess is added, when a blue coloration will indicate *copper*.

Iron may be detected in the acid, after its previous dilution with a little water, by a blue coloration or precipitate on the addition of solution of potassium ferrocyanide, or by a red coloration on the addition of potassium sulphocyanide.

Arsenic.—The presence of arsenic, if sulphurous acid is absent, will have been indicated by the previously described test for the latter, page 154; it may also be recognized by the addition of a few drops of a saturated solution of stannous chloride, or a strip of pure tin-foil and a little pure concentrated sulphuric acid, to the concentrated acid, in a test-tube, and warming very gently. If arsenic be present, brown flakes will be deposited, or, if the amount be very small, only a brown coloration of the liquid will ensue.

The recognition of very small quantities of arsenic may be best accomplished by the application of *Marsh's* test, as described on pages 33 to 36.*

Estimation:

The estimation of pure hydrochloric acid is most conveniently accomplished volumetrically by the process of neutralization. About 5 grams of the acid are accurately weighed in a small beaker, diluted with a small amount of water, a few drops of litmus solution added, and a normal solution of potassium or sodium hydrate (page 87) allowed to flow into the liquid from a burette until, with constant stirring, by means of a glass rod, the liquid assumes a permanent blue tint. One cubic centimeter of normal alkali solution corresponding to 0.0365 gram HCl, corrected if necessary by its proper factor, the number of cubic centimeters employed will at once indicate by simple calculation the amount of absolute hydrochloric acid in the quantity of liquid taken, and from which its percentage strength may then be calculated. For the confirmation of the correctness of the result the specific gravity of the acid may be taken, and compared with the strength of that indicated in the subjoined table, page 158.

Hydrochloric acid may also be estimated volumetrically by the process of precipitation. About one gram of the acid is first accurately weighed in a beaker or small flask, subsequently diluted with from 50 to 100 cubic centimeters of water, and, after exact neutralization with pure sodium carbonate, and the addition of a few drops of a solution of potassium chromate, as an indicator, a decinormal solution of argentic nitrate (page 98) is allowed to flow into the liquid from a burette until, with constant stirring, by means of a glass rod, a permanent red coloration is produced. One cubic centimeter of decinormal argentic nitrate

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* In the application of the above tests for arsenic, sulphurous acid should be excluded, as, in the first instance, it produces of itself with stannous chloride a yellowish or brown coloration, and, in the second instance, by the formation of hydrogen sulphide in contact with nascent hydrogen, the arsenic would be deposited as insoluble arsenious sulphide; when sulphurous acid is present, it should, therefore, first be eliminated by the addition of a very small quantity of a solution of iodine in potassium iodide, when the tests as described may be applied.

solution corresponding to 0.00365 gram HCl, this number, when multiplied by the number of cubic centimeters of silver solution employed, will represent the amount of absolute hydrochloric acid in the quantity under examination, from which the percentage strength of the acid may be readily calculated.

The estimation of hydrochloric acid may be also accomplished gravimetrically, by adding to a weighed portion, diluted, if necessary, with water, a solution of argentic nitrate until no further precipitate is produced, and subsequently rendering the liquid slightly acid, by the addition of a few drops of nitric acid. The precipitate of argentic chloride is collected on a tared filter, washed with water, and, after drying at 100° C. (212° F.) until of constant weight, weighed; or, the dried precipitate, if sufficient in amount, is brought into a small, previously weighed porcelain crucible, and ignited at a gentle heat. 100 parts of argentic chloride correspond to 25.43 parts of absolute hydrochloric acid, HCl.

Rules for the dilution of Hydrochloric Acid.

For the purpose of diluting a concentrated acid with water, or with a weaker acid, in order to obtain an acid of some special strength, the following simple and concise rules are applicable and convenient:—

If a stronger acid (*a*) is to be diluted to form an acid of the strength (*b*) by mixing it with water, or with a weak acid (*c*), the difference in percentage strength is sought, on the one hand, between *a* and *b*, and, on the other, between *b* and *c*, and *a* and *c* are then mixed in the proportion shown by the difference in the numbers. It has, however, to be taken into consideration that when the difference between *a* and *b* is greater than between *b* and *c*, less must be taken of *a* than of *c* in order to obtain *b*; but when the difference between *a* and *b* is less than between *b* and *c*, more must be taken of *a* than of *c* in order to obtain *b*.

Example:

I. Hydrochloric acid, containing 29 per cent. HCl, is to be mixed with water to form an acid containing 25 per cent. HCl:

	(*a*)	(*b*)	(*c*)
	29 per cent.	25 per cent.	0 per cent.
Difference		4	25

Accordingly 25 parts of the 29 per cent. acid are to be mixed with 4 parts of water,

or 100 grams Hydrochloric Acid = 29 grams HCl
16 grams water = —

116 grams Hydrochloric Acid = 29 grams HCl
or 100 grams " " = 25 grams "

II. Hydrochloric acid, containing 32 per cent. HCl, is to be mixed with an acid containing 8 per cent. HCl, to form an acid containing 14 per cent. HCl.

	(*a*)	(*b*)	(*c*)
	39 per cent.	14 per cent.	8 per cent.
	18		6
Difference	(3)		(1)

Accordingly 1 part of the 32 per cent. acid is to be mixed with 3 parts of the 8 per cent. acid,

or 100 grams Hydrochloric Acid = 32 grams HCl
300 grams " " = 24 " "
400 grams Hydrochloric Acid = 56 grams HCl
or 100 grams " " = 14 grams "

TABLE *of the quantity by weight of Hydrochloric Acid Gas, and the corresponding equivalent of Chlorine, contained in* 100 *parts by weight of Aqueous Hydrochloric Acid of different specific gravities* (*Ure*).

Temperature 15° C. (59° F.).

Specific gravity.	Per ct. of hydrochl. acid.	Per cent. of chlorine.	Specific gravity.	Per ct. of hydrochl. acid.	Per cent. of chlorine.	Specific gravity.	Per ct. of hydrochl. acid.	Per cent. of chlorine
1.2000	40.777	39.675	1.1328	26.913	26.186	1.0637	13.049	12.697
1.1982	40.369	39.278	1.1308	26.545	25.789	1.0617	12.641	12.300
1.1964	39.961	38.882	1.1287	26.098	25.392	1.0597	12.233	11.903
1.1946	39.554	38.485	1.1267	25.690	24.996	1.0577	11.825	11.506
1.1928	39.146	38.089	1.1247	25.282	24.599	1.0557	11.418	11.109
1.1910	38 728	37.692	1.1227	24.874	24.202	1.0537	11.010	10.712
1.1893	38.330	37.269	1.1206	24.466	23.805	1.0517	10.602	10.316
1.1875	37.923	36.900	1.1185	24.058	23.408	1.0497	10.194	9.919
1.1857	37.516	36.503	1.1164	23.650	22.012	1.0477	9.786	9.522
1.1846	37.108	36.107	1.1143	23.242	22.615	1.0457	9.379	9.126
1 1822	36.700	35.707	1.1123	22.834	22.218	1.0437	8.971	8.729
1.1802	36.292	35 310	1.1102	22.426	21.822	1.0417	8.563	8.332
1.1782	35.884	34.913	1.1082	22.019	21.425	1.0397	8.155	7.935
1.1762	35.476	34.517	1.1061	21.611	21.028	1.0377	7.747	7.538
1.1741	35.068	34.121	1.1041	21.204	20.632	1.0357	7.340	7.141
1.1721	34.660	33.724	1 1020	20.796	20.235	1.0337	6 932	6.745
1.1701	34.252	33.328	1.1000	20.388	19.837	1.0318	6.524	6.348
1.1681	33.845	32.931	1.0980	19.980	19.440	1.0298	6.116	5.951
1.1661	33.437	32.535	1.0960	19.572	19.044	1.0279	5.709	5.554
1.1641	33.029	32.136	1.0939	19.165	18.647	1.0259	5.301	5.158
1.1620	32.621	31.745	1.0919	18.757	18.250	1.0239	4.894	4.762
1.1599	32.213	31.343	1.0899	18.349	17 854	1.0220	4.486	4.365
1.1578	31.805	30.946	1.0879	17.941	17.457	1.0200	4.078	3.968
1.1557	31.398	30.550	1.0859	17.534	17.060	1.0180	3.670	3.571
1.1537	30.990	30.153	1.0828	17.126	16.660	1.0160	3.262	3.174
1.1515	30.582	29.757	1.0818	16 718	16.267	1.0140	2.854	2.778
1.1494	30.174	29.361	1.0708	16.310	15.870	1.0120	2.447	2.381
1.1473	29.767	28.964	1.0778	15.902	15.474	1.0100	2.039	1.984
1.1452	29.359	28.567	1.0758	15.494	15.077	1.0080	1.631	1.588
1.1431	28.951	28.171	1.0738	15.087	14.580	1.0060	1.124	1.191
1.1410	28.544	27.772	1.0718	14.679	14.284	1.0040	0.816	0.795
1.1389	28.136	27.376	1.0697	14.271	13.887	1.0020	0.408	0.397
1.1369	27.728	26.979	1.0677	13.863	13.490			
1.1349	27.321	26.583	1.0657	13.457	13.094			

The specific gravity of the aqueous acid being decreased by an increase of temperature, and increased by a decrease of temperature, the consequent change of the specific gravity amounts for each degree of the centigrade thermometer in either direction—

For acids of a specific gravity of 1.1741 to those of 1.1389 to about 0.0005
" " " 1.1349 " 1.0980 " 0.0004
" " " 1.0939 " 1.0637 " 0.0003

For instance: An acid of a specific gravity of 1.1234 at 16° C., containing 25 per cent. of hydrochloric-acid gas, will have at 18.5° C. a specific gravity of $1.1234 - (0.0004 \times 2.5) = 1.1224$, and at 13.5° C. a specific gravity of $1.1234 + (0.0004 \times 2.5) = 1.1244$.

ACIDUM HYDROCYANICUM DILUTUM.

ACIDUM HYDROCYANATUM.

Diluted Hydrocyanic Acid. Prussic Acid.

Ger. Cyanwasserstoffsäure, Blausäure; Fr. Acide hydrocyanique; Sp. Ácido hidrociánico.

Pure hydrocyanic acid is a thin, colorless, and exceedingly poisonous, volatile, and unstable liquid. Its odor is very powerful and characteristic, resembling that of peach-blossoms or oil of bitter almonds. It mixes with water, alcohol, and ether, in all proportions. The officinal acid is a very dilute hydro-alcoholic solution, containing two per cent. of absolute acid. It imparts a faint evanescent color to litmus, and forms a white curdy precipitate with a solution of argentic nitrate. This precipitate is soluble in solution of potassium cyanide, ammonia-water, and boiling nitric acid, but insoluble in dilute acids, and does not readily change color on exposure to solar light; when strongly heated it is completely decomposed into metallic silver and cyanogen gas. If the acid is rendered slightly alkaline by potassium hydrate, a few drops of a solution of ferrous sulphate and ferric chloride added, and the mixture subsequently acidulated with hydrochloric acid, a precipitate of ferric ferrocyanide or Prussian blue will be produced.

Hydrocyanic acid may also be recognized by the following characteristic reactions. When neutralized with a dilute solution of potassium or sodium hydrate, a few drops of yellow ammonium sulphide added, and the mixture carefully evaporated in a porcelain capsule to dryness, a residue is obtained which, when dissolved in water, acidulated with hydrochloric acid, and filtered, yields on the addition of a drop of solution of ferric chloride an intense blood-red color. When the acid is neutralized with a dilute solution of potassium or sodium hydrate, a little picric acid added, and the mixture warmed, an intense blood-red color, due to the formation of picrocyanic acid, $C_8H_5N_5O_6$, is produced. If a solution of mercurous nitrate is added to a solution of hydrocyanic acid, a gray precipitate of metallic mercury is at once produced, with the simultaneous formation of mercuric cyanide, which remains in solution.

Examination:

A small portion of the acid, when allowed to evaporate on a watch glass, should leave no residue.

Mineral acids in general may be detected by producing a permanent red coloration with litmus, as also by causing the precipitation of red mercuric iodide upon the addition of a solution of the double salt of mercuric cyanide and potassium iodide, $HgK(CN)_2I$,* the latter being decomposed by all acids, with the exception of hydrocyanic and carbonic acids.

Hydrochloric and *phosphoric acids* may be detected by the addition of an excess of ammonia-water, and evaporating the solution in a porcelain capsule, at a gentle heat, to dryness; the residue is dissolved in dilute nitric acid, and a portion of the filtered solution examined with argentic nitrate for *hydrochloric acid*, which is indicated by a white precipitate. To another portion of the solution ammonium molybdate is added, and heated to boiling; an ensuing yellowish precipitate indicates *phosphoric acid.*

Formic acid, if present, will be detected by its property of reducing red oxide of mercury to gray metallic mercury, when a little of the acid is warmed and agitated with the oxide; or by the reduction of metallic silver on the addition of a solution of argentic nitrate, which will impart a grayish color to the precipitated argentic cyanide.

Sulphuric acid is detected by the formation of a white precipitate upon the addition of a few drops of barium nitrate to the acid.

Estimation of the Strength of Hydrocyanic Acid:

There are two simple methods of ascertaining the quantity of absolute acid contained in hydrocyanic acid. The one depends upon the fact that one part of absolute hydrocyanic acid forms 5 parts of argentic cyanide; that, accordingly, 100 parts of the officinal acid should yield 10 parts of argentic cyanide.

The second method is the volumetric one, and depends upon the property of argentic cyanide to form a soluble double salt with alkaline cyanides. When, therefore, the officinal hydrocyanic acid is converted into sodium or potassium cyanide by the addition of sodium or potassium hydrate, no permanent precipitate will appear upon the addition of argentic nitrate until more than sufficient argentic cyanide is produced to form the soluble compound.

I. Ten grams of the acid are completely precipitated by a solution of argentic nitrate. Then two filters of exactly the same size and paper are cut; through the one the liquid is filtered, the pre-

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* Obtained by mixing hot concentrated alcoholic solutions of 3 parts of mercuric cyanide and 2 parts of potassium iodide; the compound crystallizes out upon cooling, and may be dissolved in water for use.

cipitate washed, and then both the empty filter and the one containing the argentic cyanide are dried, at a temperature not exceeding 100° C. (212° F.). When the weight of the latter filter remains constant, both filters are weighed, the empty one serving as a counterpoise of the one containing the precipitate; the excess of weight of the latter is argentic cyanide, of which—

1. gram represents 2.015 per cent. of absolute hydrocyanic acid.
1.05 " " 2.10 " " " "
1.10 " " 2.20 " " " "

II. The principle involved in the volumetric estimation of hydrocyanic acid has been fully described on page 100. 5.4 grams of the acid are accurately weighed, and diluted, in a beaker, with about 200 cubic centimeters of water. The liquid is then made slightly alkaline with a solution of potassium or sodium hydrate, a few drops of a saturated solution of sodium chloride added, and a decinormal solution of argentic nitrate (page 98) allowed to flow into the liquid from a burette until, with constant stirring, a slight permanent turbidity is produced in the solution. The number of cubic centimeters of silver solution required to produce this reaction with the above-mentioned quantity of acid, divided by 10, will give at once the percentage strength of the acid in hydrogen cyanide.

Separation and Detection of Hydrocyanic Acid in Forensic Investigations.—Hydrocyanic acid, being one of the most formidable of poisons, is sometimes the object of search in forensic investigations, and the process for its isolation, and subsequent recognition and estimation will, therefore, be briefly described.

The organic materials or substances to be examined are brought into a flask, a little water added, if necessary, and the mixture slightly acidulated with tartaric acid. A preliminary test is then first made by inserting in a cork adapted to the flask containing the mixture a small strip of paper, moistened first with a little tincture of guaiac, and, after drying, with a very dilute solution of cupric sulphate,* and subsequently gently warming the mixture to about 50° C. (122° F.). In the presence of the vapor of hydrocyanic acid the paper will assume a deep blue color. As, however, other substances, ammonia, nitric oxide, etc., are capable of producing a similar blue coloration, this reaction does not afford unqualified proof of the presence of hydrocyanic acid; and when thus indicated by the above reaction, or by the odor of the mixture under examination, the isolation and identification of the acid must in all cases be effected.

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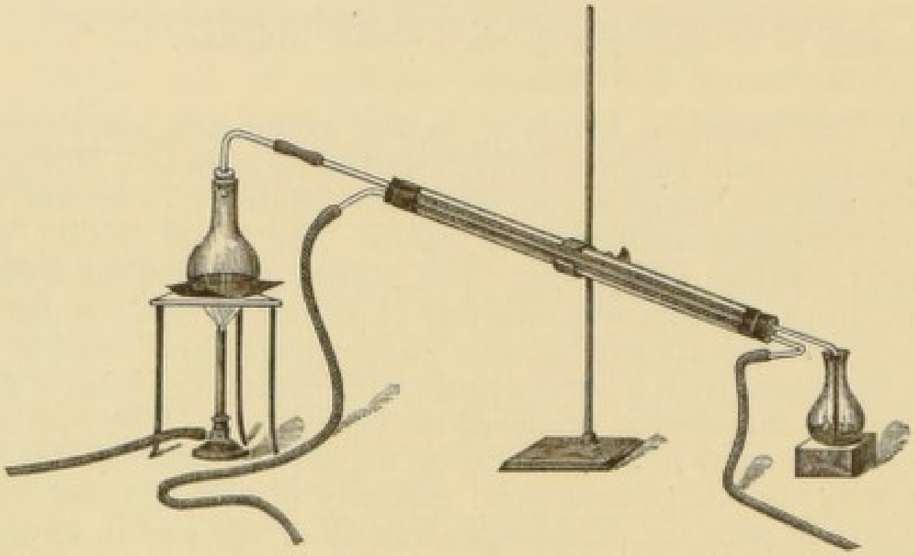
* The tincture of guaiac is best freshly prepared, in the proportion of one part of the wood to ten parts of alcohol, or one part of the resin to twenty parts of alcohol; the solution of cupric sulphate in the proportion of one part of the salt to two thousand parts of water, by which dilution it forms a perfectly colorless solution.

The substance to be examined, therefore, after acidulation with tartaric acid, and dilution, if necessary, with water, is subjected to distillation in a flask or retort, provided with a condenser, and the distillate collected in a receiver containing a little water (Fig. 72);

FIG. 72.



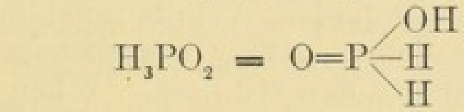
the distillation being continued until about one-quarter or one-third of the liquid has distilled over. The distillate is then examined by its odor, action upon litmus, and by the application of the previously described reactions, viz., the formation of argentic cyanide, Prussian blue, and ferric sulphocyanide. If a quantitative estimation of the acid is required, it may be converted into argentic cyanide, by the addition of solution of argentic nitrate to the distillate until a precipitate ceases to be produced, and from the argentic cyanide, dried at 100° C. (212° F.) until of constant weight, the amount of pure hydrocyanic acid calculated: 100 parts of argentic cyanide corresponding to 20.15 parts of absolute hydrocyanic acid. As the distillate, however, may contain hydrochloric acid in addition to hydrocyanic acid, the former should be tested for, and, when present, must be eliminated by the rectification of the distillate over a little powdered borax or precipitated calcium carbonate, previous to its precipitation with argentic nitrate; these substances serving to combine the free hydrochloric acid, but are not acted upon by hydrocyanic acid, which is thus obtained in a pure form.

In view of the possibility of the occurrence of potassium ferrocyanide in the substance under examination, which would also yield hydrocyanic acid by distillation with an acid, and of the fact that it is a non-poisonous salt, the examination should be invariably preceded by a test for ferrocyanides, by digesting a portion of the substance with water, filtering the solution, and, after acidulating with hydrochloric acid, applying the well-known reaction with ferric chloride. For the separation of potassium ferrocyanide when associated with hydrocyanic acid, or a soluble simple cyanide, the organic materials, if not already possessing an acid reaction, should be first slightly acidulated with sulphuric acid, and then sufficient of a neutral solution of ferric chloride added to precipitate the entire amount of ferrocyanide as Prussian blue. After standing for some time the mixture is filtered, and the filtrate, after the addition of a sufficient quantity of neutral potassium tartrate to insure the complete combination of the free sulphuric acid, is subjected to distillation. By operating in this manner the distillate can only contain hydrocyanic acid when originally present as such, or in the form of potassium cyanide.

ACIDUM HYPOPHOSPHOROSUM.

Hypophosphorous Acid.

Ger. Unterphosphorigesäure ; Fr. Acide hypophosphoreux ;
Sp. Acido hipofosfórico.



$$H_3PO_2 = O{=}P\begin{cases}-OH\\-H\\-H\end{cases} ; \quad 66.$$

A dense, syrupy, strongly acid liquid, which, at low temperatures, forms large, colorless laminar crystals. The crystals melt at 17.4° C. (63.3° F.), and deliquesce gradually at ordinary temperatures. By exposure to the air it becomes slowly oxidized to phosphorous acid, and by the action of chlorine or nitric acid it is converted into phosphoric acid.

Hypophosphorous acid in its aqueous solution possesses strongly reducing properties, precipitating gold and silver from solutions of their salts, and, when added to a solution of mercuric chloride, either mercurous chloride or metallic mercury is separated, according to the amount of acid present. When the acid, in excess, is gently warmed with a few drops of solution of cupric sulphate, at a temperature not exceeding 60° C. (140° F.), a reddish-brown precipitate of cupric hydride, CuH, is produced; with an excess of the cupric solution, and upon more strongly heating, metallic copper is separated.

The acid, when strongly heated, is decomposed into hydrogen phosphide and phosphoric acid: $2H_3PO_2 = PH_3 + H_3PO_4$.

Examination:

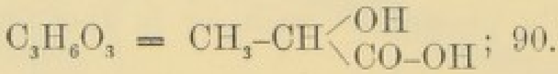
Lead and *Calcium Salts* and *Phosphoric Acid.*—A small portion of the acid is neutralized with ammonia-water, and is then tested, in separate portions, as follows: A dark coloration or precipitate on the addition of ammonium sulphide will indicate *lead*, a white precipitate on the addition of ammonium oxalate, *calcium salts*, and a white precipitate with barium chloride, *phosphoric acid*.

Hydrogen sulphide may be recognized by a dark coloration on the addition of a solution of plumbic acetate.

ACIDUM LACTICUM.

Lactic Acid. Oxy-propionic Acid.

Ger. Milchsäure; Fr. Acide lactique; Sp. Ácido láctico.



$$C_3H_6O_3 = CH_3\text{–}CH\left\langle\begin{matrix}OH\\ CO\text{–}OH\end{matrix}\right.;\ 90.$$

A limpid, odorless, syrupy liquid, colorless, or of a pale-yellowish tint, of a sour taste, and having the specific gravity 1.212 at 15° C. (59° F.), corresponding to 75 per cent. of absolute lactic acid. It is miscible, in all proportions, with water, glycerin, alcohol, and ether, and also, without being colored, with cold, concentrated sulphuric acid. Lactic acid dissolves zinc and iron, with effervescence, and cannot be distilled without undergoing partial decomposition. Heated upon platinum-foil, it emits inflammable vapors, which burn with a pale flame, leaving a carbonaceous residue, which is completely dissipated at a red heat. When heated with a solution of potassium permanganate, lactic acid emits the odor of aldehyde.

Examination:

Gum, *Mannite*, and *Glucose*.—A few drops of the acid are diluted with water in a test-tube, and slightly supersaturated with sodium carbonate; to the clear liquid are added a few drops of Fehling's solution, and the whole gently warmed; a blue coagulation upon the addition of the cupric solution before warming, would indicate the presence of gum; a brick-colored precipitate, after heating, indicates glucose.

The presence of gum and mannite may also be recognized by the occurrence of a turbidity upon dropping the acid into a mixture of equal parts of alcohol and ether.

Glycerin may be detected by mixing, in a porcelain capsule, a small portion of the acid with a slight excess of zinc oxide, previously triturated with a little water; the whole is then evaporated, upon a water-bath, to dryness, the residue treated with strong alcohol, and the obtained alcoholic solution evaporated upon a watch-glass; a neutral, syrupy, sweet residue would indicate glycerin.

Sarcolactic acid may be detected by an ensuing blue precipitate, when tested with a solution of cupric sulphate.

Foreign Organic Acids.—Two drops of the lactic acid are added in a test-tube to so much lime-water that the alkaline reaction predominates; if a turbidity takes place at once, *oxalic*, *tartaric*, or *phosphoric acids* are indicated; if the turbidity does not ensue before the liquid is heated to boiling, *citric acid* is indicated. *Acetic* and *butyric acids* are recognized by their respective odors when the acid is gently heated in a porcelain capsule.

Sulphuric, *hydrochloric*, and *phosphoric acids* may be detected in the diluted aqueous solution of the acid by testing it, in separate portions, with barium chloride for the former, and with argentic nitrate for the two latter.

Acid calcium phosphates or other calcium salts would be indicated by a white turbidity of the dilute solution of the acid when tested with ammonium oxalate.

Metals are detected in the acid, when neutralized with ammonia-water, and then tested with hydrogen sulphide; a white turbidity or precipitate would indicate *zinc*, a brown or blackish coloration or precipitate, *copper*, *lead*, or *iron*.

Estimation:

Ninety parts by weight of the officinal acid should be neutralized by not less than seventy-five parts by weight of crystallized potassium bicarbonate, corresponding to 75 per cent. of absolute lactic acid. The acid may be also estimated volumetrically by the process of neutralization, whereby 6 grams of the officinal acid should require for exact neutralization 50 cubic centimeters of a normal solution of potassium or sodium hydrate, which likewise corresponds to 75 per cent. of absolute acid. By the employment of other quantites of the acid than that above indicated, the calculation may be made with the consideration that 1 cubic centimeter of normal potassium or sodium hydrate corresponds to 0.09 gram of absolute lactic acid.

ACIDUM NITRICUM.

Nitric Acid.

Ger. Salpetersäure; Fr. Acide nitrique; Sp. Acido nitrico.

Nitric acid, in its most concentrated form, is a colorless, fuming, corrosive liquid, having the spec. grav. of 1.530 at 15° C. (59° F.). It begins to boil at 86° C. (186.8° F.), and becomes of a dark-yellow color, due to the partial decomposition of the acid into nitrogen tetroxide, oxygen, and water. When a strong acid is subjected to distillation, it loses nitric acid, and the boiling point is gradually increased until, at the temperature of 120.5° C. (248.9° F.), an acid of constant composition distils over; a weak acid, under the same conditions, loses water until, at 120.5° C.

(248.9° F.), the boiling point remains constant. This acid having a constant boiling point has the spec. grav. of 1.414 at 15.5° C. (60° F.), and contains 68 per cent. of absolute nitric acid.

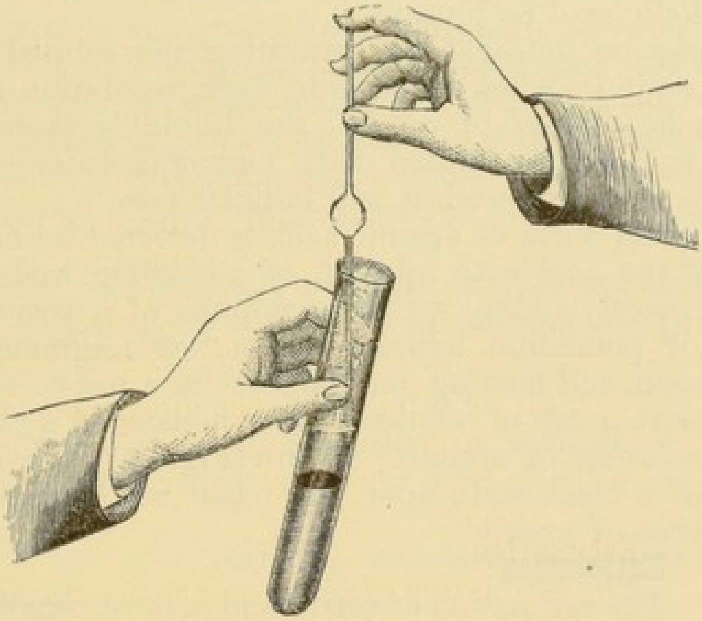
The crude commercial nitric acid is of two strengths: the so-called double acid has a spec. grav. of 1.36, containing about 57 per cent. of absolute nitric acid; and the single acid, of 1.22 spec. grav., containing about 35 per cent. of absolute acid.

The officinal nitric acid has the spec. grav. of 1.420 (1.185 Pharm. Germ. = 30 per cent. HNO_3), and contains 69.4 per cent. of absolute nitric acid. The Acidum Nitricum Dilutum, of 1.059 spec. grav. (1.101 Brit. Pharm. = 16.8 per cent. HNO_3), contains 10 per cent. of absolute nitric acid.

Nitric acid is readily decomposed, and is a powerful oxidizing agent, acting violently upon most of the metals, and upon organic compounds, converting many non-nitrogenous vegetable substances into explosive bodies. From its tendency to decompose, nitric acid has frequently a yellowish color from nitrogen oxides, held in solution, which, upon dilution of the acid with water, or upon heating, cause a further decomposition and consequent disengagement of nitric peroxide. Nitric acid may be recognized by its property of dissolving copper-turnings to a blue solution, with the evolution of colorless nitric-oxide gas, which, however, at once unites with atmospheric oxygen, forming red fumes of nitric peroxide; by the ready decoloration of diluted solution of indigo; by its coloring pine-wood bright yellow; and by deep red or brown compounds with ferrous salts. An exceedingly delicate test for nitric acid depends upon its reaction with the alkaloid brucine. A few drops of concentrated sulphuric acid, and one or two drops of a saturated aqueous solution of brucine, are added to the solution to be tested, when a fine rose or dark-red coloration will be produced. By means of this reaction a solution containing but one part of nitric acid in 100,000 parts of water will assume a distinct pink coloration. Another excellent test, but somewhat less delicate than the preceding, depends upon the reaction of nitric acid with aniline. About 0.5 cubic centimeter (approximately 5 drops) of a solution of 10 drops of aniline in 50 cubic centimeters of 15 per cent. sulphuric acid (Acid. Sulph. Dil., U. S. P., may be employed) is brought into a small porcelain capsule, and a glass rod, moistened with the liquid to be tested, is then brought in contact with the liquid. If the nitric acid be very dilute, a rose-red coloration will be produced, but, if concentrated, the entire liquid will assume a brown or dark brownish-red tint.

The characteristic reaction of nitric acid with ferrous salts extends also to the nitrates, when previously acted upon by strong sulphuric acid. The test is performed either by placing a crystal of ferrous sulphate in the liquid under examination, mixed with concentrated sulphuric acid, or by mixing the liquid with a concentrated solution of ferrous sulphate, and pouring this mixture carefully upon concentrated sulphuric acid in a test-tube, so as to form in either case two layers (Fig. 73). If a large quantity of nitric acid is present, the surfaces of the crystal, or the line of contact between the liquids, become black; if but a small quantity is present, they become reddish-brown or purple.

FIG. 73.



Examination:

Hydrochloric acid may be detected in the acid diluted with about five times its volume of water, by the formation of a white precipitate, when tested with argentic nitrate.

Sulphuric acid is detected in the acid, previously diluted with at least five times its volume of water, by the production of a white precipitate, either immediately or upon standing, on the addition of a solution of barium nitrate.

Nitrous and *hyponitric acids* (nitrogen tetroxide) are detected in the diluted acid, by the addition of one or two drops of a very dilute (1 : 100) solution of potassium permanganate: their presence is indicated by decoloration. They may also be recognized by adding to the acid, previously diluted with about five times its volume of water, a few drops of a solution of potassium iodide, and a little mucilage of starch, when a blue coloration will be produced.

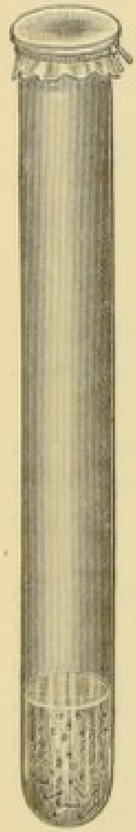
Iodine and *Iodic Acid.*—A small portion of the acid (the concentrated acid should be diluted with about five times its volume of water) is shaken, in a test-tube, with a few drops of chloroform, which, after subsiding, will appear of a reddish-violet color if free *iodine* be contained in the acid; when it remains colorless, or after the removal of the free iodine, if present, by agitation with chloroform, a very small quantity of an aqueous solution of hydrogen sulphide or sulphurous acid is added, drop by drop, with gentle agitation; if a coloration of the chloroform now takes place, *iodic acid* is indicated.

A confirmatory test is, to mix the acid, after dilution, if strong acid is under examination, with a few drops of mucilage of starch; a bluish coloration will take place after a while, when iodine is present; if no reaction occurs, a few drops of solution of sulphurous acid may be added, drop by drop, when the blue color will appear, if iodic acid be present.

Metals may be detected by saturating the diluted acid with hydrogen sulphide, when an ensuing dark coloration or precipitate will indicate *lead* or *copper;* the liquid is then filtered, if necessary, and supersaturated with ammonia-water; if a dark coloration is now produced, it will indicate *iron*.

Arsenic, in the form of arsenic acid, is detected by neutralizing a portion of the acid with solution of potassium hydrate, subsequently adding twice its volume of a strong solution of potassium hydrate and a few fragments of pure zinc, and heating the mixture in a test-tube, provided with a cap of bibulous paper moistened with a drop of solution of argentic nitrate (Fig. 74); the production of a black stain upon the paper will reveal the presence of arsenic.

FIG. 74.



Estimation:

The estimation of nitric acid is most conveniently accomplished volumetrically by the process of neutralization. About 5 grams of the acid, accurately weighed in a beaker, are diluted with about 50 cubic centimeters of water, a few drops of litmus solution added, and a normal solution of potassium or sodium hydrate (page 87) allowed to flow into the liquid from a burette until, with constant stirring, the liquid assumes a permanent blue tint. One cubic centimeter of the normal alkali solution corresponding to 0.063 gram HNO_3, the amount of absolute acid in the quantity employed, and its percentage strength, may readily be calculated. In addition thereto the specific gravity of the acid may be determined, and the result of the volumetric estimation compared with the percentage strength of an acid having a corresponding specific gravity, as indicated by the subjoined table, page 170.

Of the strong officinal acid 4.54 grams, and of the diluted acid 31.5 grams, are neutralized by 50 cubic centimeters of normal solution of potassium or sodium hydrate.

Rules for the Dilution of Nitric Acid.

If a strong acid, *a*, has to be diluted with water, or with a weaker acid, *c*, in order to obtain an acid of some special strength, *b*, the following rules are applicable:

The difference in percentage strength is sought, on the one hand, between *a* and *b*, and, on the other, between *b* and *c*, and *a* and *c* are then mixed in the proportions represented by the difference in the respective numbers. It must be observed, however, that when the difference between *a* and *b* is greater than between *b* and *c*, less of *a* than of *c* must be taken in order to obtain *b*; and when the difference between *a* and *b* is less than between *b* and *c*, more of *a* than of *c* must be employed in order to obtain *b*; for example:

I. Nitric acid, containing 29 per cent. of absolute acid, is to be mixed with water, to form an acid containing 25 per cent. of absolute acid:

	a.	*b.*	*c.*
	29 per cent.	25 per cent.	0 per cent.
Difference	4	25	

25 parts of 29 per cent. acid are, therefore, to be mixed with 4 parts of water, or

100 grams of nitric acid = 29 grams HNO_3
16 " " water =

116 grams of nitric acid = 29 grams HNO_3
or 100 " " " " = 25 " "

II. Nitric acid, containing 32 per cent. of absolute acid, is to be mixed with an 8 per cent. acid, to form an acid containing 14 per cent. of absolute acid:

	a.	*b.*	*c.*
	32 per cent.	14 per cent.	8 per cent.
Difference	18 (3)	6 (1)	

1 part of 32 per cent. acid is, therefore, to be mixed with 3 parts of 8 per cent. acid, or

100 grams of nitric acid = 32 grams NHO_3
300 " " " " = 24 " "

400 grams of nitric acid = 56 grams HNO_3
or 100 " " " " = 14 " "

TABLE *of the quantity by weight of absolute Nitric Acid, and the corresponding equivalent of Nitric Anhydride, contained in* 100 *parts by weight of Nitric Acid, of different specific gravities.*

Temperature 15° C. (59° F.).

Specific gravity.	Per cent. of HNO_3	Per ct. of N_2O_5.	Specific gravity.	Per ct. of HNO_3.	Per cent. of N_2O_5.	Specific gravity.	Per ct. of HNO_3.	Per cent. of N_2O_5.
1.530	100.00	85.71	1.435	73.00	62.57	1.298	47.18	40.44
1.530	99.84	85.57	1.432	72.39	62.05	1.295	46.64	39.97
1.530	99.72	85.47	1.429	71.24	61.06	1.284	45.00	38.57
1.529	99.52	85.30	1.423	69.96	60.00	1.274	43.53	37.31
1.523	97.89	83.90	1.419	69.20	59.31	1.264	42.00	36.00
1.520	97.00	83.14	1.414	68.00	58.29	1.257	41.00	35.14
1.516	96.00	82.28	1.410	67.00	57.43	1.251	40.00	34.28
1.514	95.27	81.66	1.405	66.00	56.57	1.244	39.00	33.43
1.509	94.00	80.57	1.400	65.07	55.77	1.237	37.95	32.53
1.506	93.01	79.72	1.395	64.00	54.85	1.225	36.00	30.89
1.503	92.00	78.85	1.393	63.59	54.50	1.218	35.00	29.29
1.499	91.00	78.00	1.386	62.00	53.14	1.211	33.86	29.02
1.495	90.00	77.15	1.381	61.21	52.46	1.198	32.00	27.43
1.494	89.56	76.77	1.374	60.00	51.43	1.192	31.00	26.57
1.488	88.00	75.43	1.372	59.59	51.08	1.185	30.00	25.71
1.486	87.45	74.95	1.368	58.88	50.47	1.179	29.00	24.85
1.482	86.17	73.86	1.363	58.00	49.71	1.172	28.00	24.00
1.477	85.00	72.89	1.358	57.00	48.86	1.166	27.00	23.14
1.474	84.00	72.00	1.353	56.10	48.08	1.157	25.71	22.04
1.470	83.00	71.14	1.346	55.00	47.14	1.138	23.00	19.71
1.467	82.00	70.28	1.341	54.00	46.29	1.120	20.00	17.14
1.463	80.96	69.39	1.339	53.81	46.12	1.105	17.47	14.97
1.460	80.00	68.57	1.335	53.00	45.40	1.089	15.00	12.85
1.456	79.00	67.71	1.331	52.33	44.85	1.077	13.00	11.14
1.451	77.66	66.56	1.323	50.99	43.70	1.067	11.41	9.77
1.445	76.00	65.14	1.317	49.97	42.83	1.045	7.22	6.62
1.442	75.00	64.28	1.312	49.00	42.00	1.022	4.00	3.42
1.438	74.01	63.44	1.304	48.00	41.14	1.010	2.00	1.71

With the decrease and increase of temperature, the specific gravity of nitric acid suffers a corresponding increase or decrease, amounting for each degree of the centigrade thermometer in either direction :

For acids of a specific gravity of 1.494 to those of 1.477 to 0.00213 in the average.
“ “ “ “ 1.474 “ 1.456 “ 0.002 “ “
“ “ “ “ 1.456 “ 1.435 “ 0.00186 “ “
“ “ “ “ 1.429 “ 1.410 “ 0.00171 “ “
“ “ “ “ 1.405 “ 1.381 “ 0.00155 “ “
“ “ “ “ 1.374 “ 1.353 “ 0.00141 “ “
“ “ “ “ 1.346 “ 1.317 “ 0.00128 “ “
“ “ “ “ 1.304 “ 1.274 “ 0.00114 “ “
“ “ “ “ 1.274 “ 1.237 “ 0.001 “ “
“ “ “ “ 1.237 “ 1.198 “ 0.00085 “ “
“ “ “ “ 1.192 “ 1.166 “ 0.00071 “ “
“ “ “ “ 1.157 “ 1.120 “ 0.0005 “ “

For instance: An acid of 1.179 spec. grav. at 15° C., containing 24.85 per cent. of nitric anhydride, or 29.00 of absolute nitric acid, will have at 17.5° C. a spec. grav. of $1.179 - (0.00071 \times 2.5) = 1.1773$, and at 13° C. a spec. grav. of $1.179 + (0.00071 \times 2) = 1.1804$.

ACIDUM OLEICUM.

ACIDUM OLEINICUM.

Oleic Acid.

Ger. Oelsäure; Fr. Acide oléique; Sp. Acido oléico.

$C_{18}H_{34}O_2 = C_{17}H_{33}\text{–CO–OH}$; 282.

An oily liquid, without odor or taste, and colorless or having but a slight yellow color. It solidifies at 4° C. (39° F.) to a compact, white crystalline mass, and from its solution in alcohol it crystallizes in brilliant white needles, which melt at 14° C. (57° F.) to a colorless oil. Its specific gravity is 0.808 at 19° C. (66° F.). When perfectly pure, and unoxidized, it is neutral in its action upon litmus, but on exposure to the air, especially when slightly impure, it rapidly absorbs oxygen, acquiring thereby a yellow or brownish-yellow color, a rancid taste and smell, and an acid reaction. When strongly heated, it becomes decomposed, but with super-heated steam it may be distilled unchanged at 250° C. (482° F.). By treatment with nitrous acid, oleic acid is converted into the solid isomeric elaïdic acid, which crystallizes in laminæ, melting at 44 to 45° C. (111 to 113° F.). Oleic acid is insoluble in water, but freely soluble in alcohol, ether, chloroform, benzol, petroleum benzin, and the volatile and fatty oils; it is also soluble in cold, concentrated sulphuric acid without decomposition.

Examination:

Stearic and *palmitic acids* will be indicated by a higher congealing point than 4° C. (39° F.), and may be also detected by the following test: A portion of the acid is completely saponified by potassium carbonate, with the aid of a gentle heat, the resulting soap dissolved in water, exactly neutralized with acetic acid, and the solution precipitated with plumbic acetate; the ensuing precipitate of plumbic oleate, after being twice washed with boiling water, should be completely or almost completely soluble in ether; any considerable insoluble residue will indicate an undue proportion of an admixture of stearic or palmitic acids.

Fixed oils, with the exception of ricinus or castor oil, may be detected by the formation of a turbid mixture or the separation of oily drops, when the acid is mixed with an equal volume of strong alcohol, and heated to 25° C. (77° F.).

Lead may be detected by a brown or blackish coloration or precipitate when the alcoholic solution of the acid is saturated with hydrogen sulphide.

ACIDUM OXALICUM.

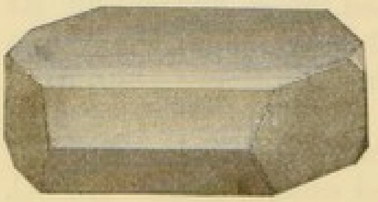
Oxalic Acid.

Ger. Oxalsäure ; Fr. Acide oxalique ; Sp. Acido oxálico.

$$C_2H_2O_4 + 2H_2O = \begin{array}{c} CO\text{–}OH \\ | \\ CO\text{–}OH \end{array} + 2H_2O ;\ 126.$$

Colorless, transparent, oblique-rhombic prisms (Fig. 75), containing two molecules (28 per cent.) of water of crystallization, which they lose gradually upon exposure in a warm and dry atmosphere, or quickly upon heating at 100° C. (212° F.), becoming reduced to a soft white powder. By cautiously heating at a temperature not exceeding 150° C. (302° F.), the anhydrous acid may be completely sublimed; exposed to a strong heat it develops irritating inflamable vapors, and is resolved, without carbonization, into carbon dioxide, carbon monoxide, formic acid, and water, and is finally completely dissipated.

FIG. 75.



Oxalic acid is soluble in 14 parts of water at 15° C. (59° F.), and in its own weight or less of boiling water, in 6 to 7 parts of 90 per cent., and 4 parts of absolute, alcohol ; it is also soluble in 7 parts of glycerin, but sparingly soluble in ether and chloroform. Its solution has a very sour taste, and a strong acid reaction ; it forms with the alkali metals soluble, with all other bases, for the most part, insoluble, salts, which, however, are soluble in dilute mineral acids.

When a cold saturated aqueous solution of oxalic acid is dropped into strong alcohol, it should not produce a turbidity ; when dropped into lime-water, a copious white precipitate must ensue at once, which remains unchanged upon the addition of acetic acid, as well as of ammonium chloride, but which is readily dissolved by hydrochloric and nitric acids. Added to a solution of calcium sulphate, a precipitate is also produced after a while.

When heated with concentrated sulphuric acid, oxalic acid is resolved into water and equal volumes of carbon monoxide and carbon dioxide gases, without being charred.

Examination:

Binoxalates and *quadroxalates of potassium* (sorrel and lemon salts) are detected by heating a small portion of the oxalic acid in a platinum or porcelain capsule, to redness, and until no more fumes are emitted; a white fused residue, turning red litmus-paper blue, and effervescing with a few drops of hydrochloric acid, would indicate potassium or traces of calcium.

The crude commercial acid mostly leaves a very small trace of residue, too insignificant, however, to impair the quality of the acid, or to render it unfit for its common technical applications.

Tartaric, *citric*, and *racemic acids*, and their salts, as accidental admixtures in oxalic acid, may be detected by gently heating a small quantity of the acid on platinum-foil, when they will be recognized by the development of a peculiar caramel-like odor, and a voluminous carbonaceous residue; when heated, in a test-tube, with concentrated sulphuric acid, the crystals, as well as the sulphuric acid, must not become dark-colored or blackened, otherwise the presence of one or the other of such admixtures is indicated.

The acid should dissolve perfectly in water, forming a clear solution, and, when saturated with hydrogen sulphide, should afford no coloration or precipitate.

Estimation:

Oxalic acid may be estimated volumetrically, either by the process of neutralization with a normal alkali, or by oxidation in its warm aqueous solution, slightly acidulated with sulphuric acid, with a standard or decinormal solution of potassium permanganate; it being resolved by the latter, through absorption of oxygen, into carbon dioxide and water.

I. Three grams of the air-dry, but uneffloresced, acid are dissolved in about 50 cubic centimeters of water, and, after the addition of a few drops of litmus solution, a normal solution of potassium or sodium hydrate (page 87) is allowed to flow into the liquid from a burette until, with constant stirring, a permanent blue coloration is produced. Oxalic acid being dibasic, each cubic centimeter of alkali solution employed, corrected if necessary by its proper factor, corresponds to 0.063 gram of crystallized acid, from which the percentage amount of pure acid in the specimen under examination may be readily determined.

II. 0.2 gram of the crystallized acid are dissolved in about 200 cubic centimeters of water, in a beaker, 5 to 10 grams of dilute sulphuric acid are then added, and, after gently heating, a standard solution of potassium permanganate (page 89) is allowed to flow into the liquid from a burette until, with constant stirring, a permanent pink coloration is produced.

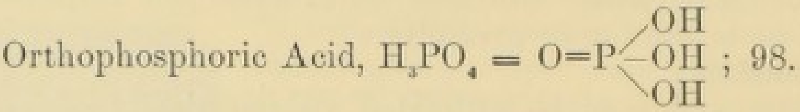
The reaction may be expressed as follows: $C_2H_2O_4 + O = 2CO_2 + H_2O$. One atom of oxygen thus oxidizes one molecule of oxalic acid, and the same amount of oxygen would oxidize two atoms of iron from the ferrous to the ferric state: $2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$. From these deductions one molecule of oxalic acid corresponds to two atoms (one molecule) of iron; and placing then the molecular weight of iron (112) as the first term, the molecular weight of crystallized oxalic acid (126) as the second term, and the amount of metallic iron, expressed in grams, corresponding to the number of cubic centimeters of permanganate solution employed, as the third term, a simple proportion will determine the amount of pure crystallized oxalic acid contained in the specimen under examination.

ACIDUM PHOSPHORICUM.

Phosphoric Acid.

Ger. Phosphorsäure; Fr. Acide phosphorique; Sp. Acido fosfórico.

$$\text{Metaphosphoric Acid, } HPO_3 = O{=}P\Big\langle\begin{matrix}O\\OH\end{matrix}\text{; 80.}$$



$$\text{Orthophosphoric Acid, } H_3PO_4 = O{=}P\Bigg\langle\begin{matrix}OH\\OH\\OH\end{matrix}\text{ ; 98.}$$

Monobasic or *metaphosphoric acid*, HPO_3, when perfectly pure, forms a soft pasty mass, which, on exposure to the air, readily absorbs moisture, and deliquesces to a thick syrupy liquid. The *glacial phosphoric acid* (Acidum Phosphoricum Glaciale) is an impure metaphosphoric acid, containing frequently considerable amounts of sodium or calcium phosphates, and forms colorless, transparent, glass-like, fusible masses, deliquescent, and slowly but freely soluble in water and in alcohol, yielding colorless, inodorous, acid solutions. The aqueous solution of metaphosphoric acid, when freshly prepared, produces white precipitates with albumen and with solutions of argentic nitrate and barium and calcium chlorides, which are soluble in an excess of the acid, while free orthophosphoric acid precipitates none of the above mentioned reagents. When its solution is allowed to stand for some time, or by continued boiling, the monobasic acid is converted into the tribasic acid, which is contained in the medicinal Acidum Phosphoricum Dilutum. This process is accelerated by the addition of a little nitric acid to the boiling solution of the monobasic acid.

Tribasic or *orthophosphoric acid*, H_3PO_4, when free from water, forms an odorless and colorless, dense, syrupy liquid, possessing a strongly acid taste and reaction. On standing over sulphuric acid, or by exposure to cold, it crystallizes, forming six-sided prisms, terminated by six-sided pyramids, belonging to the rhombic system, which melt at 38.6° C. (101.5° F.), and readily become liquefied in the presence of a small amount of water. The specific gravity of the anhydrous acid is 1.88 at 15° C. (59° F.). At temperatures above 160° C. (320° F.) it loses water, and at 213° C. (415.4° F.) it is completely converted into pyrophosphoric acid, $H_4P_2O_7$; when heated to redness, the latter acid becomes in turn further decomposed, losing water, and metaphosphoric acid, HPO_3, is produced.

Orthophosphoric acid, as previously stated, when in the free state, does not precipitate albumen, nor a solution of argentic nitrate or barium chloride; when carefully neutralized by ammonia-water, however, it yields a white precipitate with a solution of barium chloride, soluble in nitric or hydrochloric acids; with argentic nitrate a yellow precipitate of argentic phosphate, soluble in nitric acid or ammonia-water, and with test magnesium mixture, a white crystalline precipitate of ammonio-magnesium phosphate. When heated with a solution of ammonium molybdate, acidulated with nitric acid, a yellow crystalline precipitate of ammonium phosphomolybdate is produced.

Two strengths of orthophosphoric acid are officinal:* Acidum Phosphoricum, containing 50 per cent. of absolute acid, and having a specific gravity of 1.347; and Acidum Phosphoricum Dilutum, containing 10 per cent. of absolute acid, and having a specific gravity of 1.057.

Examination of Metaphosphoric Acid:

Ammonium salts may be detected by heating a few fragments of the fused acid in a strong solution of potassium hydrate in a test-tube, when they will be recognized by the odor of ammonia, as also by the production of white fumes, when a glass rod, moistened with acetic acid, is held over the orifice of the tube.

Calcium, *magnesium*, and *aluminium salts* may be detected by dissolving a small portion of the acid in water, boiling with a few drops of nitric acid, and, after the removal of the excess of nitric acid, carefully neutralizing with ammonia-water, when the phosphates of calcium, magnesium, and aluminium will be precipitated. If a precipitate is thus obtained, it is separated by filtration, the filtrate reserved for subsequent examination for sodium or potassium salts, and the precipitate further examined as follows: It is first digested with a concentrated solution of potassium or sodium hydrate, the solution filtered, and to the filtrate solution of ammonium chloride added, when a transparent, flocculent precipitate will indicate *aluminium*. The portion of the precipitate insoluble in the alkaline hydrate is then dissolved in hydrochloric acid, an excess of a solution of sodium acetate, and subsequently a little ferric chloride added, until the liquid assumes a yellowish hue, heated to boiling, and filtered; to a portion of the filtrate solution of ammonium oxalate is added, when a white precipitate will indicate *calcium;* to another portion of the filtrate ammonium carbonate in slight excess is added, the solution filtered, and to the filtrate ammonium phosphate and ammonia-water then added, when a white crystalline precipitate will indicate *magnesium.*

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* The phosphoric acid of the Pharmacopœia Germanica has a specific gravity of 1.120, corresponding to 20 per cent. of absolute acid; and the diluted phosphoric acid of the British Pharmacopœia a specific gravity of 1.08, corresponding to 14 per cent. of absolute acid.

Sodium or *potassium salts* may be detected in the filtrate from the precipitate produced by ammonia-water, as above described, by the following method: The phosphoric acid is first completely precipitated by neutral plumbic acetate, the filtrate freed from lead by hydrogen sulphide, filtered, and the filtrate evaporated and ignited. If a residue is thus obtained, it will contain the sodium or potassium salts in the form of carbonates, and may be further examined or identified by the color imparted to the non-luminous flame, when tested on platinum wire.

Silicic acid may be detected by evaporating a portion of the solution of the acid, to which a small quantity of hydrochloric acid has been added, to dryness, with the aid of a gentle heat; the residue is then dissolved in water, slightly acidulated with hydrochloric acid, when the silicic acid, if present, will remain behind as an insoluble granular powder.

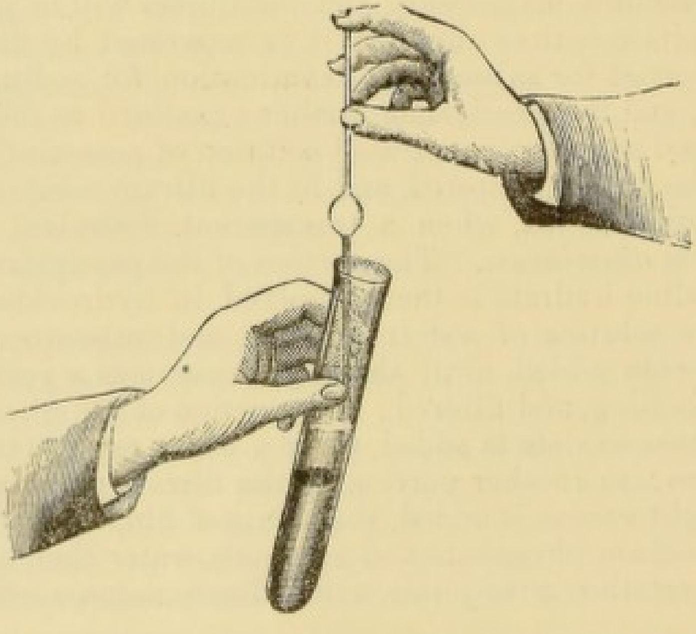
Metallic and *other impurities* may be detected by the methods described under orthophosphoric acid.

Examination of Orthophosphoric Acid:

Monobasic or *metaphosphoric acid* may be detected by a white precipitate on the addition of a solution of barium chloride, and by the formation of a gelatinous white precipitate when tested with solution of albumen.

Phosphorous acid may be detected in the diluted acid by the addition of a few drops of a solution of argentic nitrate or mercuric chloride, and gently warming; a brown or blackish coloration or precipitate with the first reagent, and a grayish-colored precipitate with the latter, will indicate phosphorous acid. A dilute solution of the acid, to which one or two drops of a solution

FIG. 76.



of potassium permanganate is added, will also become readily decolorized on warming, if phosphorous acid is present.

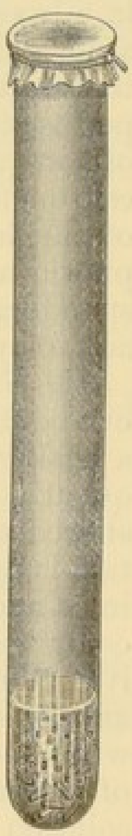
Hydrochloric acid is detected in the diluted acid, to which a few drops of concentrated nitric acid have been added, by a white precipitate on the addition of a solution of argentic nitrate.

Nitric acid is indicated by ensuing decoloration when a little of the acid is gently heated with one drop of indigo-solution. Its presence may be confirmed by mixing with the acid nearly an equal bulk of concentrated solution of ferrous sulphate, and placing this mixture upon concentrated sulphuric acid, with the precaution that the two fluids do not mix (Fig. 76); a red-brown coloration upon the line of contact between the two fluids will confirm the presence of nitric acid.

Sulphuric acid is detected in the diluted acid, to which a few drops of nitric acid have been added, by a white precipitate with barium nitrate.

Metals are detected by saturating the diluted acid with hydrogen sulphide, and allowing the liquid to stand for 12 hours in a corked test-tube or flask; the occurrence of a coloration or precipitate will indicate metals;* a light-yellow, flocculent one, arsenic; a brown or black one, copper or lead.

FIG. 77.



Arsenious as well as *arsenic acid*, besides having been detected in the test for metals with hydrogen sulphide, may be specially tested for by the application of Marsh's test, as described on pages 33 to 35, or by the following modification of the same. To a small quantity of the dilute phosphoric acid, contained in a test-tube, one drop of solution of potassium permanganate is added, and the liquid gently warmed; if decoloration takes place, the addition of solution of permanganate is continued, drop by drop, until decoloration of the reagent ceases; dilute sulphuric acid and fragments of pure zinc (both of which should have been previously tested for arsenic) are then added, not allowing the liquid to occupy more than one-fourth of the capacity of the tube. A small cap of bibulous paper, previously moistened with a drop of solution of argentic nitrate, is then placed over the mouth of the tube (Fig. 77), and the reaction accelerated, if necessary, by gently warming; the production of a purplish-black spot on the paper, due to the reduction of metallic silver, will confirm the presence of arsenic.

Estimation:

The strength of officinal phosphoric acid may be approximately determined by ascertaining its specific

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* Upon long standing, a separation of sulphur, from the decomposition of hydrogen sulphide, may ensue, but this may be readily recognized.

gravity, and subsequent reference to the subjoined table (page 180). Unlike most other acids, it cannot be estimated by direct neutralization with an alkali, since the point of neutralization, as indicated by means of litmus, cannot be distinctly observed, and in connection therewith is the fact of its forming three classes of salts—NaH_2PO_4, which has an acid reaction, and Na_2HPO_4 and Na_3PO_4, both of which possess an alkaline reaction.

Among the various methods employed for the quantitative estimation of the officinal or orthophosphoric acid, the two following will be found expedient and sufficiently accurate.

I. *Volumetric.*—This method depends upon its indirect estimation by the process of neutralization. A convenient quantity of the acid (about 10 grams of the officinal diluted acid, or 2 grams of the stronger acid) is accurately weighed, in a beaker, a normal solution of potassium or sodium hydrate (page 87) then allowed to flow in from a burette, until sufficient of the latter has been employed to insure the formation of the neutral sodium salt, Na_3PO_4. To the strongly alkaline liquid a solution of barium chloride is then added until no further precipitate is produced, the resulting barium phosphate $Ba_3(PO_4)_2$, after being allowed to stand for a few hours, filtered off, the precipitate well washed with water, and the filtrate together with the washings collected in a beaker; after the addition of a few drops of litmus solution, a normal solution of oxalic or sulphuric acid (page 82) is allowed to flow into the liquid from a burette until, with constant stirring, a permanent pink tint is produced. The number of cubic centimeters of normal acid solution required, deducted from the number of cubic centimeters of alkali solution first employed, will give the amount of the latter required for the exact neutralization of the phosphoric acid; one cubic centimeter of the normal alkali corresponding to 0.0327 gram H_3PO_4, the percentage strength of the acid may be readily calculated.

II. *Gravimetric.*—About 10 grams of the officinal diluted acid, or about 2 grams of the stronger acid, are accurately weighed, in a beaker, ammonia-water, in slight excess, then added, and subsequently test magnesium mixture, until, after having been well stirred and allowed to stand for a short time, no further precipitate is produced on the addition of the reagent. Ammonia-water, in an amount equal to about one-fourth of the volume of the liquid contained in the beaker, is then added, and the latter being covered, it is allowed to stand for about twelve hours. The precipitate of ammonio-magnesium phosphate is then collected on a filter, washed with a solution consisting of 1 part of ammonia-water and 3 parts of water until the washings no longer produce a turbidity in a solution of argentic nitrate acidulated with nitric acid, dried at 100° C. (212° F.), and finally ignited in a weighed porcelain crucible at a low, red heat. From the weight of the resulting magnesium pyrophosphate, $Mg_2P_2O_7$, the amount of phosphoric acid contained in the solution, or the percentage strength of the same, is readily calculated: 100 parts of magnesium pyrophosphate corresponding to 88.39 parts of phosphoric acid, H_3PO_4, or 64.28 parts of phosphoric anhydride, P_2O_5.

The U. S. Pharmacopœia directs that on pouring 5 grams of the stronger acid upon 10 grams of plumbic oxide free from plumbic carbonate and from moisture, evaporating and igniting, the obtained residue should weigh 11.81 grams; and that 5 grams of the diluted acid with 5 grams of plumbic oxide, under the same conditions, should yield a residue weighing 5.36 grams.

Rules for the Dilution of Phosphoric Acid.

If a strong acid, *a*, has to be diluted with water, or with a weaker acid, *c*, in order to obtain an acid of some special strength, *b*, the following rules are applicable:

The difference in percentage strength is sought on the one hand between *a* and *b*, and, on the other, between *b* and *c*, and *a* and *c* are then mixed in the proportions represented by the difference in the respective numbers.

It must be considered, however, that when the difference between *a* and *b* is greater than between *b* and *c*, less of *a* than of *c* must be taken in order to obtain *b*; and when the difference between *a* and *b* is less than between *b* and *c*, more of *a* than of *c* must be employed in order to obtain *b*; for example:

I. Phosphoric acid, containing 45 per cent. of absolute acid, is to be mixed with water, to form an acid containing 10 per cent. of absolute acid:

	a.	*b.*	*c.*
	45 per cent.	10 per cent.	0 per cent.
Difference	35	10	

10 parts of 45 per cent. acid are therefore to be mixed with 35 parts of water, or

100 grams of phosphoric acid = 45 grams H_3PO_4
350 " " water = ———
450 grams of phosphoric acid = 45 grams H_3PO_4
or 100 " " " " = 10 " "

II. Phosphoric acid, containing 32 per cent. of absolute acid, is to be mixed with an 8 per cent. acid, to form an acid containing 10 per cent. of absolute acid:

	a.	*b.*	*c.*
	32 per cent.	10 per cent.	8 per cent.
Difference	22	2	
	(11)	(1)	

1 part of 32 per cent. acid is therefore to be mixed with 11 parts of 8 per cent. acid, or

100 grams of phosphoric acid = 32 grams H_3PO_4.
1100 “ “ “ “ = 88 “ “

1200 grams of phosphoric acid = 120 grams H_3PO_4.
100 “ “ “ “ = 10 “ “

TABLE *of the quantity by weight of Orthophosphoric Acid, and the corresponding amount of Phosphoric Anhydride, contained in* 100 *parts by weight of aqueous Phosphoric Acid of different specific gravities (Schiff).*

Temperature 15° C. (59° F.).

Specific gravity.	Per ct. of H_3PO_4.	Per cent. of P_2O_5.	Specific gravity.	Per ct. of H_3PO_4.	Per cent. of P_2O_5.	Specific gravity.	Per ct. of H_3PO_4.	Per cent. of P_2O_5.
1.0054	1	0.726	1.1262	21	15.246	1.2731	41	29.766
1.0109	2	1.452	1.1329	22	15.972	1.2812	42	30.492
1.0164	3	2.178	1.1397	23	16 698	1.2894	43	31.218
1.0220	4	2.904	1.1465	24	17.424	1.2976	44	31.944
1.0276	5	3.630	1.1534	25	18.150	1.3059	45	32.670
1.0333	6	4 356	1.1604	26	18.876	1.3143	46	33.496
1.0390	7	5.082	1.1674	27	19 602	1.3227	47	34.222
1.0449	8	5.808	1.1745	28	20.328	1 3313	48	34.948
1.0508	9	6.534	1.1817	29	21.054	1.3399	49	35.674
1.0567	10	7.260	1.1889	30	21.780	1.3486	50	36.400
1.0627	11	7.986	1.1962	31	22.506	1.3573	51	37.126
1.0688	12	8.712	1.2036	32	23.232	1.3661	52	37.852
1.0749	13	9.438	1.2111	33	23.958	1.3750	53	38 578
1.0811	14	10.164	1.2186	34	24.684	1.3840	54	39.304
1.0874	15	10.890	1.2262	35	25.410	1.3931	55	40.030
1.0937	16	11.616	1.2338	36	26.136	1.4022	56	40.756
1.1001	17	12.342	1.2415	37	26.862	1.4114	57	41.482
1.1065	18	13.068	1.2493	38	27.588	1.4207	58	42.208
1.1130	19	13.794	1.2572	39	28.314	1.4301	59	42.934
1.1196	20	14.520	1.2651	40	29.040	1.4395	60	43.660

With the decrease or increase of temperature, the specific gravity of phosphoric acid suffers a corresponding increase or decrease, amounting for each degree of the centigrade thermometer in either direction :

For acids of a specific gravity of	1.0567	to those of	1.1196	to about	0.00035
“ “ “ “	1.1262	“	1.1889	“	0.00040
“ “ “ “	1.1962	“	1.2651	“	0.00052
“ “ “ “	1.2731	“	1.3486	“	0.00068
“ “ “ “	1.3573	“	1.4395	“	0.00082

For instance: An acid of 1.1262 spec. grav. at 15° C., containing 15.246 per cent. of phosphoric anhydride or 21 per cent. of phosphoric acid, will have at 20° C. a spec. grav. of $1.1262 - (0.0004 \times 5) = 1.1242$, and at 13° C. a spec. grav. of $1.1262 + (0.0004 \times 2) = 1.127$.

ACIDUM SALICYLICUM.

Salicylic Acid. Ortho-oxybenzoic Acid.

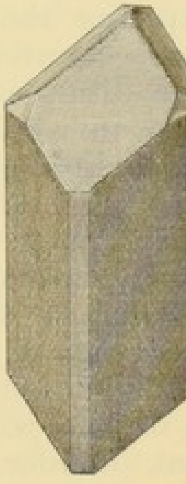
Ger. Salicylsäure; Fr. Acide salicylique; Sp. Acido salicílico.

$$C_7H_6O_3 = C_6H_4\begin{cases} HO \\ CO\text{-}OH \end{cases}; 138.$$

Fine, light, colorless needles, or four-sided prisms (Fig. 78), odorless, or having but a slight aromatic odor, and permanent in the air. They fuse at 156° C. (312.8° F.), and when carefully heated may be sublimed without decomposition; when quickly or more strongly heated, they are resolved into carbon dioxide and phenol, a decomposition which takes place to a slight extent when aqueous solutions of the acid are boiled; when strongly heated on platinum-foil they are completely dissipated.

Salicylic acid is soluble in 450 parts of water, and in 2.5 parts of alcohol at 15° C. (59° F.); in 14 parts of boiling water, and very freely in boiling alcohol; in 2 parts of ether or absolute alcohol, in 3.5 parts of amylic alcohol, and in 80 parts of chloroform; and sparingly soluble in benzol, carbon bisulphide, glycerin, and the volatile and fatty oils; it is readily soluble in solutions of the alkaline hydrates, forming crystallizable salts; and is also soluble in cold, concentrated sulphuric acid, without coloration, being precipitated from the latter solution unchanged on the addition of water. The solubility of the acid in water is greatly increased by the presence of various salts, such as the alkaline carbonates and acetates, borax, etc., which form with the acid readily soluble compounds.

FIG. 78.



The aqueous solution of the acid has an agreeable, somewhat sweetish taste, and an acid reaction, and assumes with a trace of ferric chloride an intense violet color; this reaction, however, is modified by the presence of alkaline hydrates, carbonates, acetates, and phosphates, as also by borax, potassium iodide, oxalic, citric, tartaric, phosphoric, and arsenic acids. With bromine-water the aqueous solution yields a white precipitate of bromo-salicylic acid, $C_7H_5BrO_3$. If to an aqueous solution of salicylic acid, or preferably a perfectly neutral solution of its sodium salt, a solution of cupric sulphate be added, a bright emerald-green color is produced, but which is destroyed by the presence of free alkalies or acids.

Examination:

Fixed impurities may be recognized by a non-volatile residue when a small portion of the acid is strongly heated on platinum-foil.

Organic admixtures may be detected by the separation of carbon when a little of the acid is heated on platinum-foil, or in a dry test-tube; or by a dark coloration when a small portion of the acid is agitated with about fifteen times its weight of cold, concentrated sulphuric acid.

Chlorides or *hydrochloric acid* may be detected by an ensuing white precipitate when a little of the acid, dissolved in about ten times its weight of alcohol, and acidulated with nitric acid, is tested with solution of argentic nitrate.

Phenol or *carbolic acid* may in most instances be detected by its odor; smaller quantities may be readily recognized by agitating the acid with a small quantity of warm water, and, after being allowed to cool, and the addition of a little ammonia-water, exposing the solution to the vapor of bromine, when a deep blue coloration will be produced; or, about 5 cubic centimeters of a saturated solution of salicylic acid are poured into a test-tube, in which 2 cubic centimeters of strong hydrochloric acid and a little granular potassium chlorate have just been mixed; some ammonia-water is then, by means of a pipette, carefully placed upon the mixture; the former will assume a reddish or brownish tint, if carbolic acid be present.

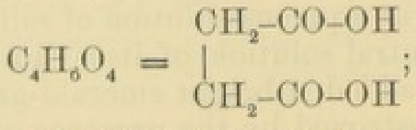
Detection of Salicylic Acid in Syrups, Extracts, Articles of Food, etc.:

A sufficient quantity of the substance to be examined is mixed or diluted with water, if necessary, and evaporated at a gentle heat, in order to expel any alcohol which may be present. After being allowed to cool, the clear filtered liquid is strongly acidulated with sulphuric acid, and subsequently shaken with ether. The ether is then carefully separated from the aqueous liquid, allowed to evaporate spontaneously, and the residue dissolved in a little water and tested with ferric chloride; if salicylic acid be present a deep violet coloration will be produced.

ACIDUM SUCCINICUM.

Succinic Acid.

Ger. Bernsteinsäure; Fr. Acide succinique; Sp. Ácido succínico.



$$C_4H_6O_4 = \begin{array}{l} CH_2\text{-}CO\text{-}OH \\ | \\ CH_2\text{-}CO\text{-}OH \end{array} ;\ 118.$$

Colorless, oblique-rhombic prisms, or rhombohedral plates, without odor when pure, and with a more or less strong odor when the acid is obtained from amber by sublimation, and is only imperfectly freed from the empyreumatic oils.

It melts at 180° C. (356° F.), but may be sublimed at a much lower temperature, and boils at 235° C. (455° F.), at the same time undergoing decomposition into water and succinic anhydride. When heated upon platinum-foil, it emits irritating, inflammable vapors, without the separation of carbon, and is entirely dissipated at a red heat.

Succinic acid is soluble in 18 parts of water at 17° C. (62.6° F.) and in 0.8 part of boiling water, in 10 parts of cold 90 per cent. alcohol, in 1.5 parts of boiling alcohol, and in 80 parts of pure ether, but is insoluble in carbon bisulphide, petroleum benzin, and turpentine oil (distinction from benzoic acid); it is also soluble in warm nitric acid, and in concentrated sulphuric acid, without decomposition, and, if perfectly pure, produces with the latter no coloration.

The aqueous solution of the acid has an acid taste and reaction, and, when carefully neutralized with ammonia-water, yields on the addition of a solution of ferric chloride a reddish-brown, flocculent precipitate of basic ferric succinate, which is dissolved upon the addition of hydrochloric acid (further distinction from benzoic acid).

Examination:

Fixed Admixtures.—If a residue remains when the acid is heated upon platinum-foil, a small portion of it should be completely incinerated in a porcelain crucible, and the residue, when cold, tested with moist turmeric- as well as with red litmus-paper. It is then divided into two parts, one of which is mixed with a little strong alcohol, and this ignited; a green color of the flame, especially toward the termination of the ignition, indicates *boracic acid;* the second portion of the residue is dissolved in a small quantity of water acidulated with a few drops of nitric acid; effervescence would indicate *carbonates*, originally present as such, or produced by the decomposition of some organic salts, if carbonization occurred upon ignition. The acid solution is then tested in separate portions, with argentic nitrate for *chlorides*, and with barium nitrate for *sulphates*, which will be indicated in either instance by an ensuing white precipitate.

Ammonium salts are detected by the odor of ammonia, and by white fumes when a glass rod, moistened with acetic acid, is held over the orifice of the test-tube, when the acid is heated in solution of potassium hydrate.

Foreign organic acids may be detected as follows:

Tartaric acid will be indicated by a white crystalline precipitate of acid ammonium tartrate, upon partial saturation of the acid with ammonia-water; or, by the production of a white crystalline precipitate of acid potassium tartrate, upon the addition of a few drops of a concentrated solution of potassium acetate to the aqueous solution of the acid.

Oxalic acid will be detected in the aqueous solution of the acid, after neutralization with ammonia-water, and the addition of a solution of calcium chloride, calcium sulphate, or lime-water, by the formation of a white precipitate, which is insoluble in acetic acid, or a solution of ammonium chloride.

Citric acid will be detected by the addition of a few drops of a solution of the acid to an excess of lime-water, so that the alkaline reaction still predominates, and subsequently heating to boiling; an ensuing white precipitate will indicate citric acid.

Benzoic acid may be detected by its solubility in carbon bisulphide or warm petroleum benzin; or by its separation, when the precipitate produced in the neutralized solution of the acid by ferric chloride is digested with a little hydrochloric acid.

Sugar may be detected, in the absence of other organic acids or their salts, by a corbonaceous residue on gently heating a little of the acid on platinum-foil; and, in the presence of other organic acids, by heating a small portion of the solution with a few drops of dilute sulphuric acid, and subsequently testing with Fehling's solution, when a red precipitate of cuprous oxide will be formed.

Metallic impurities may be detected in the concentrated solution of the acid, by a dark coloration or a precipitate upon saturation with hydrogen sulphide, or upon subsequent supersaturation with ammonia-water.

The following may serve as a general test for the purity of succinic acid: 1 part of the acid is dissolved in 15 parts of strong or absolute alcohol; the solution is aided by dipping the test-tube in hot water; when cold it is divided into two parts, one of which is mixed with an equal volume of chloroform, the other with an equal volume of ammonia-water; a complete solution must take place in the first test, and a clear mixture in the second, otherwise one or more of the above-mentioned adulterations are present.

When a crude acid, containing empyreumatic substances, has to be examined, it is first agitated and washed with a little ether, and is then dissolved in boiling water, and the solution, when cold, passed through a filter previously moistened with water.

ACIDUM SULPHURICUM.

Sulphuric Acid.

Ger. Schwefelsäure; Fr. Acide sulfurique; Sp. Ácido sulfúrico.

$$H_2SO_4 = SO_2\left\langle\begin{matrix}OH\\OH\end{matrix}\right.;\ 98.$$

A dense, colorless, inodorous, highly corrosive liquid, of a spec. grav. of 1.8426 at 15° C. (59° F.). When the pure acid of the above composition is heated, it is partially decomposed into water and sulphur trioxide. This dissociation increases with increase of temperature, until at 338° C. (640.4° F.) a liquid acid of constant composition and boiling-point distils over without further alteration, which contains from 98.4 to 98.8 per cent. of absolute acid. The commercial concentrated acid usually has a spec. grav. varying from 1.834 to 1.836 at 15° C. (59° F.), corresponding to from 93 to 94 per cent. of absolute acid. Two strengths of sulphuric acid are officinal, an acid having a spec. grav. not less than 1.840 (1.836–1.840 Pharm. Germ.; 1.843 Brit. Pharm.), and containing not less than 96 per cent. of absolute sulphuric acid; and Acidum Sulphuricum Dilutum, spec. grav. about 1.067 (1.110–1.114 Pharm. Germ.; 1.094 Brit. Pharm.), containing 10 per cent. of absolute acid.

Sulphuric acid has a strong attraction for water, absorbing it from the atmosphere, and withdrawing it or its elements from organic compounds immersed in, or mixed with, the acid; sulphuric acid, therefore, when in contact with organic substances, or with air containing dust, gradually loses its colorless appearance, and becomes more or less brown, and rapidly chars and destroys most organic substances.

Sulphuric acid is miscible with water, glycerin, alcohol, and other solvents, with evolution of heat, and produces, with most organic liquids, a more or less vehement decomposition; in its relations to other compounds, it maintains the character of one of the strongest acids, its affinity for bases being so powerful as to withdraw them from most of their compounds, forming sulphates, which, with the exception of those of barium, strontium, calcium, and lead, are freely soluble in water, the latter three being very sparingly soluble, while barium sulphate is practically insoluble in both water and dilute acids. By the same powerful affinity, sulphuric acid, in its dilute condition, dissolves most of the metals (iron, zinc, magnesium, cobalt), with the evolution of hydrogen and formation of sulphate of the metal; when concentrated it does not act in the cold upon many of the metals, but, when heated, most of them (copper, mercury, silver, lead, tin, etc.) are attacked, with the evolution of sulphur dioxide, in consequence of the reduction of the acid by the liberated hydrogen at the high temperature.

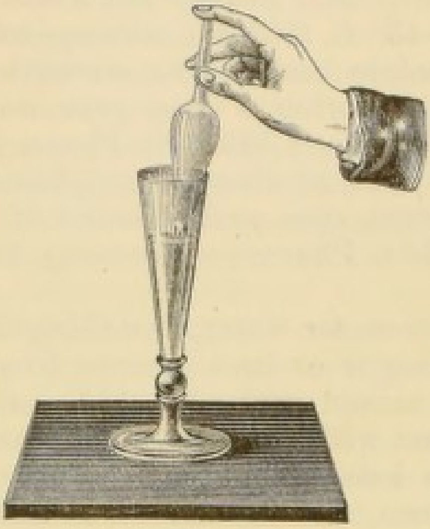
In consequence of its affinity for water, a piece of pine wood dipped into concentrated sulphuric acid becomes black from separation of carbon, and when a fragment of cane-sugar is placed in contact with the acid the latter will likewise assume a dark coloration, and upon heating develop the odor of sulphurous acid. When one drop of the acid is diluted with a test-tubeful of water, a white precipitate will be produced on the addition of a few drops of a solution of barium chloride.

Examination:

Fixed impurities are recognized by a residue after the complete evaporation of a small quantity of the acid in a platinum or porcelain capsule.

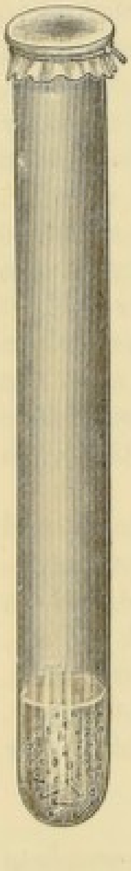
Lead is indicated by a white turbidity taking place upon the careful admixture of one part of the acid with about four or five times its volume of alcohol. Another method of readily recognizing the presence of lead in sulphuric acid is, to about half fill a small conical cylinder with concentrated hydrochloric acid, and then to place below the acid, by means of a pipette, a nearly equal volume of the sulphuric acid, with care that the fluids do not mix (Fig. 79); an ensuing white turbidity at the junction of the two fluids would confirm the presence of lead.

FIG. 79.



The presence of metallic impurities in general may be detected, after the previous dilution of the acid with several times its volume of water, and warming it gently, by saturating with hydrogen sulphide. The liquid, after standing for several hours, is filtered from any precipitate which may have been formed, subsequently supersaturated with ammonia-water, ammonium sulphide added, and, when required, further examined by the methods described in the course of analytical investigation (pages 51 to 59).

FIG. 80.

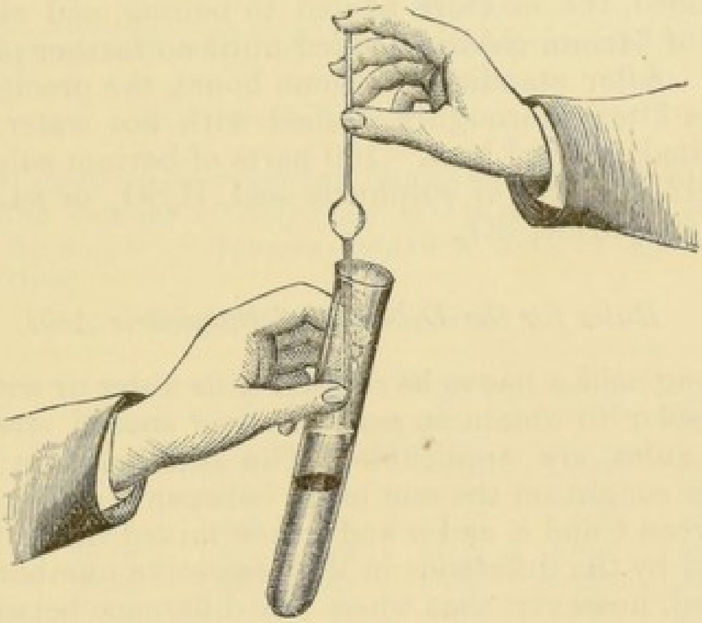


Arsenic may be detected in the acid, previously diluted with about five times its volume of water, and gently warmed, by the production of a yellow precipitate upon saturation with hydrogen sulphide, as indicated in the preceding test. If specially sought for, it may, together with *sulphurous acid*, be readily detected by heating the diluted acid, in a test-tube, with a few fragments of pure zinc, and placing over the orifice of the tube a cap of bibulous paper moistened with a drop of solution of argentic nitrate (Fig. 80); the production of a black stain upon the paper will indicate either arsenious or sulphurous acids.

Nitric and *nitrous acids* may be detected by the addition of a drop of indigo solution to a small portion of the acid, and gently warming, when decoloration of the liquid will ensue; or a crystal of ferrous sulphate is added to the acid, or a solution of the latter salt carefully poured upon it, without mixing, so as to form two distinct layers (Fig. 81), when, in either case, a brown coloration of the crystal, or a brown zone at the point of contact of the two liquids, will indicate the above-mentioned impurities.

By carefully mixing the concentrated acid with about half its volume of a solution of 5 drops of pure aniline in 25 cubic centimeters of dilute sulphuric acid, so as to form at first two layers, the mixture will assume a rose-red coloration in the presence of nitric or nitrous acids. A special test for nitric acid consists in the production of a rose-red coloration on the addition of a few drops of an aqueous solution of brucine.

FIG. 81.



Hydrochloric acid will be detected in the acid, diluted with twenty times its volume of water, by the production of a white, curdy precipitate on the addition of solution of argentic nitrate.

Estimation:

Sulphuric acid may be most conveniently estimated volumetrically by the process of neutralization. From 2 to 3 grams of the strong acid, or a corresponding quantity of dilute acid, is accurately weighed in a beaker, about 50 cubic centimeters of water, and a few drops of litmus solution added, and a normal solution of potassium or sodium hydrate (page 87) allowed to flow into the liquid from a burette until, with constant stirring, a permanent blue tint is produced. Sulphuric acid being dibasic, 1 cubic centimeter of the normal alkali solution corresponds to 0.049 gram H_2SO_4, which, multiplied by the number of cubic centimeters of normal alkali solution employed, will give the amount of absolute acid in the specimen under examination, and from which the percentage strength may be calculated. By determining the spec. grav. of the acid, the correctness of the result may be verified by comparing it with the percentage strength of an acid of the same specific gravity, as indicated in the subjoined table, page 189.

To neutralize 2.45 grams of the strong officinal acid, diluted with about 10 volumes of water, not less than 48 cubic centimeters of normal solution of potassium or sodium hydrate should be required; and to neutralize 9.8 grams of the officinal diluted acid should require from 19.2 to 20 cubic centimeters of normal alkali.

The gravimetric estimation of sulphuric acid is readily accomplished, although less quickly than by the preceding method, by its conversion into barium sulphate. To a weighed quantity of the acid, largely diluted with water, a few drops of hydrochloric acid are added, the mixture heated to boiling, and subsequently a solution of barium chloride added until no further precipitate is produced. After standing for some hours, the precipitate is collected on a filter, thoroughly washed with hot water, dried, and finally ignited at a red heat. 100 parts of barium sulphate correspond to 42.06 parts of sulphuric acid, H_2SO_4, or 34.33 parts of sulphuric anhydride, SO_3.

Rules for the Dilution of Sulphuric Acid.

If a strong acid *a* has to be diluted with water or with a weaker acid *c*, in order to obtain an acid of some special strength *b*, the following rules are applicable: The difference in percentage strength is sought on the one hand between *a* and *b*, and on the other between *b* and *c*, and *a* and *c* then mixed in the proportions represented by the difference in the respective numbers. It must be observed, however, that when the difference between *a* and *b* is greater than between *b* and *c*, less of *a* than of *c* must be taken in order to obtain *b*; and when the difference between *a* and *b* is less than between *b* and *c*, more of *a* than of *c* must be employed in order to obtain *b*; for example:

I. Sulphuric acid containing 29 per cent. of absolute acid is to be mixed with water to form an acid containing 25 per cent. of absolute acid:

	a.		*b.*		*c.*
	29 per cent.		25 per cent.		0 per cent.
Difference		4		25	

25 parts of 29 per cent. acid are therefore to be mixed with 4 parts of water, or

100 grams of sulphuric acid = 29 grams H_2SO_4.
16 " " water = ———
116 grams of sulphuric acid = 29 grams H_2SO_4.
or 100 " " " " = 25 " "

II. Sulphuric acid containing 32 per cent. of absolute acid is to be mixed with an 8 per cent. acid to form an acid containing 14 per cent. of absolute acid:

	a.	*b.*	*c.*
	32 per cent.	14 per cent.	8 per cent.
Difference	18 (3)	6 (1)	

1 part of 32 per cent. acid is therefore to be mixed with 3 parts of 8 per cent. acid, or

100 grams of sulphuric acid = 32 grams H_2SO_4.
300 " " " " = 24 " "
400 grams of sulphuric acid = 56 grams H_2SO_4.
or 100 " " " " = 14 " "

TABLE *of the quantity by weight of Sulphuric Acid* (H_2SO_4), *and the corresponding amount of Sulphuric Anhydride* (SO_3), *contained in* 100 *parts by weight of Aqueous Sulphuric Acid of different specific gravities* (*Otto*).

Temperature 15° C. (59° F.).

Specific gravity.	Per ct. of H_2SO_4.	Per cent. of SO_3.	Specific gravity.	Per ct. of H_2SO_4.	Per cent. of SO_3.	Specific gravity.	Per ct. of H_2SO_4.	Per cent. of SO_3.
1.8426	100	81.63	1.578	66	53.87	1.239	32	26.12
1.842	99	80.81	1.557	65	53.05	1.231	31	25.30
1.8406	98	80.00	1.545	64	52.24	1.223	30	24.49
1.840	97	79.18	1.534	63	51.42	1.215	29	23 67
1.8384	96	78.36	1.523	62	50.61	1.2066	28	22.85
1.8376	95	77.55	1.512	61	49.79	1.198	27	22.03
1.8356	94	76.73	1.501	60	48.98	1.190	26	21.22
1.834	93	75.91	1.490	59	48.16	1.182	25	20.40
1.831	92	75.10	1.480	58	47.34	1.174	24	19.58
1.827	91	74.28	1.469	57	46.53	1.167	23	18.77
1.822	90	73.47	1.4586	56	45.71	1.159	22	17.95
1.816	89	72.65	1.448	55	44.89	1.1516	21	17.14
1.809	88	71.43	1.438	54	44.07	1.144	20	16.32
1.802	87	71.02	1.428	53	43.26	1.136	19	15.51
1.794	86	70.10	1.418	52	42.45	1.129	18	14.69
1.786	85	69.38	1.408	51	41.63	1.121	17	13.87
1.777	84	68.07	1.398	50	40.81	1.1136	16	13.06
1.767	83	67.75	1.3886	49	40.00	1.106	15	12.24
1.756	82	66.94	1.379	48	39.18	1.098	14	11.42
1.745	81	66.12	1.370	47	38.36	1.091	13	10.61
1.734	80	65.30	1.361	46	37.55	1.083	12	9.79
1.722	79	64.48	1.351	45	36.73	1.0756	11	8.98
1.710	78	63.67	1.342	44	35.82	1.068	10	8.16
1.698	77	62.85	1.333	43	35.15	1.061	9	7.34
1.686	76	62 04	1.324	42	34.28	1.0536	8	6.53
1.675	75	61.22	1.315	41	33.47	1.0464	7	5.71
1.663	74	60.40	1.306	40	32.65	1.039	6	4.89
1.651	73	59.59	1.2976	39	31.83	1.032	5	4.08
1.639	72	58.77	1.289	38	31.02	1.0256	4	3.26
1.627	71	57.95	1 281	37	30.20	1.019	3	2.445
1.615	70	57.14	1.272	36	29.38	1.013	2	1.63
1.604	69	56.32	1.264	35	28.58	1.0064	1	0.816
1.592	68	55.59	1.256	34	27.75			
1.580	67	54.69	1.2476	33	26.94			

With the decrease and increase of temperature, the specific gravity of sulphuric acid suffers a corresponding increase or decrease, amounting for each degree of the centigrade thermometer in either direction :

For acids of a specific gravity of	1.842	to those of	1.786	to about	0.0014
" " " "	1.777	"	1.663	"	0.0012
" " " "	1.651	"	1.306	"	0.001
" " " "	1.297	"	1.215	"	0.00075
" " " "	1.206	"	1.144	"	0.00045
" " " "	1.136	"	1.068	"	0.00047

ACIDUM SULPHUROSUM.

Sulphurous Acid.

Ger. Schweflige Säure ; Fr. Acide sulfureux ; Sp. Acido sulfuroso.

A colorless liquid, possessing the characteristic suffocating odor of burning sulphur. The most concentrated acid which can be obtained by saturating water with the gas at ordinary temperatures contains 9.54 per cent. of sulphur dioxide, and has a specific gravity of 1.046. The officinal acid is stated to have a specific gravity of 1.022 to 1.023 (1.04 Brit. Pharm. = 9.2 per cent SO_2), corresponding to about 5.7 per cent. of sulphur dioxide. It possesses a very acid, sulphurous taste, and has a strongly acid reaction upon litmus, which it first reddens and afterwards bleaches. When heated to boiling, it loses sulphur dioxide, becoming finally completely volatilized ; and when exposed to the light it becomes gradually decomposed with the formation of pentathionic acid, $H_2S_5O_6$, and in contact with the air is readily oxidized to sulphuric acid.

Sulphurous acid possesses a strongly reducing action, to which are due also its bleaching properties ; it separates metallic gold, silver, and mercury from solutions of their salts, and liberates iodine from a solution of potassium iodate, which imparts a blue color to mucilage of starch. When hydrogen is generated by the action of dilute sulphuric acid upon a few fragments of pure metallic zinc, contained in a test-tube, and a few drops of sulphurous acid are added, the latter will become reduced to hydrogen sulphide, and impart a black stain to a piece of bibulous paper moistened with a solution of plumbic acetate, and placed over the mouth of the tube.

Examination :

Sulphuric acid may be detected by a white precipitate, insoluble in hydrochloric acid, upon the addition of a solution of barium chloride. The amount of sulphuric acid present should not be sufficient to produce more than a very slight turbidity, when to 10 cubic centimeters of sulphurous acid 1 cubic centimeter of diluted hydrochloric acid is added, and subsequently 1 cubic centimeter of test-solution of barium chloride.

Estimation:

The strength of an aqueous solution of sulphurous acid may be approximately determined by ascertaining its specific gravity, and subsequent reference to the subjoined table, or, more accurately, by the following method of volumetric estimation:

About 2 grams of the acid, diluted with 50 cubic centimeters of water, are placed in a flask, a little mucilage of starch added, and then a decinormal solution of iodine, the exact strength of which has been previously determined, page 93, allowed to flow into the liquid from a burette until, with constant stirring, a permanent blue coloration is produced;* the sulphurous acid becomes thus oxidized to sulphuric acid, according to the equation:

$$\underbrace{I_2}_{\substack{254\\(127)}} + \underbrace{H_2SO_3}_{\substack{82\\(41)}} + H_2O = H_2SO_4 + 2HI.$$

From the number of cubic centimeters of iodine solution employed, the amount of sulphur dioxide or of absolute sulphurous acid may be calculated; one cubic centimeter of the iodine solution, corrected if necessary by its proper factor, page 95, corresponding to 0.0032 gram of sulphur dioxide, SO_2, or 0.0041 gram of absolute sulphurous acid, H_2SO_3.

The U. S. Pharmacopœia directs that 1.28 grams of sulphurous acid, diluted with 20 volumes of water, and a little mucilage of starch added, should require the addition of at least 14 cubic centimeters of the volumetric solution of iodine before a permanent blue tint is developed, corresponding to at least 3.5 per cent. of sulphur dioxide.

TABLE *of the parts by weight of Sulphur Dioxide contained in* 100 *parts by weight of aqueous Sulphurous Acid, of different specific gravities* (*Anthon*).

Temperature 15° C. (59° F.).

Specific gravity.	Per cent. of SO_2.	Specific gravity.	Per cent. of SO_2.
1.046	9.54	1.020	4.77
1.036	8.59	1.016	3.82
1.031	7.63	1.013	2.86
1.027	6.68	1.009	1.90
1.023	5.72	1.005	0.95

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* On account of the volatility of sulphurous acid, it is important that such estimations be performed as quickly as possible, in order to prevent loss by evaporation.

ACIDUM TANNICUM.

Tannic Acid. Tannin.

Ger. Gerbsäure; Fr. Acide tannique; Sp. Acido tánico.

$$C_{14}H_{10}O_9 = \left.\begin{array}{l} C_6H_2(OH)_2CO\text{–}OH \\ C_6H_2(OH)_3CO \end{array}\right\} O; \; 322.$$

Amorphous, friable, porous, and inodorous masses, or thin shining scales, of a pale greenish-yellow color, and feeble, mild odor* (mostly combined with a faint odor of ether); when heated upon platinum-foil, tannic acid fuses, swells up, and burns away without residue.

Tannic acid is soluble in 6 parts of water or glycerin, in 0.6 part of alcohol, and in less than its own weight of diluted alcohol, and very freely soluble in boiling water and in boiling alcohol; it is but sparingly soluble in absolute alcohol and in commercial ether, and almost insoluble in absolute ether, chloroform, carbon bisulphide, benzol, benzin, and the fixed and volatile oils. Its aqueous solution reddens litmus-paper, and has an astringent taste, without bitterness; it becomes turbid when boiled, and gradually dark-colored and mouldy, when exposed to the air; it suffers precipitation by the alkaline salts, and by the mineral acids, and forms soluble compounds with the alkaline hydrates, sparingly soluble ones with the earthy oxides, and more or less insoluble ones with most of the metallic oxides; its solution coagulates solutions of gelatin, albumen, and starch (distinction from gallic acid), and affords white precipitates, soluble in acetic acid, with the alkaloids;† it produces no reaction with ferrous salts, if completely free from ferric salts, but it gives a bluish-black precipitate with the latter, which is soluble in oxalic and mineral acids. When solution of tannic acid is dropped into lime-water, it produces a white turbidity, which soon becomes gray and dingy green, and passes through various shades to a dark purple-brown color.

If to a very dilute aqueous solution of tannic acid a small quantity of iodine-water be added, a colorless solution will be obtained, which, on the addition of a very little ammonia-water, assumes a transient, fine red coloration; if the iodine-water be added in such an amount as of itself to impart a slight reddish tint to the liquid, and lime-water, instead of ammonia, be then added, a blue coloration will be produced.

Examination:

The absence of admixtures of *resinous substances*, *gum*, *dextrin*, and of *sugar*, may be ascertained by the property of the acid to yield a clear or nearly clear solution with about four or five parts of warm water, which should remain so when tested in two portions, the one by addition of twice its volume of strong alcohol,

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* The color and odor are due to traces of a greenish resin.

† Morphine is precipitated only from very concentrated solutions, and the precipitate is readily dissolved by a slight excess of tannic acid.

the other by dilution with water; if any such adulterations be present, they may be separated and recognized by making two solutions of the acid, one in strong alcohol, when gum, sugar, and dextrin will remain behind, and another one in boiling water, when resinous substances will remain undissolved or be separated on cooling.

Estimation:

In consequence of the variable nature of tannic matters as derived from different sources, and the impurities with which they are frequently accompanied, their exact quantitative estimation in technical products, vegetable extracts, etc., is often attended with considerable difficulty. Of the various methods proposed, two of the less complicated will here be given, which, however, in most instances afford sufficiently accurate results.

I. The substance to be examined is extracted with strong alcohol, the alcoholic liquid evaporated at a gentle heat to the consistence of a soft extract, and the residue taken up with just sufficient water to insure the complete solution of the tannic matter. To the clear aqueous solution a solution of neutral plumbic acetate is then added until a precipitate ceases to be produced, the precipitate collected upon a tared filter, washed three or four times with small portions of water, dried at 100° C. (212° F.) until of constant weight, and its weight finally determined. The precipitate is then removed from the filter, the latter, together with a little ammonium nitrate, brought into a porcelain crucible and ignited, and afterward the precipitate added, and the whole ignited at a strong heat until the weight remains constant. The weight of the ignited plumbic oxide, subtracted from the previously determined weight of the lead precipitate, will represent the amount of tannic acid, together with other organic acids or bitter principles precipitable by plumbic acetate, which may be contained in the substance under examination.

II. This method depends upon the precipitation of the tannic acid as zinc tannate, and the estimation of the latter by means of a solution of potassium permanganate. A solution of zinc acetate in an excess of ammonia water yields with tannic acid a precipitate of zinc tannate, insoluble in an excess of the reagent, in water or ammonia-water, but is not precipitated by alcohol, glycerin, potassium or calcium tartrate, albumen, or by ferric and ferrous salts of the organic acids; with gallic acid and aluminium salts it yields a precipitate, which, however, is soluble in an excess of the reagent and in ammonia-water.

The solutions required in this process of estimation are: 1. A solution of zinc acetate, prepared by dissolving 10 grams of crystallized zinc acetate in 200 cubic centimeters of water, and the subsequent addition of 130 grams of ammonia-water, spec. grav. 0.960. 2. Diluted sulphuric acid, prepared by mixing 1 part of sulphuric acid, spec. grav. 1.84, with 5 parts of water; and 3. A solution of 1.333 grams of crystallized potassium permanganate in 1 liter of water. In order to determine the oxidizing power of the permanganate solution, a solution of pure tannic acid of known strength is prepared; for instance, 1 gram of pure tannin dissolved in 1 liter of water. If it be found, for example, that 20 cubic centimeters of this tannin solution require the addition of 10 cubic centimeters of permanganate solution in order to produce a permanent pink tint, then 1 cubic centimeter of the permanganate solution corresponds to 0.002 gram of pure tannin. The estimation is then performed as follows: To about 50 cubic centimeters of the liquid to be examined, a slight excess of the solution of zinc acetate above that required to completely precipitate the tannin is added, the mixture heated to boiling, subsequently evaporated to about one-third of its volume, and allowed to cool. The precipitate of zinc tannate is then collected on a filter, washed with hot water, subsequently dissolved in diluted sulphuric acid, and the solution titrated with potassium permanganate until a permanent pink tint is produced. If, for example, 15 cubic centimeters of the potassium permanganate solution are employed, and, as by the above determination, 1 cubic centimeter of permanganate solution corresponds to 0.002 gram of tannin, consequently 15 cubic centimeters of permanganate solution correspond to 0.002 × 15 = 0.03 gram of tannin. As this amount is contained in 50 cubic centimeters of the liquid under examination, 100 cubic centimeters will contain 0.06 gram, or 0.06 per cent. of pure tannic acid.

TABLE *of the amount by weight of pure Tannic Acid contained in* 100 *parts by weight of its aqueous solutions of different specific gravities* (*Hammer*).

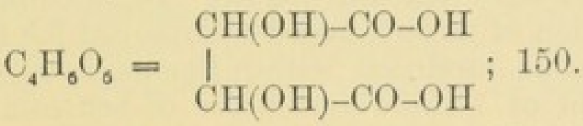
Temperature 15° C. (59° F.).

Specific gravity.	Per cent. of tannic acid.	Specific gravity.	Per cent. of tannic acid.	Specific gravity.	Per cent. of tannic acid.	Specific gravity.	Per cent. of tannic acid.
1.0010	0.25	1.0211	5.25	1.0416	10.25	1.0625	15.25
1.0020	0.50	1.0222	5.50	1.0427	10.50	1.0635	15.50
1.0030	0.75	1.0232	5.75	1.0437	10.75	1.0646	15.75
1.0040	1.00	1.0242	6.00	1.0447	11.00	1.0656	16.00
1.0050	1.25	1.0252	6.25	1.0458	11.25	1.0666	16.25
1.0060	1.50	1.0263	6.50	1.0468	11.50	1.0677	16.50
1.0070	1.75	1.0273	6.75	1.0479	11.75	1.0688	16.75
1.0080	2.00	1.0283	7.00	1.0489	12.00	1.0698	17.00
1.0090	2.25	1.0293	7.25	1.0499	12.25	1.0709	17.25
1.0100	2.50	1.0304	7.50	1.0510	12.50	1.0719	17.50
1.0110	2.75	1.0314	7.75	1.0520	12.75	1.0730	17.75
1.0120	3.00	1.0324	8.00	1.0530	13.00	1.0740	18.00
1.0130	3.25	1.0334	8.25	1.0541	13.25	1.0751	18.25
1.0140	3.50	1.0345	8.50	1.0551	13.50	1.0761	18.50
1.0150	3.75	1.0355	8.75	1.0562	13.75	1.0772	18.75
1.0160	4.00	1.0365	9.00	1.0572	14.00	1.0782	19.00
1.0171	4.25	1.0375	9.25	1.0583	14.25	1.0792	19.25
1.0181	4.50	1.0386	9.50	1.0593	14.50	1.0803	19.50
1.0191	4.75	1.0396	9.75	1.0604	14.75	1.0814	19.75
1.0201	5.00	1.0406	10.00	1.0614	15.00	1.0824	20.00

ACIDUM TARTARICUM.

Tartaric Acid.

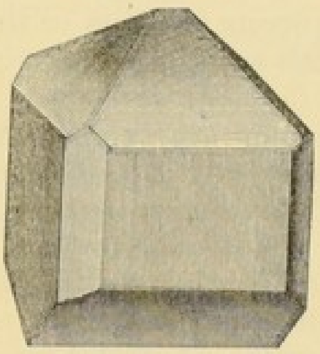
Ger. Weinsäure ; Fr. Acide tartarique ; Sp. Acido tartárico.



$$C_4H_6O_6 = \begin{array}{l} CH(OH)\text{–}CO\text{–}OH \\ | \\ CH(OH)\text{–}CO\text{–}OH \end{array} ; 150.$$

Colorless, transparent, monoclinic prisms (Fig. 82), permanent in the air; they contain no water of crystallization, and, when cautiously heated in a glass tube, fuse at 135° C. (275° F.) to a transparent, vitreous, very deliquescent mass of metatartaric acid, $C_4H_6O_6$; when strongly heated, with exposure to the air, they are decomposed with the evolution of inflammable vapors of a peculiar odor, resembling that of burnt sugar, and with the separation of carbon, and are finally wholly dissipated.

Fig. 82.



Tartaric acid is soluble in 0.7 part of cold, and in 0.5 part of boiling, water; in 2.5 parts of cold, and in 0.2 part of boiling, alcohol; in 36 parts of absolute alcohol, in 23 parts of commercial ether, or 250 parts of absolute ether; and is nearly insoluble in chloroform, benzol, and benzin. Its solutions possess a strongly acid taste and reaction, and, when dropped into solutions of neutral potassium salts, give rise to the formation of a white granular precipitate, at once in concentrated solutions, and after a time in diluted ones. This reaction, however, does not take place in solutions containing free mineral acids or acid salts thereof. When solution of tartaric acid is dropped into lime-water, so that the alkaline reaction predominates, a white turbidity occurs (distinction from citric acid), which disappears again upon the addition of solution of ammonium chloride (distinction from racemic acid), and also upon the addition of acetic acid (distinction from oxalic acid); solution of calcium sulphate remains unchanged upon the addition of tartaric acid (additional distinction from oxalic and racemic acids).

Crystals of tartaric acid, when immersed in concentrated sulphuric acid, dissolve gradually without coloration, unless warmed, when they become black, and, on more strongly heating, with the development of carbon monoxide, carbon dioxide, and sulphurous acid gas.

Examination:

Salts.—An admixture of salts is recognized by the addition of an equal volume of alcohol to a cold saturated aqueous solution of the acid, or by dissolving the powdered acid in 6 parts of strong alcohol; a complete and permanent solution must ensue in either case.

Sulphuric acid or *sulphates* may be detected in the diluted solution, to which a little hydrochloric acid has been added, by a white turbidity with barium nitrate. If 10 cubic centimeters of a strong solution of tartaric acid be employed for the test, no precipitate should be produced within five minutes upon the subsequent addition of 1 cubic centimeter of test-solution of barium chloride, and an excess of hydrochloric acid.

Chlorides may be detected in the diluted solution, by a white precipitate, insoluble in nitric acid, on the addition of a solution of argentic nitrate.

Oxalic acid or *oxalates* may be detected in the concentrated aqueous solution of the acid, by a white precipitate when tested with solution of calcium sulphate.

Calcium salts may be detected in the diluted solution, previously nearly neutralized with ammonia-water, so that the acid reaction still predominates, by a white precipitate on the addition of ammonium oxalate.

Metallic impurities (copper or lead) are detected by a brown or blackish coloration or precipitate, when a concentrated aqueous solution of the acid is saturated with hydrogen sulphide; after filtering, if necessary, and subsequent super-saturation with ammonia-water, an ensuing dark coloration would indicate *iron*.

Estimation:

One hundred parts of tartaric acid require for exact neutralization 92.2 parts of anhydrous potassium carbonate, 133.33 parts of crystallized potassium bicarbonate, 190.66 parts of crystallized sodium carbonate, 112 parts of sodium bicarbonate, and 63.33 parts of magnesium carbonate.

The estimation of tartaric acid may also be conveniently accomplished volumetrically with sufficient accuracy, since, unlike citric acid, its point of neutralization as indicated by means of litmus may be distinctly observed.

About 3 grams of the crystallized acid, accurately weighed, are dissolved in about 50 cubic centimeters of water, a few drops of litmus solution added, and a normal solution of potassium or sodium hydrate (page 87) allowed to flow into the liquid from a burette until, with constant stirring, a distinct blue tint is produced. Tartaric acid being disbasic, one cubic centimeter of normal alkali corresponds to 0.075 gram of the crystallized acid, and from the number of cubic centimeters of alkali solution employed, the purity or percentage strength of the acid may be readily calculated. If 3.75 grams of acid, and a strictly normal solution of alkali are employed, the number of cubic centimeters of the latter required for neutralization, when multiplied by 2, will represent at once the percentage purity of the acid.

Another method of estimation consists in adding to a solution of 1 part of tartaric acid in 3 parts of cold water, a solution of 1 part of potassium acetate in 3 parts of cold water, and subsequently adding a volume of alcohol equal to that of the whole mixture; after being allowed to stand for 2 hours, the white, crystalline precipitate of acid potassium tartrate is collected upon a tared filter, well washed with diluted alcohol, and dried at 100° C. (212° F.), when it should weigh between 1.25 and 1.26 parts.

TABLE *of the parts by weight of crystallized Tartaric Acid contained in 100 parts by weight of aqueous solutions of the acid of different specific gravities (Gerlach).*

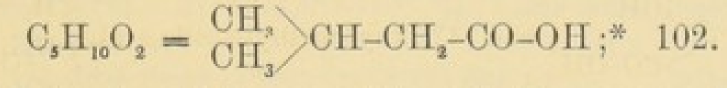
Temperature 15° C. (59° F.).

Specific gravity.	Per cent. of tartaric acid.	Specific gravity.	Per cent. of tartaric acid.	Specific gravity.	Per cent of tartaric acid.
1.0045	1	1.09693	20	1.2019	39
1.0090	2	1.1020	21	1.20785	40
1.0136	3	1.1072	22	1.2138	41
1.0179	4	1.1124	23	1.2198	42
1.0224	5	1.1175	24	1.2259	43
1.0273	6	1.1227	25	1.2317	44
1.0322	7	1.1282	26	1.2377	45
1.0371	8	1.1338	27	1.2441	46
1.0420	9	1.1393	28	1.2504	47
1.04692	10	1.1449	29	1.2568	48
1.0517	11	1.15047	30	1.2632	49
1.0565	12	1.1560	31	1.26962	50
1.0613	13	1.1615	32	1.2762	51
1.0661	14	1.1670	33	1.2828	52
1.0709	15	1.1726	34	1.2894	53
1.0761	16	1.1781	35	1.2961	54
1.0813	17	1.1840	36	1.3027	55
1.0865	18	1.1900	37	1.3093	56
1.0917	19	1.1959	38	1.3169	57

ACIDUM VALERIANICUM.

Valerianic Acid. Isopropyl-acetic Acid.

Ger. Valeriansäure, Baldriansäure; Fr. Acide valérianique;
Sp. Ácido valeriánico.



$$C_5H_{10}O_2 = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH\text{–}CH_2\text{–}CO\text{–}OH;^{*}\quad 102.$$

Pure valerianic acid forms a thin, colorless, or nearly colorless liquid, having the persistent odor of valerian-root, and a pungent, acid taste; it reddens litmus, bleaches the skin, and burns when

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* Of the acids having the empirical formula $C_5H_{10}O_2$, four modifications are theoretically possible, all of which are at present known:

(1) Normal valerianic acid, $CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CO\text{–}OH$. (2) The medicinal

inflamed with a bright, smoky light. In contact with water, it absorbs about 20 per cent. of its weight without losing its oily consistence, and is itself soluble in 25 parts of water at 15° C. (59° F.); it is miscible with ammonia-water, alcohol, and ether, in all proportions. Its spec. grav. is 0.934 at 15° C. (59° F.), and it boils at 175° C. (347° F.). The commercial acid is generally the hydrate $C_5H_{10}O_2 + H_2O$, formed as above mentioned from the absolute acid by the absorption of about 20 per cent. of its weight of water, and, with reference to the old notation, was formerly known as the trihydrated acid, $C_{10}H_9O_3.3HO$; it has the specific gravity 0.945, boils at 165° C. (329° F.), and may be also distinguished from the absolute acid by its limited solubility in carbon bisulphide. When pure concentrated valerianic acid is added to an excess of mercuric oxide, a fine red solution of basic, uncrystallizable valerianate is obtained; the same coloration is produced by a less concentrated acid on warming the solution, a considerable excess of the mercuric oxide being always maintained.

Examination:

Inorganic salts (valerianates) may be detected by a non-volatile residue on the evaporation of a small quantity of the acid in a small porcelain capsule.

Foreign fatty acids will be indicated by a higher specific gravity of the acid, and may also be recognized as follows: One gram of the acid is weighed in a tared flask, and water, of a temperature of from 12 to 15° C. (53.6 to 59° F.), is carefully added, with constant agitation, until the acid is just dissolved. The flask is weighed again, and the quantity of water required for solution must be not less than twenty-five times the weight of the acid; in this instance, not less than twenty-five grams. If the acid dissolves in less water, it is not pure, containing admixtures (alcohol, acetic acid, and butyric acid), which by their greater solubility increase that of the valerianic acid. On the other hand, the quantity of water required for solution must not exceed thirty times (30 grams) the weight of the valerianic acid, in which case it would contain less soluble or insoluble admixtures (caproic and similar monatomic acids, valeric aldehyde, etc.). The presence of valeric aldehyde, as also of amylic alcohol and amyl valerianate,

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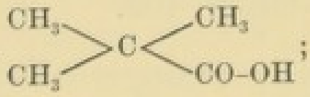
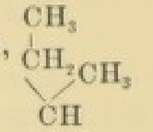
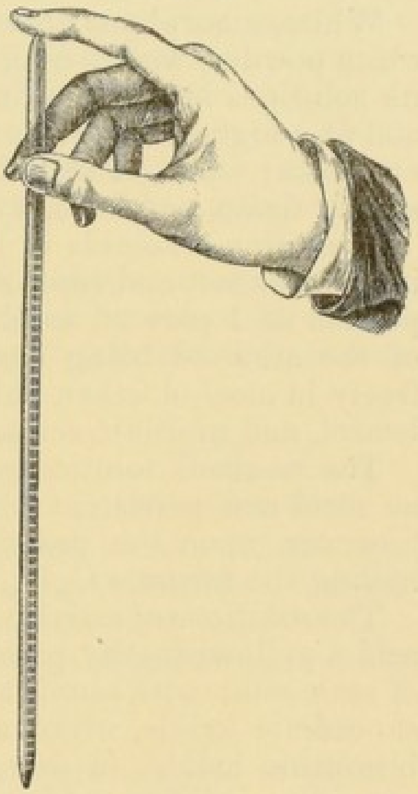
acid, or isopropyl-acetic acid,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH{-}CH_2{-}CO{-}OH$. (3) Trimethyl-acetic acid, ; and (4) Ethyl-methyl-acetic acid, 

These acids, however, with the exception of the second or medicinal acid, are principally of theoretical interest, being formed for the most part by difficult synthetical methods, and differ materially in their physical and chemical properties.

may likewise be detected by neutralizing the acid with ammonia-water, when they will either separate as an oily layer or impart a turbidity to the liquid.

If the preceding tests leave doubt as to the purity of the acid, or if a more conclusive examination be required, five grams of the acid are weighed in a beaker, and mixed with about ten grams of hot water; then from a burette, or a graduated pipette (Fig. 83), a solution of potassium carbonate, of 1.289 spec. grav. (containing 29 per cent. of anhydrous carbonate), is added drop by drop, until the acid is exactly neutralized. The quantity by weight of the solution of potassium carbonate used must not exceed twice the quantity of the acid; if a greater quantity be required, the presence of butyric, acetic, and similar homologous acids, is evident. When, in this test, oily drops are separated upon the surface of the liquid, the admixture of some neutral oily compound is indicated.

FIG. 83.



Acetic acid may be detected by carefully neutralizing a small portion of the acid with ammonia-water, and subsequently adding a dilute solution of ferric chloride until no further precipitate is produced; after the subsidence of the amorphous reddish-brown precipitate of ferric valerianate, the supernatant liquid should appear colorless or nearly so; a bright red color will indicate the presence of acetic acid.

Mineral acids may be detected in the aqueous solution of the valerianic acid by adding a few drops of nitric acid, and subsequently testing portions of it with barium nitrate for sulphuric acid, and with argentic nitrate for hydrochloric acid.

ACONITINA.

ACONITINUM.

Aconitine. Aconitia.

Ger. Aconitin ; Fr. Aconitine ; Sp. Aconitina.

$C_{33}H_{43}NO_{12}$; 645.

White, amorphous pulverulent grains, or a white or yellowish-white powder, which, with some difficulty, may be obtained from its solutions in a crystalline form. It melts at 120° C. (248° F.), and at a higher temperature is decomposed, with the evolution of ammonia; when strongly heated on platinum-foil, it burns with a smoky flame, and is finally completely dissipated.

Aconitine is soluble in 150 parts of cold water; with hot water it becomes soft and resin-like, and dissolves gradually in the proportion of 1 part of aconitine to 50 parts of boiling water, most of the alkaloid being again separated on cooling; it dissolves freely in alcohol, ether, chloroform, amylic alcohol, benzin, warm benzol, and in dilute acids.

The aqueous solution possesses a feeble alkaline reaction, and an acrid and persistent bitter taste; the latter being dependent, however, upon the presence of another alkaloid, *Picraconitine*, having the formula $C_{31}H_{45}NO_{10}$.

The solutions of aconitine in water yield with phospho-molybdic acid a yellowish-gray precipitate, becoming blue on the addition of ammonia; with tannic acid, potassio-mercuric iodide, and potassio-cadmic iodide, white, amorphous precipitates; with potassio-bismuthic iodide an orange-red precipitate, and with iodine in potassium iodide a reddish-brown precipitate, but are not precipitated by platinic or mercuric chlorides, or picric acid. The solutions of the salts of aconitine show the same behavior towards reagents, but are precipitated by picric acid, as also by solutions of sodium hydrate, sodium carbonate, and ammonia-water.

Aconitine dissolves in nitric acid with but a slight yellowish coloration; with concentrated sulphuric acid, it forms a coherent mass, which dissolves upon agitation, with a bright yellow color, and, at ordinary temperatures, gradually passes through brown or reddish-brown to violet-red. When dissolved in dilute phosphoric acid, and the solution allowed to evaporate slowly in a porcelain capsule on the water-bath, a fine violet color is also produced.

When aconitine is boiled with inorganic acids or alkalies, it is resolved into *benzoic acid*, and an uncrystallizable base, *aconine:*

$$\underbrace{C_{33}H_{43}NO_{12}}_{\text{Aconitine.}} + H_2O = \underbrace{C_7H_6O_2}_{\text{Benzoic acid.}} + \underbrace{C_{26}H_{39}NO_{11}}_{\text{Aconine.}}$$

An alkaloid formerly occasionally met with in commerce under the name of *Morson's*, or *English* aconitine, which differs in its physical, chemical, and therapeutical properties from the above described, is now recognized as consisting wholly or in part of a distinct body, and has received the name of *Pseudaconitine* or *Nepaline*, $C_{36}H_{49}NO_{12}$. It is derived from the Indian or Nepal aconite, *Aconitum ferox* Wallich, and is distinguished from aconitine by its elementary composition, its higher melting-point, 185–200° C. (365–392° F.), and much more sparing solubility in water, alcohol, ether, and chloroform, requiring about 250 parts of the latter for solution, while ordinary aconitine is soluble in 3 parts of chloroform. It crystallizes very readily from its solutions in the form of colorless, rhombic octahedra, and yields some well crystallizable salts, but does not produce the above described reactions of ordinary aconitine with sulphuric and phosphoric acids, which, however, do also not pertain to true, crystallized aconitine.

When pseudaconitine or nepaline is boiled with inorganic acids or alkalies, it appears to be first converted by dehydration into *apopseudaconitine*, $C_{36}H_{47}NO_{11}$, which latter is afterwards split into *veratric acid* and *apopseudaconine:*

$$\underbrace{C_{36}H_{49}NO_{12}}_{\text{Pseudaconitine.}} = \underbrace{C_8H_7(OH)_2CO\text{–}OH}_{\text{Veratric acid.}} + \underbrace{C_{27}H_{39}NO_8}_{\text{Apopseudaconine.}}$$

Commercial aconitine appears of itself not to be a definite substance, but to consist of a mixture of true crystallizable aconitine, together with pseudaconitine, picraconitine, and their various derivatives, aconine, pseudaconine, and possibly other amorphous bases.

For the isolation of aconitine from complex organic mixtures, or its separation and discrimination from other alkaloids, see also pages 108 and 109.

ÆTHER.

Ether. Ethylic Ether. Ethyl Oxide.

Ger. Aether; Fr. Ether; Sp. Éter sulfúrico.

$$C_4H_{10}O = (C_2H_5)_2O;\ 74.$$

A colorless, light, limpid, and highly refractive liquid, of a characteristic fragrant odor, very volatile and inflammable; it does not redden litmus, but gradually becomes slightly acid by the absorption of oxygen and the formation of acetic acid, from contact with the air in imperfectly stoppered bottles. When pure, its spec. grav., at 15.5° C. (60° F.), is about 0.720; it boils at 34.9° C. (94.8° F.) under a pressure of 760 mm., and does not solidify by exposure to the most intense cold.

The United States Pharmacopœia provides two strengths of ether, one of the spec. grav. 0.750, at 15° C. (59° F.), containing about 74 per cent., and æther fortior, of a spec. grav. not exceeding 0.725 at 15° C. (59° F.), or 0.716 at 25° C. (77° F.), and containing about 94 per cent. of ethylic ether.

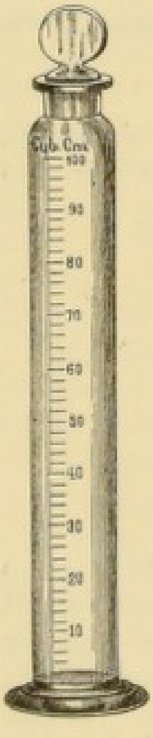
Ether is miscible, in all proportions, with alcohol, carbon bisulphide, chloroform, benzol, benzin, and the fixed and volatile oils; pure ether dissolves but one thousandth part of its weight of water, but is soluble in 20 parts by weight of water at 12° C. (53.6° F.). From its solution in ether, the water can again be almost wholly abstracted by contact with anhydrous potassium carbonate, provided that the ether be pure and free from alcohol. When completely free from alcohol and water, ether has no action on dry tannic acid, which deliquesces to a thick, syrupy fluid in æther fortior.

Ether dissolves sulphur and phosphorus sparingly, but bromine, iodine, caoutchouc, essential oils, and most of the fatty and resinous substances, freely; it is also a solvent for a number of alkaloids, and for some metallic salts, *e.g.*, mercuric, auric, platinic, and ferric chlorides, etc.

Examination:

Alcohol and Water.—Shaken with an equal bulk of water, in a small graduated cylinder (Fig. 84), officinal ether should not lose more than from one-fifth to one-fourth, and æther fortior not more than from one-tenth to one-eighth, of its volume; otherwise an excess of one or the other of the above is contained in the ether, which fact will also be indicated by a greater specific gravity of the ether than that above stated.

FIG. 84.



A still more accurate result of this test is obtained when pure glycerin is employed instead of water, whereby both water and alcohol are at the same time abstracted; the latter may then be recognized by subsequent distillation from the glycerin, and the addition of a few drops of an aqueous solution of potassium chromate and sulphuric acid to the distillate, when the green color of chromic oxide will soon appear. In the application of the preceding test, the U. S. Pharmacopœia requires that 10 cubic centimeters of ether, upon agitation with an equal volume of glycerin, should not be reduced to less than 7.5 cubic centimeters; and that when 10 cubic centimeters of æther fortior are agitated with an equal volume of glycerin, the ether layer, when fully separated, should measure not less than 8.6 cubic centimeters.

The presence of water in ether may also be detected by the appearance of a blue coloration on the addition of a little anhydrous cupric sulphate, or by forming a turbid solution when the ether is mixed with an equal volume of carbon bisulphide.

Acids.—Neutral blue litmus-paper, when previously moistened with water and immersed in both the ethereal and aqueous layers in the cylinder, should remain unaltered, as also when a small quantity of the ether is evaporated in a porcelain capsule until reduced in volume to a few drops, and then tested with litmus-paper; a slight acid reaction would indicate acetic acid, and, in crude ether, possibly sulphurous or sulphuric acid; the acid reaction may also be caused by traces of ethyl-sulphuric acid, which, together with other compound ethylic or amylic ethers, or alcohols, are also indicated when a small portion of the ether is allowed to evaporate spontaneously in a shallow porcelain capsule; when the ether has entirely evaporated, the inner surface of the capsule should be covered with a deposit of moisture, without taste or smell, and without any oily appearance.

TABLE *of the quantity by weight of pure Ethylic Ether contained in* 100 *parts by weight of Ether of different specific gravities.*

Temperature 17.5° C. (63.5° F.).

Specific gravity.	Per cent. of ethylic ether.	Specific gravity.	Per cent. of ethylic ether.	Specific gravity.	Per cent. of ethylic ether.	Specific gravity.	Per cent. of ethylic ether.
0.7185	100	0.7310	87	0.7456	74	0.7614	61
0.7198	99	0.7320	86	0.7468	73	0.7627	60
0.7206	98	0.7331	85	0.7480	72	0.7640	59
0.7215	97	0.7342	84	0.7492	71	0.7653	51
0.7224	96	0.7353	83	0.7504	70	0.7666	57
0.7233	95	0.7364	82	0.7516	69	0.7680	56
0.7242	94	0.7375	81	0.7528	68	0.7693	55
0.7251	93	0.7386	80	0.7540	67	0.7707	54
0.7260	92	0.7397	79	0.7552	66	0.7721	53
0.7270	91	0.7408	78	0.7564	65	0.7735	52
0.7280	90	0.7420	77	0.7576	64	0.7750	51
0.7290	89	0.7432	76	0.7588	63	0.7764	50
0.7300	88	0.7444	75	0.7601	62	0.7778	49

With the decrease and increase of temperature, the specific gravity of ether suffers a corresponding increase or decrease, amounting for each degree of the centigrade thermometer in either direction—

For ether of a specific gravity of 0.7198 to that of 0.7331, about 0.0013
" " " " 0.7342 " 0.7504, " 0.0011
" " " " 0.7516 " 0.7627, " 0.0009
" " " " 0.7640 " 0.7764, " 0.0008

For instance: An ether of 0.7206 spec. grav. at 17.5° C., containing 98 per cent. ethyl oxide, will have, at 20° C., a spec. grav. of 0.7206 — (0.0013 × 2.5) = 0.71735, and at 15° C., a spec. grav. of 0.7206 + (0.0013 × 2.5) = 0.72385.

ÆTHER ACETICUS.

Acetic Ether. Ethyl Acetate.

Ger. Essigäther ; Fr. Ether acétique ; Sp. Éter acético.

$$C_4H_8O_2 = C_2H_3O{-}O{-}C_2H_5;\ 88.$$

A colorless, light, limpid liquid, of an agreeable, ethereal, and fruity odor and taste ; very volatile and combustible. When perfectly pure, its specific gravity is 0.898 at 15° C. (59° F.) and its boiling point 74.3° C. (165.7° F.), but as the removal of the last traces of alcohol is effected with great difficulty, its specific gravity usually varies from 0.900 to 0.904 at 15° C. (59° F.), and its boiling-point from 74 to 76° C. (165.2 to 168.8° F.). Acetic ether is miscible in all proportions with ether, alcohol, chloroform, carbon bisulphide, and benzol, and soluble in approximately 17 parts of water. It absorbs oxygen from the air, especially if it contains some water, forming acetic acid ; both the water and the acid can be removed from the ether by shaking it with exsiccated potassium carbonate, which will become more or less liquefied when these fluids are present.

Examination :

Its aqueous solution should afford no precipitate with a solution of barium chloride (*sulphuric acid*) ; and when a portion of the ether is allowed to evaporate in a porcelain capsule, it should leave no permanent residue (*sodium or magnesium acetates*).

Alcohol.—When shaken with an equal volume of water in a graduated glass cylinder (Fig. 84, page 202), the ether, after subsiding, should not have decreased in volume more than one-tenth to one-eighth ; when pure glycerine is employed instead of water, the volume of both liquids should remain nearly unaltered. Alcohol and water are also indicated in connection with the preceding test by a lower or higher specific gravity of the ether than that above mentioned. As acetic ether may be mixed in such proportions with alcohol and ether that the presence of these admixtures is not readily detected on the one hand by the determination of the specific gravity alone, or on the other hand, by the test with absorption by water, it is necessary in its examination to apply successively both of the above mentioned tests, by which means the admixture may be readily detected.

Acids.—Neutral blue litmus-paper, when previously moistened with water, and immersed in both the ethereal and aqueous layers in the cylinder, should remain unaltered, as also when a portion of the ether is reduced to a small volume by evaporation in a porcelain capsule, and then tested with litmus-paper.

Estimation of the Ethyl Acetate contained in Acetic Ether :

The quantitative estimation of acetic ether is accurately and most conveniently accomplished volumetrically, by a process which depends upon its previous decomposition into alcohol and the acetate of an alkaline base; the amount of alkali required to effect the decomposition of a known and weighed amount of the ether being subsequently determined by the estimation of the excess of alkali employed with a standard acid.

About 3 grams of acetic ether are accurately weighed in a bottle provided with a closely fitting glass stopper, and having a capacity of at least 200 cubic centimeters; 100 cubic centimeters of a decinormal solution of crystallized barium hydrate (containing 15.75 grams $Ba(OH)_2 + 8H_2O$ in a liter) are then added, the whole well mixed, and, having fastened the stopper securely by means of twine, the mixture is heated upon the water-bath for about two hours. The decomposition of the ether which is thus effected is expressed by the equation:

$$\underbrace{2C_2H_3O_2(C_2H_5)}_{\text{Ethyl acetate.}} + \underbrace{Ba(OH)_2}_{\text{Barium hydrate.}} = \underbrace{2C_2H_6O}_{\text{Alcohol.}} + \underbrace{Ba(C_2H_3O_2)_2}_{\text{Barium acetate.}}.$$

The bottle and its contents are finally allowed to cool, then opened and the liquid tested with curcuma paper, which should indicate by its brown coloration a decided alkaline reaction, while the odor of the acetic ether must at the same time have completely disappeared. The contents of the flask are then transferred to a beaker, the flask subsequently well rinsed with several small portions of water, and, after the addition of a few drops of litmus solution, a decinormal solution of oxalic acid (containing 6.3 grams $C_2H_2O_4 + 2H_2O$ in a liter) is allowed to flow into the liquid from a burette until, with constant stirring, a permanent red coloration appears, or preferably until a drop of the solution brought upon curcuma paper no longer produces a brown coloration. The number of cubic centimeters of oxalic acid solution employed for neutralization, when subtracted from that of the barium hydrate solution originally employed (100), will represent the number of cubic centimeters of barium hydrate solution required for the decomposition of the ether, and therefrom the amount of ethyl acetate contained in the specimen under examination or its percentage strength may be subsequently readily calculated: one cubic centimeter of decinormal barium hydrate solution corresponding to 0.0088 gram of ethyl acetate.

ALCOHOL.

SPIRITUS RECTIFICATUS.

Ethyl Alcohol.

Ger. Spiritus, Weingeist; Fr. Alcool; Sp. Alcohol.

$C_2H_6O = C_2H_5\text{-}OH$; 46.

A colorless, limpid, neutral liquid, inflammable, and burning with a pale blue flame, without smoke; its spec. grav. is 0.795 at 15° C. (59° F.); its boiling-point at 78.4° C. (173.1° F.);* it is miscible in all proportions with most liquid bodies, but not with the fatty oils, with the exception of ricinus or castor oil, and, next to water, is the most extensive and important solvent, dissolving most of the organic acids and resins, alkaloids, and many other bodies which are sparingly soluble in water. It replaces water in some organic compounds (chloral alcoholate, $C_2HCl_3O + C_2H_6O$), and may be substituted for the water of crystallization in some inorganic salts; *e. g.*, $CaCl_2 + 3C_2H_6O$, $ZnCl_2 + 2C_2H_6O$, $Mg(NO_3)_2 + 6C_2H_6O$, $PtCl_4 + 2C_2H_6O$; all of which latter, however, are decomposed by water with the liberation of the alcohol, and the absorption of their normal equivalent of water.

Anhydrous alcohol has a great attraction for water, absorbing its vapor from the atmosphere, and abstracting the moisture from organic substances immersed in it. In the act of dilution, a contraction of volume and an increase of the temperature of the mixture take place. When 55 volumes of absolute alcohol are mixed with 45 volumes of water, the mixture, after cooling, will occupy only 96.2 volumes, having therefore suffered a contraction of 3.8 per cent.; and, *vice versa*, an expansion of volume takes place when diluted alcohol is mixed with water: *e. g.*, when 100 volumes of alcohol, of a spec. grav. of 0.966, containing 29 per cent., by volume, of absolute alcohol, are mixed with 50 volumes of water, 153 volumes will be obtained.

The percentage of absolute alcohol in its aqueous dilutions can be determined approximately, and with sufficient accuracy for any practical purpose, by ascertaining its specific gravity at a known temperature. The specific gravity of any sample of alcohol established will, by the aid of the following table, at once indicate the percentage of absolute alcohol:

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* The officinal alcohol has a spec. grav. of 0.820 at 15.6° C. (60° F.), or 0.812 at 25° C. (77° F.), and contains 94 per cent. by volume or 91 per cent. by weight of absolute alcohol; the diluted alcohol (Alcohol Dilutum) has a spec. grav. of 0.928 at 15.6° C. (60° F.), or 0.920 at 25° C. (77° F.), and contains 53 per cent. by volume, or 45.5 per cent. by weight of absolute alcohol.

TABLE *of the quantity of absolute Alcohol, by weight and by volume, contained in* 100 *parts of aqueous Alcohol of different specific gravities.*

Temperature 15° C. (59° F.).

Specific gravity.	100 volumes contain:		100 parts by weight contain:	Specific gravity.	100 volumes contain:		100 parts by weight contain:
	Alcohol.	Water.	Alcohol.		Alcohol.	Water.	Alcohol.
0.7951	100	0.00	100.00	0.9348	50	53.72	42.53
0.8000	99	1.28	98.38	0.9366	49	54.70	41.59
0.8046	98	2.54	96.83	0.9385	48	55.68	40.66
0.8089	97	3.77	95.35	0.9403	47	56.66	39.74
0.8130	96	4.97	93.89	0.9421	46	57.64	38.82
0.8169	95	6.16	92.45	0.9439	45	58.61	37.90
0.8206	94	7.32	91.08	0.9456	44	59.54	37.00
0.8242	93	8.48	89.72	0.9473	43	60.58	36.09
0.8277	92	9.62	88.37	0.9490	42	61.50	35.18
0.8311	91	10.76	87.04	0.9506	41	62.46	34.30
0.8344	90	11.88	85.74	0.9522	40	63.42	33.40
0.8377	89	13.01	84.47	0.9538	39	64.37	32.52
0.8409	88	14.12	83.22	0.9553	38	65.32	31.63
0.8440	87	15.23	81.96	0.9568	37	66.26	30.75
0.8470	86	16.32	80.72	0.9582	36	67.20	29.88
0.8500	85	17.42	79.51	0.9595	35	68.12	29.01
0.8530	84	18.52	78.29	0.9607	34	69.04	28.14
0.8559	83	19.61	77.09	0.9620	33	69.96	27.27
0.8588	82	20.68	75.91	0.9633	32	70.89	26.41
0.8616	81	21.76	74.75	0.9645	31	71.80	25.56
0.8644	80	22.82	73.59	0.9657	30	72.72	24.70
0.8671	79	23.90	72.43	0.9668	29	73.62	23.85
0.8698	78	24.96	71.30	0.9679	28	74.53	23.00
0.8725	77	26.03	70.16	0.9690	27	75.43	22.16
0.8752	76	27.09	69.04	0.9700	26	76.33	21.31
0.8778	75	28.15	67.93	0.9711	25	77.23	20.47
0.8804	74	29.20	66.82	0.9721	24	78.13	19.63
0.8830	73	30.26	65.72	0.9731	23	79.09	18.79
0.8855	72	31.30	64.64	0.9741	22	79.92	17.96
0.8880	71	32.35	63.58	0.9751	21	80.81	17.12
0.8905	70	33.39	62.50	0.9761	20	81.71	16.29
0.8930	69	34.44	61.43	0.9771	19	82.60	15.46
0.8954	68	35.47	60.38	0.9781	18	83.50	14.63
0.8978	67	36.51	59.33	0 9791	17	84.39	13.80
0.9002	66	37.54	58.29	0.9801	16	85.29	12.98
0.9026	65	38.58	57.25	0.9812	15	86.19	12.15
0.9049	64	39.60	56.23	0.9822	14	87.09	11.33
0.9072	63	40.63	55.21	0.9833	13	88.00	10.51
0.9095	62	41.65	54.20	0.9844	12	88.90	9.69
0.9117	61	42.67	53.19	0.9855	11	89.80	8.87
0.9139	60	43.68	52.20	0.9867	10	90.72	8.06
0.9161	59	44.70	51.20	0.9878	9	91.62	7.24
0.9183	58	45.72	50.21	0.9890	8	92.54	6.43
0.9205	57	46.73	49.24	0.9902	7	93.45	5.62
0.9226	56	47.73	48.26	0.9915	6	94.38	4.81
0.9247	55	48.74	47.29	0.9928	5	95.30	4.00
0.9267	54	49.74	46.33	0.9942	4	96.24	3.20
0.9288	53	50.74	45.37	0.9956	3	97.17	2.40
0.9308	52	51.74	44.41	0.9970	2	98.11	1.60
0.9328	51	52.73	43.47	0.9985	1	99.05	0.80

Since, however, the temperature exercises a considerable expanding and contracting influence upon alcohol and its dilution with water, it is necessary to ascertain, simultaneously with the specific gravity, also the temperature of the sample; for this reason, the areometers (alcoholometers) constructed for determining the specific gravity of alcohol are provided with a thermometer, and differences in the temperature of the alcohol under estimation may readily be corrected by calculation based upon this rule: The number of degrees of temperature of the alcohol above or below 15° must be multiplied by four-tenths; the product is then to be added to the percentage of the absolute alcohol indicated by the specific gravity, when the temperature of the liquid was lower than 15° C., and subtracted, when it was higher.

If, *e. g.*, the spec. grav. of a sample is found to be 0.861, at a temperature of 5° C., its percentage of real alcohol would be, according to the preceding table, 81 per cent., by volume; since, however, the alcohol was weighed at a temperature 10° lower than the standard temperature of the above table, its specific gravity was accordingly greater. Therefore, in order to correct this difference, 10 has to be multiplied by four-tenths; the product (= 4) must be added to the percentage of alcohol (81) inferred from the spec. grav., and the sum (= 85) expresses the real quantity of alcohol in 100 parts by volume.

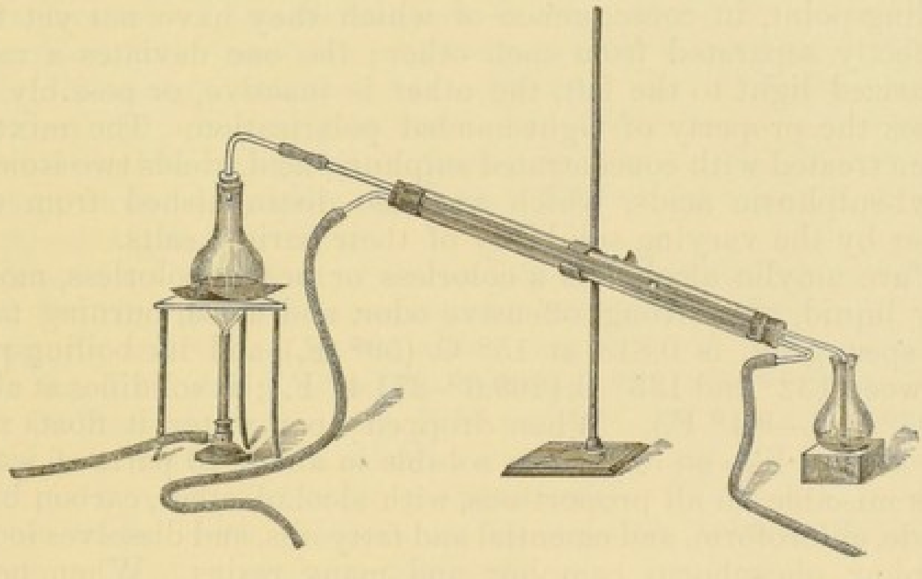
Examination:

Alcohol should be perfectly neutral in its action upon litmus, wholly vaporizable by heat, and afford no coloration on the addition of ammonia-water.

Fusel oil (consisting principally of amylic alcohol, with traces of propylic, butylic, and other alcohols, free fatty acids or compound ethers) and *aldehyde* may be detected by mixing a portion of the alcohol with an equal volume of pure ether, and subsequently adding an amount of water equal to the volume of the mixture; the whole is shaken, and, when subsidence has taken place, the ethereal layer is decanted, and allowed to evaporate spontaneously in a shallow porcelain capsule. After the evaporation of the ether, the residue will give the characteristic odor of fusel oil, or of any flavors indicative of a previous employment of the alcohol for the extraction of vegetable substances. The residue, if sufficient in amount, may be also further examined by bringing it into a test-tube with a few drops of water, subsequently adding a very small quantity of sodium acetate, and a few drops of concentrated sulphuric acid, and gently warming the mixture; if fusel oil be present, the characteristic odor of amyl acetate (pear essence) will be developed. The presence of fusel oil may likewise frequently be detected by simply pouring a few grams of alcohol upon three or four times its volume of hot water, contained in a large beaker, and causing the mixture to flow to and fro, when, in proportion as the alcohol evaporates, the odor of the fusel oil will become more distinct. Aldehyde will also be further indicated by a dark coloration on the addition of ammonia-water, or when a small portion of the alcohol is warmed with a fragment of pure potassium hydrate; as also by the reduction of metallic silver, on the addition of a few drops of a solution of argentic nitrate to the alcohol, and gently warming.

Methyl Alcohol.—Among the several methods for the detection of methyl alcohol as an admixture in ethyl alcohol, the following two are preferable: 1. About 150 cubic centimeters of the alcohol are digested for an hour with 20 grams of plumbic carbonate, and filtered, the filtrate is then distilled from a water-bath, and the first 20 cubic centimeters of the distillate treated with 1 cubic centimeter of test-solution of potassium permanganate; the color should not disappear within one or two minutes, otherwise methyl alcohol is indicated. 2. Ten grams of powdered potassium bichromate are dissolved, in a flask, in about 75 cubic centimeters of water, 15 grams of concentrated sulphuric acid are then added, and subsequently about 10 grams of the alcohol to be examined.

FIG. 85.



The flask is then connected with a condenser (Fig. 85), and, after having been allowed to stand for about a quarter of an hour, gentle heat is applied until about two-thirds of the liquid has distilled over. The distillate (which will contain aldehyde and acetic acid from the oxidation of the ethyl alcohol, and also formic acid from the oxidation of the methyl alcohol, if the latter were present) is then slightly supersaturated with crystallized sodium carbonate, and evaporated at a gentle heat, with the repeated addition of water, if necessary, until the odor of aldehyde has entirely disappeared. The solution is then filtered into a test-tube, slightly acidulated with acetic acid, a few drops of solution of argentic nitrate added, and the mixture gently warmed. If the liquid merely darkens a little, but remains quite translucent, the alcohol is free from methyl alcohol; but if a dark-brown or black precipitate of reduced silver separates, and the test-tube, after being rinsed and filled with water, shows upon its interior a bright metallic mirror, which, when seen against white paper, appears brown by transmitted light, the alcohol is methylated.

ALCOHOL AMYLICUM.

Amylic Alcohol. Fusel Oil.

Ger. Amylalcohol, Fuselöl; Fr. Alcohol amylique; Sp. Alcohol amílico.

$$C_5H_{12}O^* = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right> CH-CH_2-CH_2-OH;\ 88.$$

Amylic alcohol, as obtained by fractional distillation from fusel oil, is a mixture of two isomeric alcohols, having nearly the same boiling-point, in consequence of which they have not yet been perfectly separated from each other; the one deviates a ray of polarized light to the left, the other is inactive, or possibly possesses the property of right-handed polarization. The mixture, when treated with concentrated sulphuric acid, yields two isomeric amyl-sulphuric acids, which are also distinguished from each other by the varying solubility of their barium salts.

Pure amylic alcohol is a colorless or nearly colorless, mobile, oily liquid, of a strong, offensive odor, and acrid, burning taste; its spec. grav. is 0.818 at 15° C. (59° F.), and its boiling-point between 132° and 133° C. (269.6°–271.4° F.); it solidifies at about —23° C. (—9.4° F.). When dropped upon water, it floats upon the surface like an oil, but is soluble in about 40 parts of water; it is miscible, in all proportions, with alcohol, ether, carbon bisulphide, chloroform, and essential and fatty oils, and dissolves iodine, sulphur, phosphorus, camphor, and many resins. When mixed with an equal volume of concentrated sulphuric acid, it forms a violet-red mixture, from which, upon dilution with much water, the amylic alcohol is for the most part separated unchanged; if the mixture, however, is allowed to stand for several hours, no separation takes place upon dilution, in consequence of the forma-

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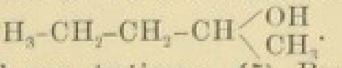
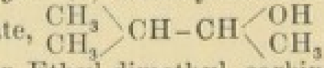
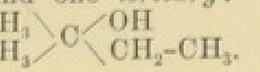
* Of the alcohols possessing the empirical formula $C_5H_{12}O$, eight modifications are theoretically possible; viz., 4 primary, 3 secondary, and 1 tertiary, of which number, five are now known, viz., two *primary:* (1) Normal amylic alcohol, $CH_3-CH_2-CH_2-CH_2-CH_2-OH$. (2) The commercial amylic alcohol of the above constitution. Two *secondary:* (3) Isoamylic alcohol,



$CH_3-CH_2-CH_2-CH\left<\begin{matrix}OH\\CH_3\end{matrix}\right.$. (4) Amylene hydrate,



$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH-CH\left<\begin{matrix}OH\\CH_3\end{matrix}\right.$. And one *tertiary:* (5) Pseudoamylic alcohol, or Ethyl-dimethyl carbinol,



$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C\left<\begin{matrix}OH\\CH_2-CH_3\end{matrix}\right.$.

tion of the above-mentioned amyl-sulphuric acid, which is soluble in water. When amylic alcohol is heated with strong sulphuric acid and a fragment of potassium bichromate, the odor of valerianic acid is evolved. Amylic alcohol does not take fire by contact with flame, and, when dropped on paper, does not leave a permanent greasy stain.

ALOINUM.

Aloin.

Ger. Aloïn ; Fr. Aloine ; Sp. Aloina.

The term *aloin*, although originally applied to a crystalline principle obtained from Barbadoes aloes, has now, in view of the discovery of allied crystalline principles in other varieties of aloes, been extended to the entire group, which, however, with the consideration of the distinctions in their physical and chemical characters, have received, according to their derivation, the appellations *barbaloin*, *nataloin*, and *socaloin*. The different varieties of aloin are apparently isomeric, and differ from each other in their chemical composition simply by the amount of combined water; thus:—Nataloin, $C_{16}H_{18}O_7$; Barbaloin, $C_{16}H_{18}O_7 + H_2O$; Socaloin, $C_{16}H_{18}O_7 + 3H_2O$.

Nataloin, $C_{16}H_{18}O_7$, crystallizes from ethyl or methyl alcohol in thin, brittle, rectangular scales, of a pale yellow color; it is very sparingly soluble in water, either hot or cold, but at 15.5° C. (60° F.), is soluble in 60 parts of alcohol, 35 parts of methyl alcohol, 50 parts of acetic ether, 1236 parts of ether, and 230 parts of absolute alcohol. By oxidation with nitric acid it affords oxalic and picric acids, and with chromic acid it yields carbonic and acetic acids; with chlorine or bromine no definite derivative products have as yet been obtained.

Barbaloin, $C_{16}H_{18}O_7 + H_2O$, is a neutral substance, crystallizing in tufts of small yellow prisms, which lose one molecule of water by drying in vacuo, or by prolonged heating at 100° C. (212° F.). It is sparingly soluble in water or in alcohol, but very freely if either liquid be slightly warmed; it is insoluble in ether. By oxidation with nitric acid it yields about one-third of its weight of chrysammic acid, $C_{14}H_4(NO_2)_4O_4$, besides aloetic acid, $C_{14}H_4(NO_2)_4O_4$, and oxalic and picric acids; with chromic acid, or a mixture of potassium bichromate and sulphuric acid, it yields, besides carbonic and acetic acids, a peculiar yellow compound, *aloxanthin*, ot the composition $C_{15}H_{10}O_6$, which is soluble in alkalies, forming a cherry-red solution, and, when heated with zinc dust, yields methylanthracene, $C_{14}H_9(CH_3)$. Aloxanthin may thus be considered as tetroxymethylanthraquinone, $C_{14}H_3(CH_3)(OH)_4O_2$; when treated with nitric acid, it is converted into chrysammic acid. With bromine or chlorine, barbaloin combines to form yellow crystallizable compounds of brom- or chloraloin.

Socaloin, $C_{16}H_{18}O_7 + 3H_2O$, forms small tufted acicular prisms of a yellow color, and is much more soluble than nataloin. It is very freely soluble in methyl alcohol, and, at ordinary temperatures, is soluble in 30 parts of alcohol, 9 parts of acetic ether, 380 parts of ether, and 90 parts of water. It melts at 118 to 120° C. (242.6 to 248° F.) to a soft mass, and parts with its water of crystallization by drying over sulphuric acid. By the action of oxidizing agents, potassium bichromate and sulphuric acid, or nitric acid, it furnishes the same products as those yielded by barbaloin, but with bromine no well-defined compound has as yet been obtained.

Zanaloin, prepared from a variety of Socotrine aloes imported from Zanzibar, is believed to be identical with socaloin.

Distinguishing Tests:

The three varieties of aloin, nataloin, barbaloin, and socaloin, may be distinguished from each other, and, to a certain extent, also themselves identified, by the following reactions: A drop of nitric acid, contained on a porcelain plate, produces with a few particles of nataloin or barbaloin a bright crimson coloration, rapidly fading in the case of barbaloin, but permanent with nataloin, unless heat be applied; with socaloin but little effect is produced. To distinguish barbaloin from nataloin, they are separately tested by adding a minute quantity to a drop or two of sulphuric acid, on a porcelain plate, and then allowing the vapor from a glass rod, moistened with nitric acid, to pass over the surface; barbaloin and socaloin undergo no change, but nataloin assumes a fine blue color.

ALUMEN.

ALUMINII ET POTASSII SULPHAS. ALUMINII ET AMMONII SULPHAS.

Alum.

Ger. Alaun; Fr. Alun; Sp. Alúmbre.

$Al_2K_2(SO_4)_4 + 24H_2O$; 948. $Al_2(NH_4)_2(SO_4)_4 + 24H_2O$; 906.*

Colorless, transparent, octahedral crystals (Fig. 86), often exhibiting the faces of a cube and dodecahedron, and containing 24 molecules (45.57 per cent.) of water of crystallization. On ex-

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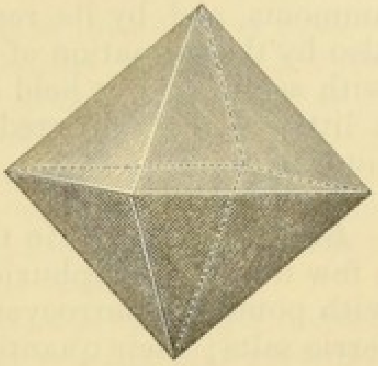
* If aluminium be accepted as trivalent, as is indicated by the molecular composition of several organic compounds, the composition of alum is more correctly expressed by the formula AlK (or NH_4)$(SO_4)_2 + 12H_2O$.

FIG. 86.



posure to the air, the surface of the crystals becomes opaque and white, which, however, is not due to the loss of water, but to the absorption of ammonia, and the formation of a basic sulphate.

Alum melts in its water of crystallization at 92° C. (197.6° F.), and loses the whole of its water very slowly by prolonged heating at 100° C. (212° F.) in a current of air, much more quickly at temperatures above 185° C. (365° F.), swelling up to a white porous mass (burnt alum), which, when moistened with a few drops of solution of cobaltous nitrate, and again strongly heated, assumes a blue color.

Potassium alum, which is the official one of the U. S. and the German Pharmacopœias, is soluble in 25.6 parts of water at 0° C. (32° F.), in 10.5 parts at 15° C. (59° F.), in 6.6 parts at 20° C. (68° F.), and in 0.27 part of boiling water; it is also soluble in glycerin, but insoluble in alcohol, ether, and chloroform. Its solution has a sweetish, astringent taste, reddens litmus-paper, and gives with the alkaline hydrates a voluminous white precipitate of aluminium hydrate, which is nearly insoluble in ammonia water, but readily soluble in an excess of potassium or sodium hydrates, from which solution, however, it is again precipitated on the addition of ammonium chloride; the alkaline carbonates and phosphates also produce white precipitates of aluminium hydrate or phosphate, insoluble in an excess of the reagents, and with solutions of barium salts a white precipitate of barium sulphate is produced. The aqueous solution of alum dissolves metallic zinc, especially when heated therewith in a platinum capsule, with the evolution of hydrogen, and the formation of zinc sulphate and a basic salt of the composition $Al_2(SO_4)_3 + 2Al_2(HO)_6 + K_2SO_4 + 3H_2O$.

Ammonium alum is very similar to potassium alum, and analogous in its composition, but differs therefrom in some of its chemical and physical properties. Its specific gravity is 1.626, whilst that of potassium alum is 1.724. It is soluble in 19.3 parts of water at 0° C. (32° F.), in 7.4 parts at 20° C. (68° F.), and in 0.24 part of boiling water; its relations to other solvents and reagents being similar to those of potassium alum.

Commercial alum frequently contains both ammonium and potassium in varying proportions, the former being substituted, to a greater or less extent, for the latter; since their properties are nearly the same, this admixture is of little consequence in the common uses of alum. Potassium alum consists, in 100 parts, of 18.33 parts of potassium sulphate, 36.14 parts of aluminium sulphate, and 45.57 parts of water of crystallization; while ammonium alum contains, in 100 parts, 14.55 of ammonium sulphate, 37.82 of aluminium sulphate, and 47.63 of water of crystallization. The presence of ammonium alum is recognized by the odor of ammonia, and by its reaction upon moistened red test-paper, as also by the formation of white fumes when a glass rod, moistened with acetic acid, is held over the mouth of the test-tube in which a little of the powdered alum is heated with a solution of potassium hydrate.

Examination:

Iron is recognized in the solution of alum, after the addition of a few drops of sulphuric acid, by a blue coloration when tested with potassium ferrocyanide; most crude alum contains traces of ferric salts; their quantity, however, should not be so considerable as to produce a purple coloration of a solution of the alum upon the addition of a few drops of solution of tannic acid, or more than a bluish coloration when one drop of test-solution of potassium ferrocyanide is added to a solution of 1 gram of alum in 30 cubic centimeters of water.

Other *metallic* impurities may be detected in the solution, after the addition of a little tartaric acid and subsequent supersaturation with ammonia-water, by hydrogen sulphide or ammonium sulphide; a dark coloration or precipitate indicates metallic impurities; a white precipitate, not disappearing upon the addition of potassium hydrate, would show *zinc*. If required, the nature of such a precipitate may be determined by the method described on pages 52 to 59.

Detection of Alum in Flour or in Bread:

From 50 to 100 grams of the substance to be examined are digested in a flask or porcelain capsule, at a gentle heat, with concentrated nitric acid, or with concentrated hydrochloric acid and a little potassium chlorate, until the organic substances are completely destroyed, and a limpid slightly yellowish solution is obtained. The liquid is then diluted with water, filtered, evaporated to a small volume, potassium hydrate (free from aluminium) in slight excess added, and the liquid afterward acidulated with hydrochloric acid, and finally supersaturated with ammonia-water; if a transparent, flocculent precipitate is thus produced, it will indicate a salt of aluminium, or alum.

ALUMINII HYDRAS.

ALUMINIUM HYDRICUM. ALUMINA HYDRATA.

Hydrate of Aluminium. Aluminium Hydrate. Hydrated Alumina.

Ger. Thonerdehydrat; Fr. Hydrate d'alumine; Sp. Hydrato de alúmina.

$Al_2(OH)_6$; 156.

A white, amorphous, inodorous, and tasteless powder, neutral in its action upon litmus, and permanent in the air. It is insoluble in water, either hot or cold, but soluble in acetic and the dilute mineral acids, particularly upon warming, and is also dissolved by solutions of potassium or sodium hydrate, but is insoluble in ammonia-water. Its solution in the fixed alkaline hydrates is not rendered turbid by boiling, but it is separated therefrom as a transparent flocculent precipitate, on the addition of a solution of ammonium chloride. When a small portion of aluminium hydrate, contained on the looped end of a platinum-wire, is moistened with a drop of a solution of cobaltous nitrate, and strongly heated, a beautiful blue color will be imparted to the bead.

One hundred parts of aluminium hydrate, when strongly heated in a weighed porcelain crucible, until after cooling and repeated weighing the weight remains constant, should afford a residue of aluminium oxide Al_2O_3, weighing 65.4 parts.

Examination:

Soluble salts in general may be detected by boiling a portion of the powder with about twenty times its weight of water, filtering, and evaporating the filtrate to dryness. If a residue is obtained, it is dissolved in water, and acidulated with a few drops of nitric acid; effervescence will indicate *carbonates.* The solution is then tested, in separate portions, with argentic nitrate for *chlorides*, and with barium chloride for *sulphates*, when a white precipitate in either case will reveal the presence of such impurities.

Barium, *calcium*, and *zinc*, when in the form of soluble salts or carbonates, may be detected by dissolving a portion of the powder in acetic acid, with the aid of a gentle heat, and testing the solution, in separate portions, as follows: To a portion of the solution, solution of potassium chromate is added, when a yellow precipitate will indicate *barium*, or possibly lead; after filtration, if necessary, solution of ammonium oxalate is added, when an ensuing white precipitate will indicate *calcium.* To another portion of the acetic solution ammonia-water in considerable excess is added, the mixture filtered, and tested with ammonium sulphide, when an ensuing white precipitate will indicate *zinc.*

Silica and *insoluble sulphates* will be indicated by an insoluble residue when a portion of the powder is treated with warm dilute hydrochloric acid. Such a residue may be further tested by mixing it with about three times its weight of exsiccated sodium carbonate, and fusing in a small porcelain crucible; the fused mass is then treated with warm water, filtered, the filtrate acidulated with hydrochloric acid, and tested with barium chloride, when a white precipitate will indicate *sulphates.* The portion of the fused mass insoluble in water is supersaturated with acetic acid, the solution evaporated to dryness by the aid of a gentle heat, and the residue dissolved in water acidulated with acetic acid, when *silica* will remain behind as an insoluble powder; the clear solution is then tested, in separate portions, with ammonium oxalate for *calcium*, and with sulphuric acid for *barium.*

Metallic impurities may be detected by dissolving a portion of the aluminium hydrate in dilute hydrochloric acid, and testing with hydrogen sulphide; a dark coloration or precipitate will indicate *copper* or *lead*.

Another portion of the dilute acid solution may be subsequently tested with a drop of solution of potassium ferrocyanide, when an ensuing blue coloration or precipitate will reveal the presence of *iron*.

ALUMINII SULPHAS.

ALUMINIUM SULFURICUM.

Sulphate of Aluminium. Aluminium Sulphate.

Ger. Schwefelsaures Aluminium; Fr. Sulfate d'alumine; Sp. Sulfato de alúmina.

$$Al_2(SO_4)_3 + 18H_2O;\ 666.$$

A white crystalline powder, or small pearly, six-sided, monoclinic tablets, permanent in the air, and containing 18 molecules (48.6 per cent.) of water of crystallization. When exposed to heat, it first melts in its water of crystallization, which it loses at about 200° C. (392° F.), swelling up to a light, porous mass of anhydrous salt, which dissolves but slowly again in water. At a red heat it is decomposed with the liberation of sulphuric acid, leaving behind aluminium oxide (alumina or argilla), which, when moistened with solution of cobaltous nitrate and reheated, assumes a blue color.

Aluminium sulphate is soluble in 1.2 parts of water at 15° C. (59° F.), and very soluble in boiling water, but is almost insoluble in alcohol. Its aqueous solution possesses an acid reaction and an astringent taste, and yields a white precipitate with barium chloride, insoluble in hydrochloric acid; with the alkaline hydrates it also yields a voluminous white precipitate, of which that with the fixed hydrates is soluble in an excess of the precipitant (evidence of the absence of magnesium), but is precipitated again upon the addition of ammonium chloride. The alkaline solution should yield no reaction upon the addition of a few drops of ammonium sulphide; the occurrence of a brown or yellowish-red precipitate would indicate *ferric* and *manganic* salts, and of a white one *zinc*.

The presence of *salts of the alkalies* may be detected by adding to a solution of the salt a slight excess of ammonia-water, heating until the odor of ammonia has disappeared, filtering, evaporating the filtrate to dryness, and igniting the residue at a gentle heat; no fixed residue, or but a very slight one, not exceeding 5 per cent. of the weight of the salt, should remain.

AMMONII BENZOAS.

AMMONIUM BENZOICUM.

Benzoate of Ammonium. Ammonium Benzoate.

Ger. Benzoësaures Ammonium ; Fr. Benzoate d'ammoniaque ;
Sp. Benzoato de amoniaco.

$NH_4C_7H_5O_2 = C_6H_5\text{-}CO\text{-}ONH_4$; 139.

Small, colorless, shining, thin, four-sided, tabular crystals, permanent in the air, and having a feeble odor of benzoic acid, and a saline, somewhat balsamic, and bitterish taste. When heated to 120° C. (248° F.), the salt melts; at 239° C. (462.2° F.) it boils, but becomes thereby partially decomposed, with the elimination of two molecules of water, and the formation of benzo-nitrile (phenyl cyanide), $C_6H_5\text{-}CN$, a colorless, limpid liquid, having an odor resembling that of bitter-almond oil; when strongly heated on platinum-foil, the salt first fuses, emits vapors having the odor of ammonia and of benzoic acid, and is finally completely dissipated.

Ammonium benzoate is soluble in 5 parts of cold, or 1.2 parts of boiling water; in 28 parts of cold, or 7.6 parts of boiling alcohol; and is also soluble in glycerin. Its aqueous solution loses ammonia upon evaporation, and is converted into the more sparingly soluble acid salt, $NH_4C_7H_5O_2 + C_7H_6O_2$; if not too dilute, it emits the odor of ammonia when heated with potassium hydrate, and gives a white precipitate of benzoic acid upon the addition of hydrochloric acid, and a copious, pale, reddish-yellow precipitate of basic ferric benzoate with ferric salts. The diluted solution of ammonium benzoate must remain clear when mixed with lime-water (evidence of the absence of ammonium oxalate), and, when acidulated with nitric acid, should afford no turbidity or precipitate on the addition of a solution of barium chloride (absence of sulphates), or with argentic nitrate (absence of chlorides).

AMMONII BROMIDUM.

AMMONIUM BROMATUM.

Bromide of Ammonium. Ammonium Bromide.

Ger. Bromammonium ; Fr. Bromure d'ammonium ; Sp. Bromuro de amonio.

NH_4Br; 97.8.

Colorless, transparent, anhydrous, prismatic crystals, or a white, granular salt, which, by exposure to the air, gradually assumes a yellow color, from the liberation of a minute quantity of free bromine. When strongly heated, the salt is completely volatilized, without decomposition or charring.

Ammonium bromide is soluble in 1.5 parts of water and in 150 parts of alcohol at 15° C. (59° F.), in 0.7 part of boiling water and in 15 parts of boiling alcohol, and very sparingly soluble in ether. Its aqueous solution has a saline, pungent taste, is neutral to test-paper, and, when acidulated with a few drops of nitric acid, yields on the addition of a solution of argentic nitrate a yellowish curdy precipitate of argentic bromide, which is sparingly soluble in ammonia-water; when the aqueous solution is added to a very dilute solution of mercuric chloride, no precipitate is produced (distinction from alkaline iodide). An aqueous solution of the salt, mixed with a little mucilage of starch, and a few drops of chlorine-water subsequently added, produces a yellowish-brown coloration, without exhibiting a blue tint (absence of iodide).

Heated with potassium hydrate, it emits the odor of ammonia.

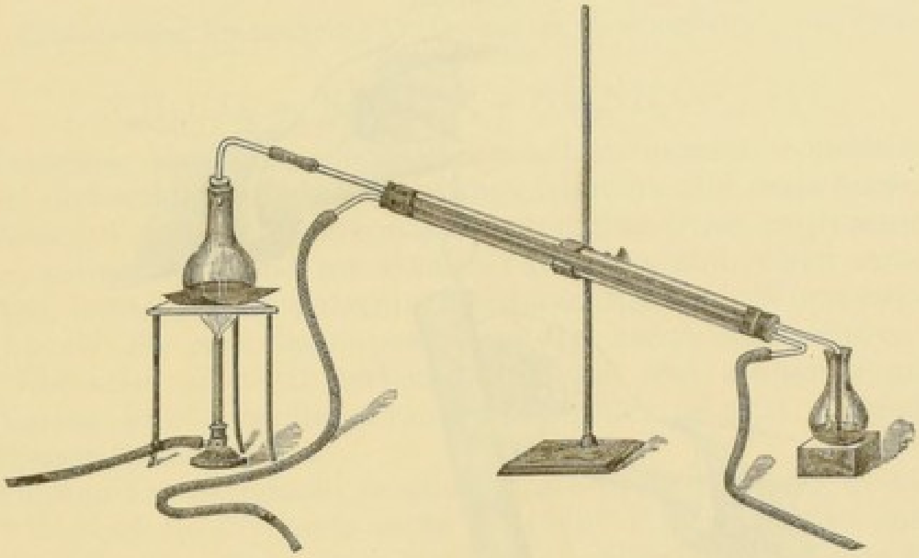
Examination:

Ammonium bromate is detected in the aqueous solution by a yellow coloration on the addition of a few drops of dilute sulphuric or nitric acid, due to the liberation of bromine, which is rendered more evident by subsequent agitation with a few drops of carbon bisulphide or chloroform.

Ammonium chloride, or other alkaline chlorides, when present in any considerable amount, may be detected by precipitating the aqueous solution with argentic nitrate, and digesting the moist, well-washed precipitate with a cold, saturated solution of ammonium carbonate. After standing for some time, the solution is filtered, and the filtrate supersaturated with nitric acid; if the bromide is pure, but a slight turbidity will occur, whereas, if chlorides are present, a white, curdy precipitate will be produced. In order to ascertain, in this case, the presence of not more than three per cent. of chlorides, three grams of the dry salt are dissolved in so much distilled water as to make the solution measure 100 cubic centimeters. Then to 10 cubic centimeters of this solution a few drops of test-solution of potassium bichromate are added, and subsequently, with constant stirring, standard solution of argentic nitrate; not more than 31.4 cubic centimeters of the latter should be required, before the red color ceases to disappear, otherwise the salt contains more than three per cent. of chlorides.

Smaller quantities of chloride may be detected by mixing 5 grams of the powdered and well-dried salt with 6 grams of pure powdered potassium bichromate, bringing the mixture into a small, perfectly dry flask, which is connected with a receiver containing a small amount of water (Fig. 87), and subsequently adding to the mixture in the flask 15 parts of pure concentrated sulphuric acid; the reaction being finally aided by the application of a gentle heat. If chlorides are present, chloro-chromic anhydride, CrO_2Cl_2, will be volatilized, and may be subsequently recognized in the distillate, after neutralization with ammonia-water, by the yellow color of the solution, and by the application of the several reactions for chromates; or, by its reduction to green chromic oxide, on the addition of a little hydrochloric acid and alcohol, and gently warming.

FIG. 87.



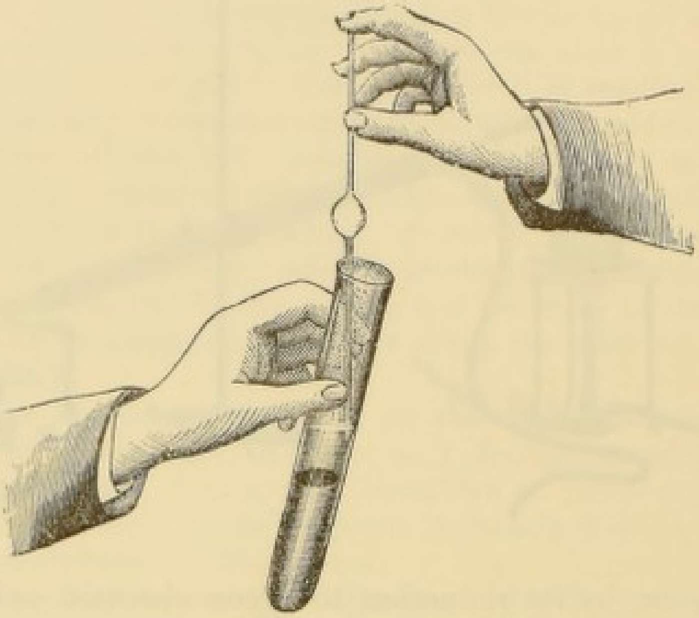
Nitrates will be indicated in the aqueous solution of the salt by a brown coloration, when a little dilute sulphuric acid is added, and the mixture heated to boiling. The presence of nitrates may, however, be more conclusively established by precipitating an aqueous solution of the salt with plumbic acetate, or preferably argentic acetate, in slight excess, filtering from the precipitate of plumbic or argentic bromide, and subsequently adding to the filtrate a solution of ferrous sulphate, and afterward concentrated sulphuric acid, so as to form two layers (Fig. 88); a brown or purplish zone at the line of contact of the two liquids will reveal the presence of nitrates.

Sulphates may be detected in a solution of 1 part of the salt in about 20 parts of water, by a white turbidity or precipitate on the addition of a few drops of solution of barium chloride.

Estimation:

One part of the dry salt, when completely precipitated by argentic nitrate, yields, if perfectly pure, 1.917 parts of argentic bromide. Upon the relation of the amount of argentic nitrate required to completely precipitate a definite amount of the salt, the following volumetric method of estimation is based: Two grams of ammonium bromide, previously reduced to powder, and carefully dried, are dissolved in water to the measure of 100 cubic centimeters; 10 cubic centimeters of this solution, corresponding to 0.2 gram of ammonium bromide, are then brought into a beaker, diluted with about 50 cubic centimeters of water, and, after the addition of a few drops of a solution of potassium chromate, a decinormal solution of argentic nitrate (page 98) is allowed

Fig. 88.



to flow into the liquid from a burette until, with constant stirring, a permanent reddish-brown coloration is produced. If the salt is pure ammonium bromide, 20.41 cubic centimeters of the silver solution will be required to produce this effect, as containing 0.347 gram of argentic nitrate, which corresponds to 0.2 gram of ammonium bromide, according to the equation:

$$\underbrace{AgNO_3}_{170} : \underbrace{NH_4Br}_{98} = 0.347 : 0.2.$$

If the salt were pure ammonium chloride, 37.35 cubic centimeters of the silver solution would be required, in accordance with a similar proportion; the difference in the amount of silver solution required for 0.2 gram of the two salts, would, therefore, be $37.35 - 20.41 = 16.94$ cubic centimeters; from which it follows, that for each 0.1694 cubic centimeter of silver solution required in excess of 20.41 cubic centimeters, in order to effect complete precipitation, 1 per cent. of ammonium chloride will be represented, as $\frac{16.94}{100} = 0.1694$. It is evident, that the presence of ammonium iodide, or other alkaline chlorides or bromides, would influence the result in proportion to the quantity of the admixture.

AMMONII CARBONAS.

AMMONIUM CARBONICUM.

Carbonate of Ammonium. Ammonium Sesqui-carbonate.

Ger. Kohlensaures Ammonium ; Fr. Carbonate d'ammoniaque ; Sp. Carbonato de amoniaco.

$$N_3H_{11}C_2O_5 = NH_4HCO_3 + NH_4NH_2CO_2;\ 157.$$

Colorless, hard, translucent, crystalline masses, consisting of equal molecules of acid ammonium carbonate and carbamate. It possesses a pungent ammoniacal odor, free from empyreuma, a sharp saline taste, and an alkaline reaction, and, when strongly heated, is completely volatilized without fusion. When exposed to the air the salt decomposes rapidly, becoming opaque, with the liberation of both carbonic acid gas and ammonia, and is converted into a white, crystalline powder of acid ammonium carbonate (bicarbonate).

Ammonium carbonate is soluble in 4 parts of water at 15° C. (59° F.), and in 1.5 parts at 65° C. (149° F.); it is also soluble in about 5 parts of glycerin, and is freely dissolved by dilute acids, with the liberation of carbonic acid gas. In contact with alcohol, the salt is resolved into ammonium carbonate, which dissolves, whilst the acid carbonate remains behind ; the latter salt is soluble, however, in about 8 parts of water at 15° C. (59° F.). The aqueous solution of the salt, when heated to 47° C. (116.6° F.), becomes partially decomposed, with the liberation of carbonic acid gas ; this decomposition takes place more rapidly at 75° C. (167° F.), and at temperatures above 85° C. (185° F.) much ammonia is also evolved, so that by prolonged boiling the salt is completely decomposed and dissipated, and the solution upon evaporation leaves no residue.

Examination :

Acid ammonium carbonate (bicarbonate) will be indicated by the change from the hard crystalline state of the salt to the friable pulverulent condition, by the much less pungent ammoniacal odor, and by the more sparing solubility of the salt in water, and insolubility in alcohol, as above mentioned.

Ammonium sulphate is detected in the aqueous solution, previously acidulated with nitric acid, by a white precipitate on the addition of barium chloride.

Ammonium chloride and *hyposulphite* are recognized in the aqueous solution, previously neutralized with acetic acid, by testing it with argentic nitrate ; a white precipitate, insoluble in diluted nitric acid, will indicate chloride ; a white turbidity, which gradually turns black, indicates hyposulphite.

Calcium salts will be detected in the aqueous solution, acidulated with acetic acid, by a white precipitate on the addition of ammonium oxalate, and will also remain behind when a little of the ammonium carbonate is strongly heated on platinum foil.

Metallic impurities are detected in the aqueous solution, previously acidulated with hydrochloric acid, by the successive application of hydrogen sulphide and ammonium sulphide, according to the systematic method of analysis, as described on pages 51 to 61, with special consideration of the possible presence of arsenic, lead, copper, and iron.

Empyreumatic substances may be detected in the solution of 1 part of the salt in about 20 parts of water, supersaturated with diluted sulphuric acid, by the addition of a few drops of solution of potassium permanganate; after standing for about five minutes at the ordinary temperature, no perceptible change of color should ensue, otherwise the above mentioned impurities will be indicated.

Estimation:

The purity of the salt may be approximately determined by the amount of tartaric or citric acid required for its neutralization: one part of ammonium carbonate requiring for exact neutralization 1.33 parts of citric, or 1.43 parts of tartaric, acid. Its quantitative estimation may, however, be more conveniently and accurately accomplished volumetrically. Two grams of the salt are dissolved, in a beaker, in about 20 cubic centimeters of cold water, a few drops of litmus solution added, and a normal solution of oxalic or sulphuric acid (page 82) subsequently allowed to flow into the liquid from a burette until an excess of acid has been employed, and the liquid assumes a permanent, bright cherry-red color; after having been heated to boiling, in order to completely expel the liberated carbonic acid gas, a solution of normal alkali (page 87) is added to the liquid from a burette, until, with constant stirring, a permanent blue tint is produced. The number of cubic centimeters of acid solution required for the exact neutralization of the salt having thus been determined, its purity or percentage strength may be readily calculated: one cubic centimeter of normal acid corresponding to 0.0523 gram of pure ammonium carbonate. By the employment of 2.615 grams of the salt, and a strictly normal acid solution, the number of cubic centimeters of the latter required for neutralization, when multiplied by 2, will represent at once the percentage purity of the salt.

AMMONII CHLORIDUM.

AMMONII MURIAS. AMMONIUM CHLORATUM.
SAL AMMONIACUM.

Chloride of Ammonium. Ammonium Chloride. Sal Ammoniac.

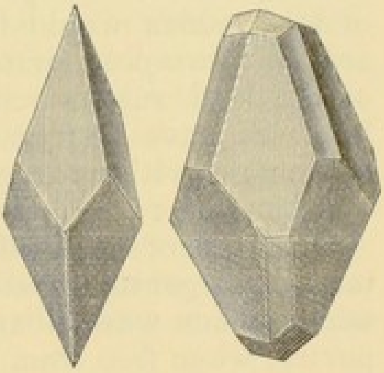
Ger. Chlorammonium; Fr. Chlorure d'ammonium; Sp. Cloruro de amoniaco.

NH_4Cl; 53.4.

A colorless, anhydrous salt, either in translucent, crystalline masses, of a tough, fibrous texture, or a granular white powder, or, as obtained by crystallization from its saturated aqueous solution, feather-like growths, consisting of an aggregation of small, regular octahedral or cubical crystals, or combinations of such, which often exhibit trapezohedric hemidedry, and thus appear to belong to the hexagonal or quadratic system (Fig. 89).

The salt has the specific gravity of 1.52. It is permanent in a dry atmosphere and at ordinary temperatures; when strongly heated, it volatilizes without fusion or charring, forming dense, white fumes, and suffers thereby a partial dissociation into ammonia and hydrochloric acid gases, which, however, again combine upon condensation in the form of a light crystalline powder of the original salt.

FIG. 89.



Ammonium chloride is soluble in 3.5 parts of water at 0° C. (32° F.), in 2.85 parts at 15.5° C. (60° F.), and in 1.37 parts of boiling water; it is also soluble in about 6 parts of glycerin, but only sparingly in alcohol, and not at all in ether or chloroform. Its aqueous solution has a sharp, saline taste, a slightly acid reaction, and becomes partially decomposed on boiling, with the loss of ammonia; it emits the odor of ammonia when heated with a solution of potassium or sodium hydrate, and yields with argentic nitrate a curdy, white precipitate, which is insoluble in nitric acid, but soluble in ammonia-water.

Examination:

Sulphates are detected in the diluted solution, acidulated with hydrochloric acid, by a white precipitate, when tested with barium nitrate.

Fixed impurities are indicated by a residue left after complete volatilization of the ammonium chloride, upon platinum-foil, or in a porcelain crucible.

Metallic impurities may be detected in the aqueous solution, previously acidulated with hydrochloric acid, by a coloration or precipitate when tested successively with hydrogen sulphide and ammonium sulphide. A precipitate thus obtained may be further examined or identified according to the systematic methods of analysis, as described on pages 51 to 61.

Iron may also be recognized at once by a blue coloration, when the solution of the salt is acidulated with hydrochloric acid, and tested with potassium ferrocyanide.

Ammonium sulphocyanide and *barium salts* having been occasionally detected as a contamination of ammonium chloride, they may be tested for as follows: The sulphocyanide may be extracted by digestion with hot alcohol, and, after the evaporation of the alcohol, and dissolving the residue in a small quantity of water, will be recognized by a blood-red color on the addition of a few drops of solution of ferric chloride. Soluble barium salts will be recognized in the aqueous solution by a white precipitate on the addition of a few drops of dilute sulphuric acid. In the presence of lead, which would likewise be precipitated by the sulphuric acid, the two precipitates may be distinguished by the solubility of the lead sulphate in basic ammonium tartrate, whereas the lead will have been also detected in the previously applied tests for metals, with hydrogen sulphide.

Estimation:

One gram of the powdered and dry salt, when completely precipitated by argentic nitrate, yields a precipitate of argentic chloride, which, when washed and dried, should weigh 2.682 grams. Its purity, when free from other chlorides, may be also conveniently and accurately determined volumetrically by dissolving 0.2 gram of the powdered and dry salt, in a beaker, in about 20 cubic centimeters of water, and, after the addition of a few drops of a solution of potassium chromate, allowing a decinormal solution of argentic nitrate (page 98) to flow into the liquid from a burette until, with constant stirring, the red coloration of argentic chromate remains permanent. The number of cubic centimeters of the silver solution which are required to produce this effect, when multiplied by the decimal 0.00535, will represent the amount of pure ammonium chloride in the quantity under estimation. By the employment of exactly 0.2675 gram of the salt, and proceeding as above, the number of cubic centimeters of the silver solution required to effect complete precipitation, multiplied by 2, will indicate at once the percentage amount of pure ammonium chloride.

AMMONII IODIDUM.

AMMONIUM IODATUM.

Iodide of Ammonium. Ammonium Iodide.

Ger. Jodammonium ; Fr. Iodure d'ammonium ; Sp. Ioduro de amonio.

NH_4I ; 144.6.

A white, granular, and deliquescent salt, crystallizing in cubes, which, when exposed to the air, becomes yellow or yellowish-brown, from oxidation and consequent liberation of a minute quantity of iodine. When heated, it is completely volatilized with the evolution of purple vapors.

Ammonium iodide is soluble in 1 part of cold, and 0.5 part of boiling, water; and in 9 parts of cold, or 3.7 parts of boiling, alcohol (distinction from ammonium and potassium bromides, which are less soluble in alcohol). Its aqueous solution has a pungent, saline taste, and emits the odor of ammonia when heated with a solution of sodium or potassium hydrate; it yields with mercuric chloride a red precipitate, soluble in an excess of either the ammonium or mercuric salt; and with argentic nitrate, a yellowish-white precipitate, which remains unchanged upon the addition of dilute nitric acid or ammonia-water; the solution assumes a blue color upon the addition of mucilage of starch and a little chlorine-water.

Examination:

An admixture of alkaline iodides, bromides, or chlorides, is approximately recognized, when a concentrated aqueous solution of the salt is dropped into strong alcohol; the liquid must remain clear; the separation of a white crystalline powder would indicate such an admixture.

Chlorides and *bromides* are detected by completely precipitating the solution of the salt with argentic nitrate, subsequently digesting the precipitate with ammonia-water, and filtering; the filtrate is then supersaturated with nitric acid, when a slight turbidity may ensue; a white precipitate would indicate chlorides and bromides. In this case, and in order to distinguish argentic chloride or bromide, the precipitate is collected and washed upon a filter, and is then rinsed through the pierced filter into a test-tube; the supernatant water is decanted as far as practicable, and good chlorine-water is poured upon and agitated with the silver salt. This will remain unchanged if it consists of argentic chloride, but, if it contains argentic bromide, the chlorine-water assumes a yellowish or reddish color, due to the elimination of free bromine, which will be absorbed by chloroform when agitated with that liquid.

Sulphates may be detected in the diluted solution, acidulated with hydrochloric acid, by a white precipitate on the addition of a few drops of a solution of barium chloride.

Estimation:

One part of the salt, in aqueous solution, when completely precipitated by argentic nitrate, yields a precipitate of argentic iodide, which, when washed and dried, should weigh 1.62 parts. The purity of the salt may also be determined volumetrically as follows: 0.2 gram of the perfectly dry salt is dissolved in a beaker in about 50 cubic centimeters of water, a few drops of neutral potassium chromate solution are then added, and subsequently a decinormal solution of argentic nitrate (page 98) is allowed to flow into the liquid from a burette until, with constant stirring, a permanent red coloration is produced. If the salt is pure ammonium iodide, 13.76 cubic centimeters of the silver solution will be required to effect its complete precipitation; one cubic centimeter of the decinormal silver solution corresponding to 0.0145 gram of ammonium iodide. If ammonium bromide or chloride is present, the number of cubic centimeters of silver solution required for precipitation will be larger in proportion to the extent of the admixture.

AMMONII NITRAS.

AMMONIUM NITRICUM.

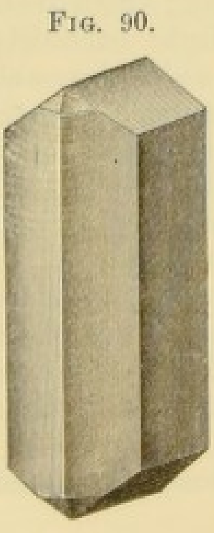
Nitrate of Ammonium. Ammonium Nitrate.

Ger. Salpetersaures Ammonium; Fr. Azotate d'ammoniaque; Sp. Nitrato de amoniaco.

NH_4NO_3; 80.

Long, flexible, colorless needles, or a fibrous crystalline mass, when obtained by crystallization at temperatures above 40° C. (104° F.); and large six-sided, rhombic prisms, terminated by six-sided pyramids (Fig. 90), when crystallized at a temperature below 38° C. (100.4° F.). The salt has the specific gravity of 1.7; it is anhydrous, and quite permanent in a dry atmosphere, but deliquesces in a moist one, losing a portion of its ammonia, and acquiring an acid reaction. When perfectly dry, and gradually heated, it fuses at 165–166° C. (329–331° F.); and at about 185° C. (365° F.) it is resolved into aqueous vapor and nitrogen monoxide (nitrous oxide gas), without leaving any fixed residue:

Fig. 90.



$$NH_4NO_3 = 2H_2O + N_2O.$$

When thrown upon a red-hot surface, it becomes decomposed, with the production of a yellow flame and a slight explosion, into nitrogen, water, and nitric oxide; and when heated with concentrated sulphuric acid, it emits nitrous vapors.

Ammonium nitrate dissolves in about half its weight of water at ordinary temperatures, a considerable reduction of temperature being produced; it is freely soluble in hot water, and is also soluble in 20 parts of cold, or 3 parts of boiling, alcohol, so that its concentrated aqueous solution remains perfectly limpid upon the addition of strong alcohol. Its aqueous solution has a sharp, bitter taste; it emits the odor of ammonia, when heated with a solution of potassium or sodium hydrate; and when mixed with a few drops of a solution of ferrous sulphate, and carefully poured upon concentrated sulphuric acid, it affords a dark zone at the junction of the liquids, characteristic of the oxides of nitrogen.

Examination:

Ammonium chloride and *sulphate* may be detected by white precipitates, when the dilute aqueous solution of the salt is acidulated with nitric acid and tested in separate portions, with argentic nitrate for the former salt, and with barium nitrate for the latter.

Fixed impurities will be recognized by a non-volatile residue, on strongly heating a small quantity of the salt upon platinum-foil.

AMMONII PHOSPHAS.

AMMONIUM PHOSPHORICUM.

Phosphate of Ammonium. Tribasic Ammonium Phosphate. Diammonio-hydric Phosphate.

Ger. Phosphorsaures Ammonium; Fr. Phosphate d'ammoniaque; Sp. Fosfato de amoniaco.

$(NH_4)_2HPO_4$; 132.

Transparent, colorless, monoclinic prisms, having the specific gravity of 1.64. They are efflorescent in dry air, and on exposure to a moist atmosphere readily lose ammonia. When heated upon platinum-foil, the salt first fuses, and is resolved into metaphosphoric acid, with the liberation of water and ammonia, and, at a bright red heat, is wholly dissipated. When heated with a solution of potassium or sodium hydrate, ammonia gas is evolved.

Ammonium phosphate is soluble in 4 parts of water at 15.5° C. (60° F.), with ensuing reduction of temperature, and soluble in 0.5 part of boiling water, but is insoluble in alcohol. The aqueous solution of the salt possesses a cooling, saline taste, and a slightly alkaline reaction, but. when the salt has been exposed to the air or is old, the solution is neutral, or even acid, a change resulting from the loss of ammonia and the formation of the primary mono-ammonium phosphate $NH_4H_2PO_4$, which takes place more rapidly when the solution of the salt is boiled.

With solution of argentic nitrate, the diluted solution of ammonium phosphate gives a yellow precipitate of argentic phosphate, soluble in ammonia-water or in nitric acid; and with solution of ammonium molybdate, acidulated with nitric acid, it yields, on warming, a yellow crystalline precipitate of ammonium phospho-molybdate. The solution of the salt should produce no coloration or precipitate with ammonium sulphide, and, after acidulation with diluted hydrochloric acid, none with hydrogen sulphide or with barium chloride. A coloration or precipitate with the first two reagents would indicate *metals*, a white precipitate with the latter reagent, insoluble in diluted nitric acid, would indicate *sulphate*.

If a solution of one gram of ammonium phosphate is completely precipitated with magnesium mixture, the precipitate collected and washed upon a filter with a mixture of one part of ammonia-water and three parts of water, dried, and subsequently heated to redness in a tared porcelain crucible, the residue of magnesium pyrophosphate obtained should weigh 0.841 gram.

AMMONII SULPHAS.

AMMONIUM SULFURICUM.

Sulphate of Ammonium. Ammonium Sulphate.

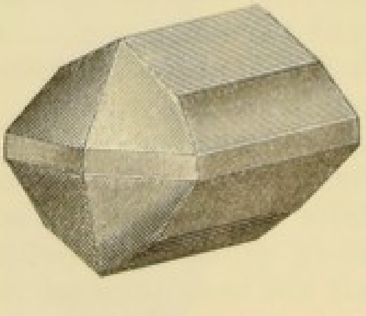
Ger. Schwefelsaures Ammonium; Fr. Sulfate d'ammoniaque; Sp. Sulfato de amoniaco.

$(NH_4)_2SO_4$; 132.

A granular powder, or large, transparent, colorless crystals, belonging to the rhombic system (Fig. 91), permanent in the air, and having the specific gravity of 1.77. The salt melts at 140° C. (284° F.) with the development of ammoniacal vapors; at a higher temperature it is decomposed into ammonia, nitrogen, water, and ammonium sulphite, which sublimes, becoming finally, at a red heat, entirely dissipated.

Ammonium sulphate is soluble in 1.3 parts of water at 15° C. (59° F.), and in its own weight of boiling water, but is sparingly soluble in aqueous, and insoluble in absolute, alcohol. The aqueous solution is neutral in its action upon litmus, possesses a strong and unpleasant saline taste, and, similarly to ammonium chloride,

FIG. 91.



is partially decomposed on boiling, with the development of ammonia. When heated with a solution of potassium or sodium hydrate, it develops the odor of ammonia, and yields with a solution of barium chloride a white precipitate, insoluble in hydrochloric acid.

Examination:

Chlorides may be detected in the dilute aqueous solution of the salt, acidulated with nitric acid, by a white precipitate on the addition of solution of argentic nitrate.

Sulphocyanides will be recognized in the aqueous solution by an ensuing deep-red coloration on the addition of a few drops of solution of ferric chloride.

Metallic impurities (lead or copper) will be detected in the aqueous solution, acidulated with hydrochloric acid, by a dark coloration or precipitate upon saturation with hydrogen sulphide; after filtration, if necessary, ammonia-water in slight excess is added, when an ensuing dark-colored precipitate will indicate *iron*, and a white one, *zinc*.

AMMONII VALERIANAS.

AMMONIUM VALERIANICUM.

Valerianate of Ammonium. Ammonium Valerianate.

Ger. Baldriansaures Ammonium; Fr. Valérianate d'ammoniaque; Sp. Valerianato de amoniaco.

$NH_4C_5H_9O_2$; 119.

Colorless, transparent, quadrangular plates, or a white, translucent, crystalline mass, having the odor of valerianic acid, a sharp, sweetish taste, and a neutral reaction. When heated, the salt melts and emits vapors of the odor of ammonia and of valerianic acid; at a stronger heat it becomes black, with the evolution of pungent, inflammable vapors, and is at last wholly dissipated. It is decomposed, and emits the odor of ammonia, when heated with a solution of potassium hydrate.

Ammonium valerianate is deliquescent in moist air, and is freely soluble in water, glycerin, and alcohol; its aqueous solution, if not very dilute, separates, upon supersaturation with acids, an oily layer of valerianic acid. The underlying aqueous liquid, when nearly saturated with ammonia-water, should not become red upon the addition of one drop of dilute solution of ferric chloride, for in this case *acetic acid* (admixture of potassium or sodium acetate) would be indicated, which may also be recognized by a fixed residue upon complete dissipation of the salt upon platinum-foil, which residue will effervesce when moistened with one drop of concentrated hydrochloric acid. The aqueous solution of the salt, when acidulated with nitric acid, and tested, in separate portions, with barium chloride and argentic nitrate, should afford no precipitate (absence of *sulphates* and *chlorides*).

AMYL NITRIS.

AMYLIUM NITROSUM. AMYLÆTHER NITROSUS.

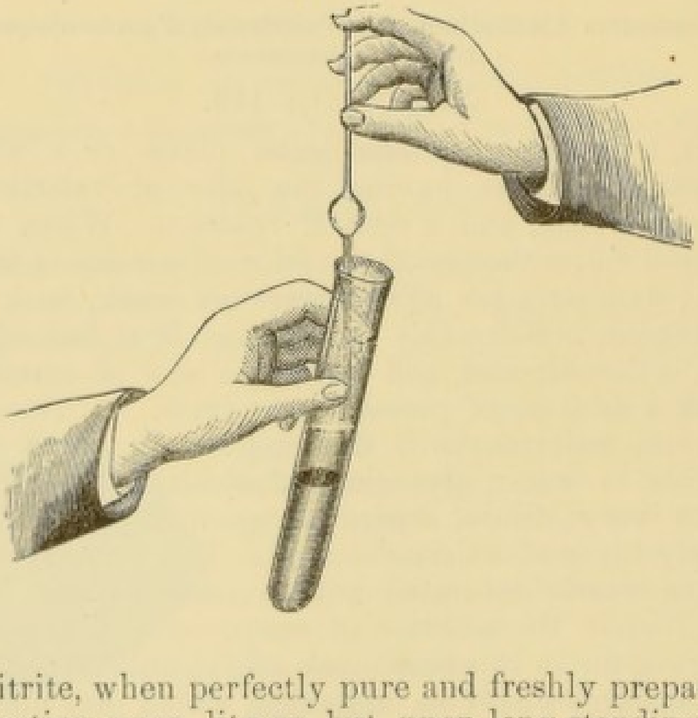
Nitrite of Amyl. Amyl Nitrite.

Ger. Salpetrigsäureamylester ; Fr. Azotite d'amyle ; Sp. Amilo nitrico.

$C_5H_{11}NO_2 = C_5H_{11}$–O–NO ; 117.

A transparent liquid, of a pale yellow color, possessing an ethereal, fruity odor, and an aromatic taste. It has the specific gravity of 0.902 to 0.9026, and boils at 94 to 95° C. (201.2 to 203° F.), yielding an orange-colored vapor, which, when ignited, burns with a yellow, luminous, and sooty flame. It is miscible, in all proportions, with alcohol, ether, chloroform, benzol, and benzin, but not with water. When carefully placed upon a mixture of a solution of ferrous sulphate and concentrated sulphuric acid (Fig. 92), a brown zone will appear at the line of contact of the two liquids.

Fig. 92.



Amyl nitrite, when perfectly pure and freshly prepared, is neutral in its action upon litmus, but, upon long standing, or by exposure to the air, especially when containing water, it gradually acquires an acid reaction, and then contains the various products of decomposition, nitrous or nitric acid, valerianic acid, amyl valerianate, and amylic alcohol. When gently warmed with an excess of a solution of potassium or sodium hydrate, it is readily resolved into nitrous acid, which combines with the alkali, and amylic alcohol, which floats upon the surface in the form of an oil; if this alkaline mixture be supersaturated with acetic acid, a few drops of solution of potassium iodide, and subsequently a little mucilage of starch added, a deep blue color will be produced.

Examination:

Alcohol and Water.—The former may be recognized, and its amount also approximately estimated, by an ensuing reduction of volume of the amyl nitrite, when shaken with an equal volume of water in a small graduated glass tube or cylinder (Fig. 93); the presence of water will be indicated by a higher specific gravity than that above stated, and by a turbid appearance of the liquid when exposed to the temperature of melting ice.

Fig. 93.

Aldehyde may be detected by mixing a small portion of the amyl nitrite with three times its volume of a mixture of equal parts of ammonia-water and absolute alcohol, subsequently adding a few drops of solution of argentic nitrate, and warming gently; an ensuing dark-brown coloration, due to the separation of metallic silver, would indicate the presence of aldehyde.

Free acids may be detected in amyl nitrite when tested with moistened blue litmus paper; and should not be present in an amount sufficient to redden the latter when 10 cubic centimeters of the amyl nitrite are agitated with 2 cubic centimeters of a mixture of 1 part of ammonia-water and 9 parts of water, and the liquid subsequently tested.

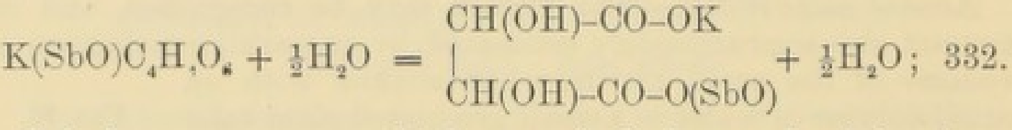
Hydrocyanic acid, resulting as a by-product from the action of nitrous acid on amylic alcohol, may be recognized by diluting about 10 drops of amyl nitrite with ten times its volume of alcohol, and adding thereto a few drops of solution of argentic nitrate; as hydrochloric acid does not occur in amyl nitrite as an impurity, an ensuing white turbidity or precipitate would indicate hydrocyanic acid.

ANTIMONII ET POTASSII TARTRAS.

ANTIMONIUM TARTARATUM. ANTIMONIUM ET POTASSIUM TARTARICUM. TARTARUS STIBIATUS.

Tartrate of Antimony and Potassium. Tartar Emetic. Potassio-antimonious Tartrate.

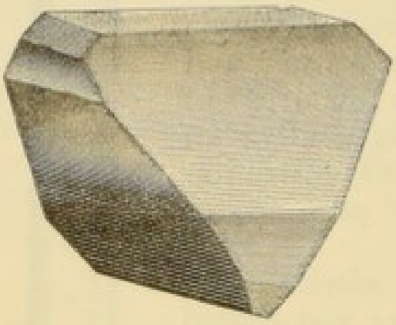
Ger. Weinsaures Antimonoxyd-kalium ; Fr. Tartrate de potasse et d'antimoine ; Sp. Tartrato de potasa y antimonio.



$$K(SbO)C_4H_4O_6 + \tfrac{1}{2}H_2O = \begin{array}{l} CH(OH){-}CO{-}OK \\ | \\ CH(OH){-}CO{-}O(SbO) \end{array} + \tfrac{1}{2}H_2O;\ 332.$$

Colorless, ransparent, shining, octahedral crystals of the rhombic system, which, in consequence of the four remaining alternating surfaces, often assume a hemihedral, tetrahedron-like form (Fig. 94); or a white, granular powder. The crystals have a specific gravity of about 2.6, and contain one-half molecule (2.7 per cent.) of water of crystallization; they effloresce slightly when exposed to the air, and lose their water of crystallization completely at 108° C. (226.4° F.), becoming white and opaque; when powdered and heated in a dry test-tube, tartar emetic emits acid empyreumatic vapors, and leaves a charred residue which, when cool, turns moist turmeric-paper brown; when the residue is placed upon charcoal and heated before the blow-pipe, white fumes are evolved, coating the coal, and brittle globules of antimony are formed.

Fig. 94.



Tartar emetic is soluble in 17 parts of water at 15° C. (59° F.), in 3 parts of boiling water, and is also soluble in glycerin, but insoluble in strong alcohol. Its aqueous solution has at first a sweetish, afterwards a nauseous metallic taste, a slightly acid reaction upon blue litmus-paper, and gradually decomposes if not concentrated or containing a small addition of alcohol; with the mineral acids (not acetic, tartaric, and citric acids) a white turbidity is produced, which disappears on the addition of a large excess of acid, and from the solution, upon the subsequent addition of water, an abundant precipitate of basic antimonious chloride, sulphate, or nitrate is produced; its solution is also precipitated by the alkaline hydrates, and by all soluble carbonates, but not by bicarbonates; the precipitate produced by the alkaline hydrates being soluble in an excess of a solution of potassium or sodium hydrate, but insoluble in ammonia-water.

Hydrogen sulphide produces an orange-red coloration in concentrated solutions of tartar emetic, and gradually a precipitate of the same color; in very dilute solutions, only a coloration takes place; but, upon warming, or upon the addition of an acid, or when the tartar emetic is contaminated with free tartaric acid or potassium bitartrate, a turbidity ensues immediately.

Solution of tartar emetic reduces a solution of mercuric chloride to mercurous chloride, gradually at common temperatures, and quickly at elevated ones; and likewise reduces a solution of auric chloride, with the separation of metallic gold.

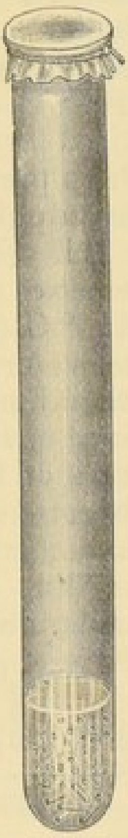
If to a solution of tartar emetic a solution of potassium or sodium hydrate be added, until the precipitate first formed is just redissolved, and a solution of argentic nitrate subsequently added, a copious dark-colored precipitate of argentous oxide, Ag_4O, is produced, which is insoluble in ammonia-water.

Examination:

Arsenic is indicated by the garlic-like odor when a small portion of the powdered tartar emetic is at first gently heated in an iron spoon, or in a porcelain crucible, and subsequently heated to redness.

If the result of this test be doubtful, or confirmatory evidence be required, a small quantity of the tartar emetic is dissolved, in a test-tube, in concentrated hydrochloric acid, a little concentrated solution of stannous chloride or a fragment of pure tin-foil added, and the mixture gently warmed; the liquid must remain clear and colorless on cooling; a brown turbidity or precipitate would indicate *arsenic*. The presence of arsenic may be also detected by adding to a little of the powdered tartar emetic, contained in a test-tube, a small quantity of powdered iron, a few fragments of metallic zinc, and a concentrated solution of potassium or sodium hydrate; the mixture is then gently heated, when, if arsenic be present, hydrogen arsenide together with free hydrogen will be developed, and impart a dark stain upon a piece of bibulous paper moistened with a drop of a solution of argentic nitrate, and placed over the orifice of the tube (Fig. 95).

FIG. 95.



Metallic impurities, *calcium salts*, *chlorides*, and *sulphates* may be detected in a solution of 1 part of tartar emetic in about 100 parts of water, acidulated with acetic acid, by testing it, in separate portions, with solution of potassium ferrocyanide, ammonium oxalate, argentic nitrate, and barium chloride; a blue coloration or precipitate with potassium ferrocyanide would indicate *iron*, a reddish-brown one, *copper;* and a white one, *zinc;* an ensuing white precipitate upon the addition of ammonium oxalate, argentic nitrate, or barium chloride, would indicate respectively *calcium salts*, *chlorides* or *sulphates*.

Potassium Bitartrate.—An admixture of this salt may be approximately recognized by the difference of the solubility of tartar emetic (1 : 17), and of cream of tartar (1 : 210) in water at 15° C. (59° F.); when, therefore, one part of the tartar emetic is agitated with 18 parts of warm water, a complete solution must take place, and remain unchanged after cooling. If cream of tartar be present, it will separate in small crystals. The presence of potassium bitartrate, as also of free tartaric acid, may be further recognized by the liberation of carbonic-acid gas, when a cold saturated solution of sodium carbonate is poured upon the crystals.

Estimation:

The determination of the amount of pure tartar emetic contained in any specimen of the salt may be accomplished by the following methods:

I. *Gravimetric.*—One gram of the uneffloresced crystals, or the same weight of the powdered tartar emetic previously dried at 110° C. (230° F.), is dissolved, in a flask, in about 50 cubic centimeters of water, the solution acidulated with hydrochloric acid, gently warmed, and completely saturated with hydrogen sulphide; the flask is then loosely stoppered and allowed to stand in a warm place for a few hours, the orange-red precipitate of antimony trisulphide, Sb_2S_3, collected on a tared filter, previously dried at 100° C. (212° F.), quickly and thoroughly washed with water to which a small quantity of water saturated with hydrogen sulphide has been added, and finally thoroughly dried at exactly 100° C. (212° F.), until of constant weight. One gram of crystallized tartar emetic should thus yield 0.510 gram, or, if the salt has been previously dried at 110° C. (230° F.), 0.523 gram of antimony trisulphide, Sb_2S_3.

II. *Volumetric.*—0.2 gram of uneffloresced crystals of tartar emetic, or, if in powder, the same quantity previously dried at 110° C. (230° F.), is dissolved, in a beaker, in 10 cubic centimeters of water; about 20 cubic centimeters of a cold saturated solution of sodium bicarbonate, and a little freshly prepared, neutral mucilage of starch are then added, and subsequently a decinormal solution of iodine (page 93) allowed to flow into the liquid from a burette until, with constant stirring, a blue coloration, which for a moment remains permanent, is produced; the antimonious oxide is thus converted into antimonic acid, as represented by the equation:

$$\underbrace{\underset{\underset{2K(SbO)C_4H_4O_6}{\|}}{Sb_2O_3}}_{650} \underbrace{+ 2I_2}_{508} + 6NaHCO_3 = 2NaSbO_3 + 4NaI + 3H_2O + 6CO_2.$$

With reference to the above proportion, one cubic centimeter of decinormal iodine solution, corrected, if necessary, by its proper factor (page 95), corresponds to 0.0072 gram of antimonious oxide, Sb_2O_3, and to 0.0162 gram of anhydrous, or 0.0167 gram of crystallized tartar emetic, $K(SbO)C_4H_4O_6 + \frac{1}{2}H_2O$; from the number of cubic centimeters of iodine solution employed, the percentage purity of the specimen under examination may be thus readily calculated.

ATIMONII OXIDUM.

ANTIMONIUM SEU STIBIUM OXYDATUM.

Oxide of Antimony. Antimonious Oxide. Antimony Trioxide.

Ger. Antimonoxyd ; Fr. Oxyde d'antimoine ; Sp. Oxido de antimonio.

Sb_2O_3; 288.

A grayish-white or pale-buff colored, crystalline powder, when obtained by precipitation; or small, colorless, transparent, brilliant needles, when obtained by sublimation (Flores Antimonii). When heated, antimonious oxide becomes yellow, and fuses at a dull-red heat, forming a yellowish liquid, which solidifies, on cooling, to a crystalline mass of a pearly color; at a higher temperature, it volatilizes in white vapors, which condense, on cooling, in colorless, shining, needle-shaped crystals; when mixed and heated with exsiccated sodium carbonate on charcoal before the blow-pipe, antimonious oxide is reduced, forming globules of metallic antimony which are brittle when cold.

Antimonious oxide is insoluble in water, ammonia-water, sulphuric, nitric, and acetic acids, but is readily dissolved by warm hydrochloric acid, with the formation of antimony trichloride; it is also soluble in warm solutions of potassium or sodium hydrate, and in solutions of tartaric acid, and the alkaline tartrates. Its acid solutions afford with hydrogen sulphide an orange-red precipitate of antimony trisulphide, Sb_2S_3; its solutions in the fixed alkaline hydrates are not acted upon by this reagent (distinction from alkaline solutions of salts of lead and zinc), but, with argentic nitrate, a black precipitate of argentous oxide is produced, which is insoluble in ammonia-water.

Examination :

Antimonic oxide may be detected by its much more sparing solubility in hydrochloric acid; and by dissolving a portion of the oxide in hydrochloric acid, diluting the solution with water, to which a little tartaric acid has been added (in order to avoid any turbidity by the separation of a basic salt), and adding a solution of potassium iodide, free from iodate; the mixture will remain colorless, if free from antimonic oxide; but, if the latter be present, it will assume a brown coloration, due to the liberation of iodine, and when agitated with a few drops of chloroform or carbon bisulphide will impart to these liquids a violet-red color.

Antimonious oxy-chloride (Algaroth's Powder) and *antimonius oxy-sulphate* are indicated by the formation of white precipitates, when a diluted solution of the oxide in an excess of tartaric acid is tested with argentic nitrate for the former, and with barium chloride for the latter. Their presence may be confirmed by digesting a little of the oxide for about one hour with a cold concentrated solution of sodium carbonate, filtering, and testing the filtrate, after supersaturation with nitric acid, with argentic nitrate for *oxy-chloride*, and with barium chloride for *oxy-sulphate;* an ensuing white precipitate in either instance will reveal the respective impurity.

Metallic antimony will be indicated by a gray color of the oxide, and will remain undissolved when the oxide is treated with hydrochloric acid.

Arsenic is recognized by the garlic-like odor, when a little of the oxide is mixed with exsiccated sodium carbonate, and then fused and reduced upon charcoal before the blow-pipe. Its presence may be confirmed by dissolving a small portion of the oxide in concentrated hydrochloric acid, subsequently adding a few drops of a concentrated solution of stannous chloride, or a fragment of pure tin foil, and warming the mixture gently; the liquid should remain clear and colorless on cooling; a brown turbidity or precipitate will indicate *arsenic.*

Estimation:

I. *Gravimetric.*—A weighed portion of the oxide (about 0.5 gram) is dissolved in hydrochloric acid, the solution largely diluted with water, to which a little tartaric acid has been added, in order to prevent precipitation, and after warming, completely saturated with hydrogen sulphide; the flask is then loosely stoppered, and allowed to repose in a warm place for a few hours; the precipitate of antimony trisulphide is collected upon a tared filter, previously dried at 100° C. (212° F.), quickly and thoroughly washed with water to which a small quantity of water saturated with hydrogen sulphide has been added, and finally thoroughly dried at exactly 100° C. (212° F.) until of constant weight; 100 parts of antimonious sulphide, Sb_2S_3, correspond to 85.71 parts of antimonious oxide, Sb_2O_3.

II. *Volumetric.*—0.1 gram of the oxide is dissolved, in a beaker, in about 10 cubic centimeters of water, to which the required quantity of tartaric acid has been added to effect solution, the solution exactly neutralized with sodium carbonate, and subsequently about 20 cubic centimeters of a cold saturated solution of sodium bicarbonate, and a little freshly prepared neutral mucilage of starch added; a decinormal solution of iodine (page 93) is then allowed to flow into the liquid from a burette until, with constant stirring, the blue coloration which is produced remains for a moment permanent; the antimonious oxide is thus converted into sodium antimoniate, as represented by the following equation:

$$\underbrace{Sb_2O_3}_{\substack{288\\(7.2)}} + \underbrace{2I_2}_{\substack{508\\(12.7)}} + 3Na_2CO_3 = 2NaSbO_3 + 4NaI + 3CO_2.$$

With reference to the above proportion, one cubic centimeter of the decinormal iodine solution, corrected, if necessary, by its proper factor (page 95), corresponds to 0.0072 gram of antimonious oxide, Sb_2O_3, which, multiplied by the number of cubic centimeters of iodine solution employed, will give the amount of pure antimonious oxide in the specimen under examination.

ANTIMONII SULPHIDUM.

ANTIMONII SULPHURETUM. ANTIMONIUM SULFURATUM NIGRUM. STIBIUM SULFURATUM CRUDUM.

Native Sulphide of Antimony. Trisulphide of Antimony. Antimonious Sulphide.

Ger. Graues Schwefelantimon (Spiessglanz); **Fr.** Sulfure d'antimoine; **Sp.** Sulfuro de antimonio.

Sb_2S_3; 336.

Heavy fused masses, which, when broken, present a striated crystalline texture, and a lead-gray metallic brilliancy; when pulverized, they form a dark iron-gray powder. Spec. grav. about 4.6. When heated upon charcoal before the blow-pipe, black antimonious sulphide fuses and burns, emitting dense white fumes and the odor of sulphurous acid; when mixed with some dried sodium carbonate and potassium cyanide, and heated in the same way, metallic globules are obtained, which are brittle when cooled.

Black antimonious sulphide, when reduced to a fine powder, is insoluble in water, alcohol, the dilute mineral acids, and organic acids, with the exception of tartaric acid, which, at the boiling temperature, dissolves it to a certain extent, with the liberation of hydrogen sulphide, and the formation of antimonious tartrate; it is readily soluble, however, in concentrated hydrochloric acid, with the formation of antimony trichloride, and the development of hydrogen sulphide; and in hot concentrated sulphuric acid, with the formation of antimonious sulphate, separation of sulphur, and development of sulphur dioxide. With concentrated nitric acid it is oxidized to antimonious nitrate, with the formation of some antimonious sulphate, separation of sulphur, and development of nitrogen dioxide; nitro-hydrochloric acid dissolves it with the formation of antimony trichloride and sulphuric acid, accompanied by the separation of sulphur. The solution in hydrochloric acid, when dropped into water, produces a copious white turbidity, which becomes orange-red in contact with hydrogen sulphide (a brown or black color of the precipitate would indicate the presence of lead or other metals). Black antimonious sulphide is also partially dissolved by boiling concentrated solutions of potassium or sodium hydrate, with the formation of sulpho-salts (sulphantimonites), leaving a brown residue, consisting of a mixture of oxysulphide and antimonite; it is almost insoluble in ammonia-water (distinction from arsenic trisulphide).

The native antimonious sulphide generally contains sulphides of iron, lead, copper, and arsenic; and there are also found, especially in the commercial black powder, silicates and mineral admixtures, while occasionally an article sold under the name of "black antimony" has been found to consist simply of a mixture of powdered lime-stone and anthracite coal.

Examination:

Metallic impurities (iron, lead, and copper), which, as previously stated, are usually present in variable proportions in native antimonious sulphide, will be indicated by a yellowish or brownish residue when about two grams of the finely-powdered sulphide are intimately mixed with four times its weight of sodium nitrate, the mixture cautiously ignited in a porcelain crucible, and the fused mass subsequently boiled with about three times its weight of water, to which a little alcohol has been added. The further identification of such impurities may be effected by the method described in detail under antimonium sulphuratum, on page 244.

Arsenic may be detected in the filtrate of the preceding test by acidulating it with nitric acid, boiling until nitrous vapors cease to be evolved, subsequently adding a few drops of solution of argentic nitrate, again filtering, if necessary, and finally pouring upon the surface of the clear solution, contained in a test-tube, a few drops of ammonia-water; a white cloud at the line of contact of the two liquids will indicate traces of arsenic, whilst if larger amounts are present, a red or reddish-brown precipitate will be produced.

Admixtures of black manganic peroxide, of pyrites, and of other crude minerals, are recognized by their infusibility when heated in the ordinary gas-flame, whereas black antimonious sulphide readily fuses at this temperature, and also by dissolving the black powder in boiling hydrochloric acid; the first-named gives rise to the evolution of chlorine, the latter remain mostly undissolved.

The artificially prepared black antimonious sulphide contains frequently more or less metallic antimony, which may be recognized by its insolubility in warm hydrochloric acid, remaining behind in minute brilliant iron-gray particles, which, however, dissolve upon the addition of potassium chlorate, and subsequent heating.

Silica may be recognized by its remaining undissolved when the sulphide is heated for a short time with about ten parts of nitro-hydrochloric acid, whilst the unoxidized sulphur will principally float upon the surface of the liquid as a spongy mass. The silica, after washing with a solution of tartaric acid, and subsequently with water, will remain unchanged upon ignition, and, when heated with a little borax on a platinum wire in the non-luminous flame, will produce the characteristic skeleton in the bead.

A mixture of *lime-stone* and *coal*, the occurrence of which as a sophistication of commercial black antimonious sulphide has been previously alluded to, may be readily recognized by treating the powder with warm hydrochloric acid; the carbon will remain undissolved, and the clear, filtered solution, after dilution with water and the addition of sodium acetate in excess, will afford, upon the addition of a few drops of a solution of ammonium oxalate, a white precipitate of calcium oxalate.

Estimation:

The estimation of the amount of pure antimony trisulphide in black antimonious sulphide may be best effected by the following method: A weighed amount (1 gram) of the very finely powdered sulphide is dissolved, in a flask, in hydrochloric acid, with the aid of a gentle heat and the addition of a small quantity of nitric acid, the solution slightly supersaturated with potassium hydrate, and subsequently a solution of potassium sulphide added, and digested at a gentle heat; the sulphides of lead, copper, and iron will thereby remain undissolved, whilst the antimonious sulphide, together with arsenic, if present, will be obtained in solution:

$$As_2S_3 + 2KHS = 2KAsS_2 + H_2S.$$

After cooling, the mixture is filtered, the undissolved portion well washed upon the filter with water, and the combined filtrate and washings saturated with sulphur dioxide gas until the latter ceases to be absorbed. The antimony, together with the arsenious sulphide, becomes thereby precipitated, but by subsequent digestion of the mixture upon the water-bath, and afterwards boiling until about two-thirds of the water has evaporated, and the escaping vapors no longer possess the odor of sulphur dioxide, the arsenious sulphide becomes redissolved, whilst the antimonious sulphide, associated with some sulphur, remains insoluble:

$$4KAsS_2 + 5SO_2 + 2H_2O = 2As_2S_3 + S_3 + 4KHSO_3;$$
$$2As_2S_3 + 16KHSO_3 = 4KAsO_2 + 6K_2S_2O_3 + 8H_2O + S_3 + 7SO_2.$$

The insoluble residue is then filtered, thoroughly washed with water, dried at 100° C. (212° F.), and the free sulphur completely removed by washing it upon the filter with pure carbon bisulphide, until the washings upon evaporation no longer leave a deposit of sulphur. After the above treatment, it is brought into a weighed porcelain crucible, moistened with a few drops of nitric acid, spec. grav. 1.42, then eight to ten times its weight of fuming nitric acid added, and the acid subsequently allowed to evaporate gradually on the water-bath. The sulphur which is at first separated becomes completely oxidized to sulphuric acid, and the antimonious sulphide converted into antimonic acid. The crucible, and its contents, are then first gently heated to expel the sulphuric acid, and finally heated to redness, whereby the antimonic acid is converted into antimony orthoantimonate, Sb_2O_4, and, after cooling, is weighed as such; 100 parts of the latter compound correspond to 110.52 parts of antimony trisulphide, Sb_2S_3.

ANTIMONII SULPHIDUM AURANTIACUM.

ANTIMONIUM SEU STIBIUM SULFURATUM AURANTIACUM. SULFUR AURATUM ANTIMONII.

Golden Sulphur. Pentasulphide of Antimony. Antimonic Sulphide.

Ger. Antimonsulfid. Goldschwefel; Fr. Soufre doré d'antimoine;
Sp. Bisulfuro de antimonio hidratado.

Sb_2S_5; 400.

A fine orange-red powder, nearly odorless and tasteless, becoming gradually lighter colored by the action of air and light, and at the same time undergoing slow oxidation with the development of sulphurous acid gas; when heated in a dry test-tube, it gives off sulphur, leaving behind black antimonious sulphide; when heated upon charcoal before the blow-pipe, it burns away with a pale, bluish flame, emitting the odor of sulphurous acid gas, and causing a white incrustation of the coal.

Antimonic sulphide is insoluble in water, alcohol, and ether, and is but slowly decomposed by the organic and dilute mineral acids. When treated with ten to fifteen times its weight of warm concentrated hydrochloric acid, it dissolves for the most part with effervescent evolution of hydrogen sulphide, leaving behind a scanty residue of red-colored sulphur; the solution, when deprived of the hydrogen sulphide by heat, produces, when dropped into water, a white turbidity, disappearing upon the addition of tartaric acid, which solution is precipitated orange-red by hydrogen sulphide.

Antimonic sulphide is completely soluble in a warm solution of potassium hydrate, in solutions of the alkaline sulphides and sulphydrates, and in warm solutions of the alkaline carbonates, with the exception of ammonium carbonate (distinction from arsenic sulphide); it is also nearly or completely dissolved by about 150 times its weight of an aqueous 10 per cent. solution of ammonia, spec. grav. 0.960; if a small residue is left, it will dissolve in a solution of tartaric acid, or of potassium hydrate, on boiling.

Examination:

Sodium Salts, *Sulphates*, and *Chlorides*.—A small portion of the antimonic sulphide is digested with frequent agitation for about 15 minutes with ten times its weight of tepid water, filtered, and the filtrate evaporated to dryness; if a residue is obtained which imparts a bright yellow color to the non-luminous flame, *sodium salts* will be indicated. The residue is then dissolved in a little water, acidulated with nitric acid, and tested, in separate portions, with barium chloride for *sulphates*, and with argentic nitrate for *chlorides;* an ensuing white precipitate in either instance will reveal the respective impurity.

Sulphur, *Kermes Minerale*, and *Antimonious Oxide*.—A portion of the antimonic sulphide is digested with frequent agitation for about 15 minutes with 150 times its weight of strong ammonia-water; the above-mentioned impurities will thus remain undissolved, and, after separation by filtration, may be further examined as follows: *Sulphur* may be detected in the insoluble residue by its complete volatilization when strongly heated, with the development of sulphurous acid gas, and, when present in the free condition in the antimonic sulphide, may be extracted and quantitatively estimated by means of carbon bisulphide, which will deposit it in a pure state upon evaporation; *kermes minerale* will be recognized by its reddish-brown color, and solubility in hydrochloric acid with the evolution of hydrogen sulphide and formation of antimony trichloride; *antimonious oxide* may be detected by its complete solubility in a solution of tartaric acid, and the solution, after acidulation with hydrochloric acid, will yield a reddish-yellow precipitate of antimony trisulphide upon saturation with hydrogen sulphide.

Arsenic may be detected by digesting the antimonic sulphide, with occasional agitation for about half an hour, in a closely stoppered flask, with a concentrated solution of ammonium carbonate, and filtering; the filtrate is then supersaturated with hydrochloric acid, when the formation of a lemon-yellow precipitate, either at once or upon subsequent saturation with hydrogen sulphide. will indicate the presence of arsenic. As traces of antimonic sulphide are also dissolved by ammonium carbonate, and would likewise be precipitated by supersaturation with an acid, the presence of small amounts of arsenic may be more accurately determined by the method of fusion with sodium nitrate, as explained in detail under antimonium sulphuratum, on page 243.

Lead, *Copper*, and *Iron*.—The sulphides of these metals will remain undissolved when a portion of the antimonic sulphide is digested with a solution of potassium sulphide. The insoluble residue, after washing with water, is dissolved in a little warm nitric acid, the solution diluted with water, heated to expel the excess of nitric acid, and, after filtering, is tested in separate portions, as follows: To a portion of the solution a few drops of a solution of potassium ferrocyanide are added, when a blue precipitate will indicate *iron;* to another portion of the solution a few drops of dilute sulphuric acid are added, when a white precipitate will indicate *lead;* and, after the removal of the latter by filtration, and subsequent supersaturation of the liquid with ammonia-water, a blue coloration will reveal the presence of *copper*.

Calcium salts may be detected by agitating the antimonic sulphide with water slightly acidulated with hydrochloric acid, and filtering; after the addition of a considerable excess of sodium acetate to the filtrate, a few drops of a solution of ammonium oxalate are added, when an ensuing white precipitate will indicate calcium.

ANTIMONIUM SULPHURATUM.

STIBIUM SULFURATUM RUBEUM.

Sulphurated Antimony. Mineral Kermes. Antimonious Oxysulphide.

Ger. Braunes Schwefelantimon; Fr. Sulfure d'antimonine hydraté;
Sp. Protosulfuro de antimonio hidratado.

$$Sb_2S_3 + xSb_2O_3.$$

An insipid powder of a reddish-brown color, becoming gradually lighter by the action of air and light. It is a mixture of antimonious sulphide with a small and variable amount of antimonious oxide, the former appearing under the microscope in amorphous globules, or laminæ, and the latter in small, colorless crystals, or fragments of such. When heated upon charcoal before the blow-pipe, sulphurated antimony fuses and burns away, with the evolution of white fumes, and the odor of sulphurous acid; heated with the addition of a little dried sodium carbonate, brittle globules of antimony are obtained.

Sulphurated antimony is insoluble in water and alcohol, but readily and wholly soluble in hydrochloric acid, which solution, after the hydrogen sulphide has been completely expelled by heat, gives a white precipitate when dropped into water, which, however, is re-dissolved upon the addition of tartaric acid; this solution yields an orange-red precipitate with hydrogen sulphide.

Sulphurated antimony is only slightly soluble in ammonia-water, but is dissolved by a warm solution of potassium hydrate, with the formation of potassium antimonite and sulphantimonite, and should also form a clear, colorless solution, with the exception of an inconsiderable insoluble residue, when heated to about 90° C. (194° F.), with 200 parts of a solution of 1 part of sodium carbonate in 2 parts of water. When treated with a solution of tartaric acid (1 part of acid to 3 parts of water), the antimonious oxide is dissolved, whilst the antimonious sulphide remains unaffected; the latter, however, is completely soluble in a solution of potassium hydrate.

Examination:

When a small quantity of sulphurated antimony is agitated with water and filtered, the filtrate must not affect either blue or red litmus-paper, nor leave a residue when evaporated upon platinum-foil; a crystalline residue effervescing upon the addition of an acid will indicate *sodium carbonate.* The residue may then be dissolved in a little water, acidulated with hydrochloric acid, and tested with barium chloride, when an ensuing white precipitate will indicate *sulphates.*

Antimonious oxide and *sodium antimonite* may be detected, and at the same time quantitatively estimated, by agitating the sulphurated antimony repeatedly with a solution of tartaric acid, when they will become dissolved, and, from the clear liquid, acidulated with hydrochloric acid, the antimony may be subsequently completely precipitated by hydrogen sulphide as antimony trisulphide, dried at 100° C. (212° F.), weighed, and therefrom the corresponding amount of antimonious oxide calculated. The amount of pure sulphide or of the oxide therein contained may likewise be determined by thoroughly washing the portion undissolved by the tartaric acid with pure water, drying, and subsequently determining the loss of weight.

Arsenic may be detected by digesting a portion of the sulphurated antimony with a cold saturated solution of ammonium carbonate, when the arsenious sulphide will be dissolved, and may be re-precipitated from the solution by supersaturation with hydrochloric acid, and subsequent saturation with hydrogen sulphide. The most reliable method, however, for the detection and separation of the arsenic is as follows: One part of the powder is intimately mixed with 3 parts of sodium nitrate, and the mixture is brought, in small portions, into a small porcelain crucible, previously heated to a low, red heat, and containing 1 part of pure sodium nitrate; the heat is then maintained until complete deflagration and oxidation of the melted mass is effected, after which the contents of the crucible may be removed while still warm, then allowed to cool, subsequently reduced to powder, and digested with the necessary quantity of a mixture of 1 part of alcohol and 5 parts of water. The antimony thus remains as insoluble sodium antimoniate, together with ferric and cupric oxides and lead antimoniate, if these metals are present, whilst the solution will contain the arsenic in the form of soluble sodium arseniate, together with sodium sulphate, nitrite, and undecomposed nitrate. The filtered solution is then acidulated with sulphuric acid, evaporated to dryness, the residue dissolved in water, and, after warming to about 60° C. (140° F.), saturated with hydrogen sulphide; the arsenic is thus, together with a little separated sulphur, completely precipitated as yellow arsenic trisulphide; or the filtered solution, as originally obtained by the extraction of the fused mass with water containing a little alcohol, is acidulated with nitric acid, boiled in order to remove all traces of nitrous acid, and a few drops of a solution of argentic nitrate subsequently added, when, in case a turbidity is produced by the separation of argentic chloride, the solution is again filtered; a few drops of ammonia-water are then carefully poured upon the surface of the solution, contained in a test-tube, when in the presence of small amounts of arsenic (not exceeding $\frac{1}{10}$ of 1 per cent.), a white cloudiness will appear at the line of contact of the two liquids, whereas with larger amounts a more or less reddish-brown precipitate of silver arseniate will be produced, soluble in an excess either of ammonia-water or of nitric acid. If the result of the above test should leave any doubt as to the presence or absence of minute quantities of arsenic, it may be made still more delicate, by rendering the above solution to which the argentic nitrate was added strongly ammoniacal, evaporating to dryness in a porcelain capsule by the aid of a gentle heat, treating the residue with water, and finally bringing the solution, together with any adhering undissolved particles of silver arseniate, upon a small filter; after thorough washing with water, the undissolved residue upon the filter is dissolved in hydrochloric acid, the solution diluted slightly with water, filtered, and tested in *Marsh's* apparatus, as described on pages 33 to 36.

Iron, *Lead*, and *Copper*.—To a portion of the sulphurated antimony, contained in a porcelain capsule, concentrated nitric acid is added, and the mixture evaporated upon the water-bath to dryness, the operation being repeated with the addition of more nitric acid, if necessary, until complete oxidation is effected; to the residue, water is added, and repeatedly evaporated to dryness, until the free nitric acid is completely eliminated; the residue is then treated with dilute nitric acid, the solution filtered and tested in separate portions as follows: To a portion of the solution a few drops of a solution of potassium ferrocyanide are added, when a blue precipitate will indicate *iron;* to another portion of the solution a few drops of dilute sulphuric acid are added, when a white precipitate will indicate *lead*, and, after the removal of the latter by filtration, and subsequent supersaturation of the liquid with ammonia-water, a blue coloration will reveal the presence of *copper*.

Admixtures of powdered silicates (brick-dust, etc.) remain unfused before the blow-pipe, and undissolved in hydrochloric acid.

APOMORPHINÆ HYDROCHLORAS.

APOMORPHINUM HYDROCHLORICUM.

Hydrochlorate of Apomorphine. Apomorphine Hydrochlorate.

Ger. Chlorwasserstoffsaures Apomorphin; Fr Hydrochlorate d'apomorphine; Sp. Clorhidrato de apomorfina.

$C_{17}H_{17}NO_2.HCl$; 303.4.

A white or grayish-white, crystalline powder, without odor, but possessing a bitter taste, and a neutral or faintly acid reaction. By exposure to light and a moist atmosphere, it readily absorbs oxygen and assumes a green color; in contact with concentrated nitric acid it produces a blood-red; with a dilute solution of ferric chloride an amethyst-red; and with molybdic acid a bright-green coloration. When strongly heated on platinum-foil, it burns entirely away, without residue.

Apomorphine hydrochlorate is soluble in 6.8 parts of water, and in 50 parts of alcohol at 15° C. (59° F.), but is slowly decomposed by boiling water or boiling alcohol, the solution acquiring an alkaline reaction, and, when concentrated, a greenish-brown color; it is almost insoluble in ether or chloroform, but soluble in an excess of a solution of sodium hydrate, forming a solution which, on exposure to the air, quickly assumes a purple-red color, and afterwards becomes black.

The aqueous solution of the salt, when freshly prepared, is colorless and neutral in its action upon litmus, and yields with a solution of sodium bicarbonate a white amorphous precipitate of apomorphine; this precipitate rapidly acquires a green color by exposure to the air, and then forms a bluish-green solution with alcohol, a purple one with ether or pure benzol, and a violet one with chloroform. The liquid from which the alkaloid has been precipitated, after supersaturation with nitric acid, yields, with a solution of argentic nitrate, a white precipitate of argentic chloride, insoluble in nitric acid, but soluble in ammonia-water.

AQUA AMMONIÆ.

LIQUOR AMMONIÆ. AQUA SEU LIQUOR AMMONII CAUSTICI.

Water of Ammonia. Solution of Ammonia.

Ger. Salmiakgeist; Fr Ammoniaque liquide; Sp. Solucion acuosa de amoniaco.

A colorless, transparent liquid, consisting of an aqueous solution of ammonia gas; the latter being soluble in water to an extraordinary degree, with the simultaneous development of heat. The degree of absorption of the gas by water is dependent upon the temperature and pressure; according to recent determinations, one volume of water absorbs:

at 0° C. (32° F.)	1050 volumes of gas,	at 15° C. (59° F.)	727 volumes of gas.
" 5° C. (41° F.)	918 " "	" 20° C. (68° F.)	654 " "
" 10° C. (50° F.)	813 " "	" 25° C. (77° F.)	586 " " .

The quantity of ammonia contained in the commercial and officinal solutions varies from 32 to 10 per cent. by weight of gas; the latter strength corresponding with a spec. grav. of 0.959 at 15° C. (59° F.), being the average strength of the aqua ammoniæ of the majority of the pharmacopœias. The United States and the British pharmacopœias include also an almost saturated solution, Aqua Ammoniæ Fortior; the former of 0.900 spec. grav., containing 28 per cent., the latter of 0.891 spec. grav., containing 32.5 per cent. of the gas.

This gas is also soluble in alcohol, which solution is officinal as Spiritus Ammoniæ, or Liquor Ammonii caustici spirituosus (Spiritus Ammoniaci caustici Dzondii), generally of a strength containing 10 to 12 per cent. of the gas.

These solutions have the properties of the gaseous ammonia, its pungent odor, sharp burning taste, and caustic action upon animal membranes; they have a strong alkaline reaction, and form white fumes when brought in contact with the vapors of chlorine or acids, however diluted with atmospheric air they may be. Solution of ammonia is miscible in all proportions with water, glycerin, and alcohol, and is neutralized by all acids with the formation of mostly well crystallizable salts; it decomposes and precipitates most of the earthy and metallic oxides from their compounds; several of these precipitates are redissolved by an excess of the precipitant. It also precipitates most of the alkaloids.

The purity of commercial aqua ammoniæ depends upon the mode of preparation, the materials employed, and the water used for the absorption of the gas. For medicinal use, distilled water ought to be employed, while this precaution is not required for solutions used in the arts and trades. The strength of solutions of ammonia may be determined by ascertaining their specific gravity; this method, however, is reliable and accurate only when the water contains ammonia alone, and is free from other, and especially from fixed substances, which would increase the specific gravity of the solution.

Examination:

Fixed substances are recognized by a residue upon the evaporation of the aqua ammoniæ in a glass capsule or on a watch-glass.

Ammonium carbonate is detected by mixing equal volumes of aqua ammoniæ and lime-water; a turbidity would indicate carbonate. The United States Pharmacopœia limits the amount of carbonic acid to the production of at most but a faint cloudiness when mixed with five times its volume of lime-water.

Empyreuma, if not recognized by the odor, will be distinctly developed when the ammonia-water is neutralized by diluted sulphuric acid, and, when slightly supersaturated with the acid, and subsequently diluted with water, the solution will decolorize a solution of potassium permanganate, if such impurities are present.

Tarry matters, which invariably contain traces of aniline and toluidine, are also detected by adding the ammonia-water, drop by drop, to a little colorless nitric acid, previously diluted with one-fourth its volume of water, in a test-tube, when the liquid will acquire a rose or deep-red coloration, gradually changing to brown upon the further addition of ammonia-water, and disappearing entirely if the latter is added in excess.

Calcium salts are recognized by a white precipitate of calcium oxalate on the addition of a solution of oxalic acid or ammonium oxalate.

Chloride, Cyanide, and *Sulphate.*—A portion of the ammonia-water is slightly supersaturated with nitric acid, and the solution evaporated on the water-bath to dryness. The residue is then dissolved in a little water, filtered, if necessary, and tested in separate portions with argentic nitrate for chloride and cyanide, and with barium nitrate for sulphate; when a precipitate has been formed with argentic nitrate, its nature may be ascertained by slightly supersaturating a little of the ammonia-water with hydrochloric acid, and subsequently adding to the solution a few drops of a solution of a ferrous and ferric salt; a blue coloration or precipitate would indicate the presence of cyanide; if such reaction does not occur, the silver precipitate, if insoluble in diluted nitric acid, consists of argentic chloride.

Metallic impurities will remain behind upon the evaporation of a little of the ammonia-water, and will also be precipitated by hydrogen sulphide, either before or after neutralization with hydrochloric acid.

Estimation:

The strength of aqueous solutions of ammonia, if free from fixed or other impurities, may be approximately determined by ascertaining the specific gravity, and reference to the subjoined table. Of the officinal Aqua Ammoniæ, containing 10 per cent. by weight of ammonia gas, 100 parts should dissolve, without effervescence, 37.058 parts of pure, crystallized oxalic acid, to form a perfectly neutral, clear, colorless, and odorless liquid.

The *ammonia strength* of pure aqua ammoniæ, or of crude ammoniacal liquors (free from other alkaline hydrates or carbonates), may be more accurately estimated, however, by the following simple method of volumetric analysis: A convenient quantity of the liquid (10 grams) is accurately weighed in a flask, a few drops of litmus solution added, and a normal solution of oxalic or sulphuric acid (page 82) allowed to flow into the liquid from a burette until, with constant stirring, a permanent red tint is produced. If exactly 10 grams of a 10 per cent. solution of ammonia are employed for the test, 59 cubic centimeters of the normal acid will be required for neutralization. As, however, one cubic centimeter of the normal acid, corrected if necessary by its proper factor, corresponds to 0.017 grams of ammonia gas, NH_3, this number, when multiplied by the number of cubic centimeters of acid required for neutralization, will indicate the exact amount of ammonia contained in the solution, and therefrom its percentage strength may be readily calculated.

TABLE *of the quantity by weight of Ammonia contained in* 100 *parts by weight of Aqua Ammoniæ of different specific gravities* (*Carius*).

Temperature 14° C. (57.2° F.).

Specific gravity.	Per cent. of Ammonia.	Specific gravity.	Per cent. of Ammonia.	Specific gravity.	Per cent. of Ammonia.	Specific gravity.	Per cent. of Ammonia.
0.8844	36 .0	0.9052	27.0	0.9314	18.0	0.9631	9.0
0·8848	35.8	0.9057	26.8	0.9321	17.8	0.9639	8.8
0.8852	35.6	0·9063	26.6	0.9327	17 6	0.9647	8.6
0.8856	35.4	0·9068	26.4	0.9333	17.4	0.9654	8.4
0.8860	35.2	0.9073	26 2	0.9340	17.2	0.9662	8.2
0·8864	35·0	0.9078	26.0	0.9347	17·0	0.9670	8.0
0.8868	34.8	0.9083	25.8	0.9353	16.8	0.9677	7.8
0.8872	34.6	0·9089	25.6	0.9360	16.6	0.9685	7.6
0.8877	34.4	0.9094	25.4	0·9366	16.4	0.9693	7.4
0.8881	34 2	0.9100	25.2	0.9373	16.2	0.9701	7.2
0.8885	34.0	0.9106	25.0	0.9380	16.0	0.9709	7.0
0.8889	33.8	0.9111	24.8	0.9386	15.8	0.9717	6.8
0.8894	33.6	0.9116	24.6	0.9393	15·6	0.9725	6.6
0.8898	33.4	0.9122	24.4	0.9400	15.4	0.9733	6.4
0.8903	33.2	0.9127	24.2	0.9407	15·2	0.9741	6.2
0.8907	33.0	0.9133	24.0	0.9414	15.0	0.9749	6·0
0·8911	32.8	0.9139	23·8	0.9420	14·8	0.9757	5.8
0·8916	32.6	0.9145	23·6	0.9427	14.6	0·9765	5.6
0.8920	32.4	0.9150	23.4	0.9434	14.4	0.9773	5.4
0.8925	32.2	0 9156	23.2	0.9441	14.2	0.9781	5.2
0.8929	32.0	0.9162	23.0	0.9449	14.0	0·9790	5.0
0.8934	31.8	0.9168	22.8	0.9456	13.8	0.9799	4.8
0.8938	31.6	0.9174	22.6	0.9463	13.6	0.9807	4.6
0.8943	31.4	0.9180	22.4	0.9470	13.4	0.9815	4.4
0.8948	31.2	0.9185	22.2	0.9477	13.2	0.9823	4.2
0.8953	31.0	0.9191	22.0	0 9484	13.0	0.9831	4.0
0.8957	30.8	0.9197	21.8	0.9491	12.8	0.9839	3.8
0.8962	30.6	0·9203	21.6	0.9498	12.6	0.9847	3.6
0.8967	30·4	0.9209	21.4	0·9505	12.4	0.9855	3·4
0.8971	30·2	0 9215	21.2	0.9512	12.2	0.9863	3.2
0.8976	30.0	0.9221	21.0	0.9520	12.0	0.9873	3.0
0.8981	29.8	0.9227	20.8	0.9527	11.8	0.9882	2.8
0.8986	29.6	0.9233	20.6	0.9534	11.6	0.9890	2.6
0 8991	29.4	0.9239	20.4	0.9542	11.4	0.9899	2.4
0.8996	29.2	0.9245	20.2	0.9549	11.2	0.9907	2.2
0.9001	29·0	0.9251	20.0	0.9556	11.0	0.9915	2.0
0.9006	28.8	0.9257	19.8	0.9563	10.8	0.9924	1.8
0.9011	28.6	0.9264	19.6	0.9571	10.6	0.9932	1.6
0.9016	28.4	0.9271	19.4	0.9578	10.4	0.9941	1.4
0.9021	28.2	0.9277	19.2	0.9586	10.2	0.9950	1.2
0.9026	28.0	0.9283	19.0	0.9593	10.0	0.9959	1.0
0.9031	27.8	0.9289	18.8	0.9601	9.8	0.9967	0.8
0.9036	27.6	0.9296	18.6	0.9608	9.6	0.9975	0.6
0.9041	27.4	0.9302	18.4	0.9616	9.4	0.9983	0.4
0.9047	27.2	0.9308	18.2	0.9623	9.2	0.9991	0.2

With the decrease and increase of temperature, the specific gravity of aqua ammoniæ suffers a corresponding increase or decrease, amounting for each degree of the centigrade thermometer in either direction—

For aqua ammoniæ of a spec. grav. of	0.9001	to that of	0.9221	to about	0.00055
" " "	0.9251	"	0.9414	"	0.0004
" " "	0.9520	"	0.9670	"	0.0003
" " "	0.9709	"	0.9831	"	0.0002

For instance: An aqua ammoniæ of 0.9593 specific gravity at 14° C., containing 10 per cent. of ammonia, will have at 18° C. a specific gravity of $0.9593 - (0.0003 \times 4) = 0.9581$, and at 12° C. a specific gravity of $0.9593 + (0.0003 \times 2) = 0.9599$.

Rules for the Dilution of Ammonia-Water.

If the amount of ammonia contained in any solution of the same is greater than desired, and it is required to be diluted with water to obtain a certain percentage strength, the same rules and method of calculation may be employed as directed for hydrochloric acid, on page 157. Thus, if the specific gravity of the ammonia-water at 14° C. is 0.940, it contains 15.4 per cent. of ammonia, and, if required to be diluted with water so that it shall contain 10 per cent. of ammonia, the following proportion will be obtained:

	15.4 per cent.	10 per cent.	0 per cent.
Difference	5.4	10	

Thus, 10 parts of the 15.4 per cent. ammonia are to be mixed with 5.4 parts of water, for

100 grams Ammonia-water = 15.4 grams NH_3
54 " water = ——

154 grams Ammonia-water = 15.4 grams NH_3
or 100 " " " = 10.0 " "

AQUA AMYGDALÆ AMARÆ.

AQUA AMYGDALARUM AMARARUM.

Bitter-Almond Water.

Ger. Bittermandelwasser; Fr. Eau d'amandes amères; Sp. Agua de almendra amarga.

Bitter-almond water, when prepared from the essential oil of bitter almonds, is a clear, when derived by distillation from bitter almonds, mostly a slightly opalescent, colorless liquid, with the odor of oil of bitter almonds, which odor must not disappear after the elimination of the hydrocyanic acid by argentic nitrate.

The preparation of the U. S. Pharmacopœia contains one part of bitter-almond oil in 1000 parts of water; that of the Pharm. German., one part of absolute hydrocyanic acid in 1000 parts of the product (corresponding to one-tenth of 1 per cent.), which is associated in the water, containing a little alcohol, with benzoic aldehyde.

Argentic nitrate and mercurous nitrate produce but a slight turbidity in bitter-almond water; but, when a few drops of ammonia-water have been previously added, and the liquid is then supersaturated with diluted nitric acid, argentic nitrate will yield a white precipitate of argentic cyanide, and mercurous nitrate, upon warming, a dark-gray precipitate of metallic mercury, while mercuric cyanide will remain in solution.

Ferrous salts produce no direct reaction with bitter-almond water; if, however, a few drops of a solution of an alkaline hydrate are first added, then a little of a solution of an oxidized ferrous salt, and the solution subsequently slightly supersaturated with hydrochloric acid, a deep blue coloration will be produced, and, upon standing, a precipitate of Prussian blue will be deposited.

Examination:

Nitrobenzol (essence of mirbane), or so-called *artificial oil of bitter almonds*, when employed as a substitute for the bitter almond or the true oil in preparing the water, may be readily recognized by warming the bitter-almond water with a few drops of nitric acid for several hours, upon the water-bath, when the odor of the nitrobenzol will still remain perceptible, whereas pure bitter-almond water will become odorless, in consequence of the volatilization of the hydrocyanic acid, and conversion of the bitter-almond oil, by oxidation, into odorless benzoic acid.

The further examination of bitter-almond water should be directed to the determination of the proper amount of contained hydrocyanic acid, for which the following volumetric method is convenient and applicable.

Estimation:

Fifty-four grams of the bitter-almond water, or the corresponding amount by volume, if it be measured, is brought into a beaker, and a few drops of solution of potassium hydrate added, sufficient to impart an alkaline reaction; if the liquid is opalescent or turbid, a few cubic centimeters of alcohol should also be subsequently added in order to render it transparent. After the addition of a few drops of a solution of sodium chloride, to serve as an indicator, a decinormal solution of argentic nitrate (page 98) is allowed to flow in from a burette until, with constant stirring, a permanent cloudiness of the liquid is just produced. The number of cubic centimeters of silver solution required for this purpose, divided by 100, will give the percentage strength of the water in hydrocyanic acid. Thus, if 10 cubic centimeters of the silver solution are employed, the bitter-almond water will contain $\frac{1}{10}$ per cent., or the proper amount of hydrogen cyanide.

If for the above estimation the bitter-almond water be measured, instead of weighed, its specific gravity should be previously determined in order to ascertain the amount by volume which will correspond to 54 grams by weight; for, if it contain alcohol, which is sometimes added for the purpose of retarding the decomposition of the hydrocyanic acid, its specific gravity will become thereby lessened, and in proportion to the amount of alcohol present. For example, if its specific gravity is 0.98, 54 grams will correspond to 55.1 cubic centimeters, according to the equation, $0.98 : 1 = 54 : 55.1$.

AQUA CHLORI.

AQUA CHLORATA. LIQUOR CHLORI.

Chlorine-Water.

Ger. Chlorwasser; Fr. Eau chlorée; Sp. Solucion de cloro.

A saturated solution of chlorine gas in distilled water, containing at 15° C. (59° F.) 2.3681 times its volume of the gas. The gas is most soluble in water at 10° C. (50° F.), when the coefficient of absorption is 2.5852, and above this temperature the solubility constantly diminishes, until at 100° C. (212° F.) the gas ceases to be absorbed. If the gas be led into water at temperatures below 10° C. (50° F.), a solid yellow crystalline compound of the gas with water (chlorine hydrate) is formed, having the composition $Cl_2 + 10H_2O$. This compound is readily decomposed by exposure to the air into an aqueous solution of chlorine and chlorine gas, but, when preserved in a sealed tube, it may be heated to 38° C. (100.4° F.) without decomposition, being resolved at this temperature into an aqueous solution of the gas and liquid chlorine.

Chlorine-water has the pale, greenish yellow color, the irritating and suffocating odor, and the chemical properties of the gas. When heated, the chlorine becomes completely volatilized, a change which takes place more gradually by simple exposure to the air; by exposure to solar light it undergoes gradual decomposition with the formation of hydrochloric acid and the elimination of oxygen, a change which also occurs, but much more slowly, when chlorine-water is protected from the light.

Chlorine-water destroys instantaneously the color of dilute indigo-solution, and all vegetable colors. By the strong affinity of chlorine for all the elements except oxygen, nitrogen, and carbon, and for many compound radicals, it is a powerful chemical agent, and, especially by its property of abstracting or displacing hydrogen, bromine, and iodine, from almost all their combinations by equivalent substitution, a most energetic oxidizer.

An aqueous solution of chlorine may be recognized, independent of its physical properties, by its property of dissolving gold leaf, and by the liberation of iodine from a solution of potassium iodide, which will impart a blue color to mucilage of starch; when added to a clear solution of barium chloride in sulphurous acid, the latter will become oxidized to sulphuric acid, and a white precipitate of barium sulphate will be immediately produced.

Chlorine-water should be preserved in small, well-stoppered bottles, in a cool place, and protected from the light. Bottles of black glass afford the best protection, although red, yellow, and green glass exert a similar action, whilst in vessels of blue or violet glass it becomes as speedily decomposed as by exposure to the direct action of light.

Examination:

Hydrochloric acid, resulting from the decomposition of the chlorine-water, or from the imperfect washing of the chlorine gas, cannot be directly tested for by means of litmus or argentic nitrate, as the former is immediately bleached, and the latter yields with pure chlorine-water a slight turbidity in consequence of its ready decomposition, and the formation of hypochlorous, chloric, and hydrochloric acids. The presence of hydrochloric acid may be readily detected, however, by agitating a portion of the chlorine-water, in a stoppered vial, with a little metallic mercury until the odor of chlorine has entirely disappeared; the latter then combines with the mercury to form mercurous chloride (calomel), whilst the hydrochloric acid remains unchanged, and, after filtration, may be recognized by its acid reaction upon litmus, and by the production of a white precipitate of argentic chloride upon the addition of solution of argentic nitrate. The loss of the strong odor of the gas, an acid reaction upon litmus, and the formation of a white precipitate with argentic nitrate, when tested after the above-mentioned treatment with metallic mercury, would indicate a degree of decomposition which renders the chlorine-water unfit for use.

Inorganic salts, as an evidence of the employment of spring-water for the absorption of the gas instead of distilled water, may be ascertained by a fixed residue remaining upon the evaporation of a little of the water on platinum-foil, or on a watch-glass; as well as by testing it, after the addition of a little ammonia-water, with oxalic acid; a white precipitate would prove the presence of calcium salts, and would be indicative of spring-water.

Estimation of the Strength of Chlorine-water:

As the value of chlorine-water depends upon the amount of contained chlorine, which, according to most Pharmacopœias, should not be less than 0.4 per cent. by weight, and, for the sake of uniformity, should not exceed 0.5 per cent. in maximum strength, the following methods may be employed for its quantitative estimation.

I. *Approximate Estimation:*

One hundred parts by weight of chlorine-water are agitated with a solution of 3 parts of crystallized or granulated ferrous sulphate (free from peroxide) in 10 parts of a mixture of equal volumes of water and dilute sulphuric acid. When, now, a few drops of diluted test-solution of potassium permanganate are added, no discharge of its color should take place. This test provides for a chlorine-water which shall contain not less than 0.383 per cent. of dissolved chlorine; if it contain a less amount, the first drops at least of the permanganate solution, which are added, will become decolorized, as a portion of its oxygen will then be applied for the oxidation of the excess of ferrous salt, and the formation of colorless manganous sulphate. If, on the other hand, the maximum strength be confined to 0.5 per cent. of chlorine, the same test may be applied, with the employment, however, of 4 parts of crystallized ferrous sulphate in dilute acid solution, which corresponds to 0.510 per cent. of free chlorine; if a greater amount of chlorine is present, it will oxidize a larger amount of ferrous sulphate, and, if it contain less than 0.51 per cent., the first few drops of a solution of potassium permangate which are added will become decolorized.

II. *Quantitative Volumetric Estimation:*

Among the several methods of volumetric estimation, the following may be recommended for its simplicity, and as affording accurate results. This method depends upon the property of chlorine of liberating an equivalent amount of iodine from a solution of potassium iodide, and of the subsequent conversion of the iodine by means of a standard solution of sodium hyposulphite (thiosulphate) into sodium iodide and tetrathionate, as explained on page 95.

25 grams, or the same number of cubic centimeters, of chlorine-water are added to 20 cubic centimeters of an aqueous 10 per cent. solution of potassium iodide, contained in a flask or beaker, and the whole well mixed by stirring with a glass rod. A standard solution of sodium hyposulphite (page 94) is then allowed to flow in from a burette, until a slight excess has been employed, and complete decoloration is effected; to the solution a little mucilage of starch is then added, and the liquid subsequently inversely titrated with a standard solution of iodine (page 93) until, with constant stirring, a permanent blue coloration is just produced. If, for example, 33.5 cubic centimeters of sodium hyposulphite solution were first employed, and subsequently 2.8 cubic centimeters of standard iodine solution, then $33.5 - 2.8 = 30.7$ cubic centimeters of sodium hyposulphite solution, or the amount required for combination with the liberated iodine. Accepting the hyposulphite solution to be of such a strength that 1 cubic centimeter corresponds to 0.012318 gram of iodine, which factor must be established by a previous experiment, as

explained on page 95, then 30.7 × 0.012318 = 0.3781 gram of iodine, which, according to the equation—

$$\underbrace{127}_{\text{I}} : \underbrace{35.5}_{\text{Cl}} = 0.3781 : 0.10435,$$

corresponds to 0.10435 gram of chlorine, and, as this is contained in 25 grams of chlorine-water, the percentage strength of the latter would be, in the instance quoted, 0.417 per cent.

The U. S. Pharmacopœia requires that on mixing 35.4 grams of chlorine-water with a solution of 0.9 gram of potassium iodide in 20 grams of water, the resulting deep red liquid should require for complete decoloration at least 40 cubic centimeters of the volumetric solution of sodium hyposulphite (corresponding to at least 0.4 per cent. of chlorine).

AQUA DESTILLATA.

Distilled Water.

Ger. Destillirtes Wasser; Fr. Eau destilleé; Sp. Agua destilada.

H_2O; 18.

An insipid, transparent and colorless, odorless liquid, which, under a pressure of 760 millimeters, boils at 100° C. (212° F.), but evaporates slowly at ordinary temperatures, and, at 0° C. (32° F.), solidifies in the form of ice, in crystals of the hexagonal system. Its greatest density is at 4° C. (39.2° F.). If, however, its expansion is prevented, it retains the liquid form even at —24° C. (—11.2° F.).

Water is an almost incompressible fluid, one million volumes becoming less by fifty volumes when the atmospheric pressure is doubled; it is a bad conductor of heat, and a still worse conductor of electricity. Pure water, from the fact of being a simple solvent for a large class of bodies, is the most valuable and indispensable chemical agent, and should respond to the following tests of purity.

Distilled water must not leave a fixed residue upon evaporation. When reduced by evaporation to one-fourth or one-sixth of its volume, and then tested in separate portions with lime-water for *carbonates*, with argentic nitrate and a few drops of nitric acid for *chlorides*, with barium nitrate for *sulphates*, with ammonium oxalate for *calcium*, and, after acidulation with hydrochloric acid, as also after subsequent supersaturation with ammonia-water, with hydrogen sulphide for *metals*, it must in no instance yield any reaction.

Ammonia or *ammonium salts* may be detected by the addition of a few drops of Nessler's reagent (page 40) or of Bohlig's reagent (page 39); a brown coloration or turbidity with the first mentioned reagent, and a white turbidity with the latter, due to the formation of a compound of mercur-ammonium chloride with mercuric oxide, $\mathrm{N}\left\{\begin{array}{l}\mathrm{H}_2\\ \mathrm{Hg}\end{array}\right.\mathrm{Cl.HgO}$, will reveal the presence of ammonia.

Nitrous acid may be detected by mixing in a beaker a little mucilage of starch, acidulated with sulphuric acid, with a solution of potassium iodide; the mixture must remain colorless; the water under examination is then added, stirring it with a glass rod; if the liquid assumes a bluish tint, traces of nitrous acid are indicated.

Nitric acid may be detected by reducing a portion of the water by evaporation to about $\frac{1}{10}$ of its volume, and to the liquid, contained in a test-tube, subsequently adding a few drops of solution of aniline sulphate, and, afterward, about 10 drops of concentrated sulphuric acid; the liquid is then slowly stirred with a glass rod, when, if nitric acid be present, rose-colored lines will appear after a while, and the whole liquid also will gradually assume this tint. Nitric acid may also be tested for by adding to about 100 cubic centimeters of the water, 2 or 3 drops of pure concentrated sulphuric acid, a few fragments of metallic zinc, and a little mucilage of starch, together with a few drops of a solution of potassium iodide; if nitric acid or nitrates are present, they will become thereby reduced to nitrous acid, which will liberate iodine from the solution of potassium iodide, and impart a blue coloration to the starch.

Organic substances may be recognized in the water, if it is free from nitrous acid, by warming to near 60° C. (140° F.) a portion of the water in a beaker, which is then placed upon white paper; then a few drops of sulphuric acid, and subsequently a very dilute solution of potassium permanganate (1 : 1000), are added, drop by drop. If the water is entirely free from organic substances, it should assume and retain, upon the addition of the first drop of the solution, a slight rose-colored hue, which increases in intensity progressively with the number of drops added. If the water, however, contains organic substances, the coloration received from the first drop will either not appear at all, or will soon disappear.

If decoloration takes place, an approximate estimate of the quantity of organic substances contained in the water may be had from the number of drops which it is necessary to use before this effect ceases, and the permanent color begins to appear.

This same decoloration is also produced when the water contains certain inorganic substances, as nitrous and sulphurous acids, hydrogen sulphide, ferrous, and other sub-salts, and other readily oxidizable substances. Organic matter in combination with the above-mentioned substances may, however, be recognized by evaporating a considerable quantity of the water by the aid of a gentle heat to dryness, and finally strongly heating the residue in a porcelain or platinum crucible. If a brown or blackish coloration is thereby produced, the presence of organic matter is indicated, and, if the latter contains nitrogen, an odor resembling that of burnt hair will be also at the same time developed.

ARGENTI CYANIDUM.

ARGENTUM CYANATUM.

Cyanide of Silver. Argentic Cyanide.

Ger. Cyansilber; Fr. Cyanure d'argent; Sp. Cianuro de plata.

$AgCN$; 133.7.

A white, amorphous powder, which becomes but slowly discolored by exposure to light (distinction from argentic chloride). When strongly heated, the salt fuses and becomes decomposed, with the development of cyanogen gas, leaving finally a grayish residue, consisting of metallic silver and argentic paracyanide. Argentic cyanide is insoluble in water, alcohol, and the dilute mineral acids, but is soluble in a solution of sodium hyposulphite or ammonia-water, and from the latter solution, upon supersaturation with nitric acid, it is precipitated unchanged.

When heated with an excess of concentrated nitric acid, it is partially dissolved, but is again precipitated on cooling; by prolonged heating with the acid it becomes decomposed, and is finally entirely dissolved. When boiled with a mixture of equal parts of concentrated sulphuric acid and water, it is decomposed, with the development of hydrocyanic acid and the formation of argentic sulphate, and can thus be separated from argentic chloride. By the action of hydrochloric acid, even in the cold, it is readily converted into argentic chloride, and, in the liquid filtered therefrom, the hydrocyanic acid may be readily detected by neutralization with ammonia-water, addition of a few drops of a solution of a ferric and ferrous salt, or partially oxidized ferrous sulphate, and subsequent supersaturation with hydrochloric acid, when a precipitate of Prussian blue will be produced. When digested with a solution of yellow ammonium sulphide, it is converted into argentic sulphide, and if the liquid filtered therefrom, which contains ammonium sulphocyanide, be cautiously evaporated to dryness, the residue dissolved in water, filtered, and, after acidulating with hydrochloric acid, tested with a few drops of a solution of ferric chloride, a deep blood-red color will be produced.

Argentic cyanide has a great tendency to enter into combination with the alkaline cyanides, with the formation of readily soluble and crystallizable double salts. Thus with potassium cyanide, it forms *potassio-argentic cyanide* $AgK(CN)_2$, which may be obtained by the evaporation of its solution in colorless, hexagonal tables, soluble in 4 parts of water at ordinary temperatures, and also soluble in alcohol; with sodium cyanide it forms *sodio-argentic cyanide*, $AgNa(CN)_2$, which crystallizes by the evaporation of its solution in colorless laminæ, soluble in 5 parts of water, and also readily soluble in alcohol. From the solutions of both of these salts, the argentic cyanide is again precipitated upon the addition of a mineral acid, with the liberation of hydrocyanic acid.

ARGENTI IODIDUM.

ARGENTUM IODATUM.

Iodide of Silver. Argentic Iodide.

Ger. Jodsilber; Fr. Iodure d'argent; Sp. Ioduro de plata.

AgI; 234.3.

An amorphous powder, of a light-yellowish color, and having the specific gravity of 5.807 at 0° C. (32° F.). When perfectly pure, it undergoes no change by exposure to solar light, but, as prepared by precipitation from a solution of argentic nitrate, it usually contains traces of the latter salt, and then assumes on exposure to the light a greenish or grayish-black color. It melts at a dull red heat, without decomposition, forming a yellow liquid, which, on further heating, assumes a red, and finally a dark reddish-brown color, and, on cooling, solidifies to a soft yellowish mass, which has then the specific gravity of 5.687 at 0° C. (32° F.).

When argentic iodide is gently heated in chlorine gas, it is converted into argentic chloride, with the liberation of iodine; the same decomposition is effected when an excess of the salt is agitated with concentrated chlorine-water, and the filtered liquid will then assume a blue color on the addition of a little mucilage of starch.

Argentic iodide is insoluble in water, alcohol, diluted acids, or solution of ammonium carbonate, and is almost insoluble in strong ammonia-water, spec. grav. 0.890, one part of the salt requiring of the latter 2493 parts for solution (distinction from argentic chloride and bromide). It is quite readily soluble in a solution of sodium hyposulphite (thiosulphate), although less freely then argentic chloride; and is soluble in a concentrated solution of potassium iodide, being re-precipitated, however, on the addition of water. It is also dissolved by an aqueous solution of potassium cyanide, and the resulting solution yields a black precipitate with hydrogen sulphide or ammonium sulphide.

If a small portion of the salt be digested with a concentrated solution of ammonium carbonate, filtered, and the filtrate slightly supersaturated with nitric acid, not more than a slight opalescence should be produced; a white turbidity or precipitate would indicate a contamination with argentic chloride.

ARGENTI NITRAS.

ARGENTUM NITRICUM.

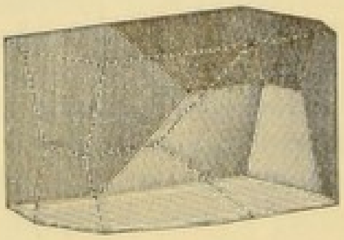
Nitrate of Silver. Argentic Nitrate.

Ger. Salpetersaures Silber (Höllenstein); Fr. Azotate d'argent;
Sp. Nitrato de plata.

$AgNO_3$; 169.7.

Anhydrous, colorless, transparent, rhombic crystals (Fig. 96), or, when fused and cast into moulds, thin, white, transparent, cylindrical sticks. Argentic nitrate, when perfectly pure, is not altered by exposure to light and air, but, in contact with organic matter, becomes rapidly blackened by exposure to the light. Its specific gravity is 4.328. When heated to 198° C. (388.4° F.), it melts without decomposition, forming a pale yellowish-colored liquid, which solidifies on cooling to a white fibrous crystalline mass; at a higher temperature it is partially decomposed with the formation of some argentic nitrite and oxide, which impart an alkaline reaction to the salt, and, at a red heat, further decomposition ensues, with the development of oxygen, nitrogen, and nitrogen dioxide vapors, leaving a residue of metallic silver. When fused upon charcoal before the blow-pipe, it deflagrates, emitting yellow vapors and sparks, while a reticular coating of metallic silver remains behind.

Fig. 96.



Argentic nitrate is soluble in 0.8 part of water and in 26 parts of alcohol at 15° C. (59° F.), and in 0.1 part of boiling water and 5 parts of boiling alcohol, but is only sparingly soluble in ether and chloroform; its strong aqueous solution, therefore, when dropped into alcohol, suffers no precipitation.

The aqueous solution of argentic nitrate must be clear, and perfectly neutral in its action upon litmus; a white turbidity would indicate argentic chloride or nitrite; a bluish color, cupric nitrate; a grayish-black turbidity in the solution of the fused salt, a partial reduction by an excess of heat in the fusion, or cupric chloride or oxide.

The solution yields, with hydrochloric acid or soluble chlorides, a white, curdy precipitate of argentic chloride; with hydrogen sulphide, a brownish-black precipitate of argentic sulphide; with the alkaline hydrates a grayish-brown precipitate of argentic oxide, readily soluble in ammonia-water; with the alkaline carbonates, a pale yellow precipitate of argentic carbonate; with sodium phosphate, a bright yellow precipitate of argentic phosphate; and with potassium chromate, a brownish-red precipitate of argentic chromate, all of which are soluble in nitric acid or ammonia-water. From a solution of argentic nitrate many of the metals effect the separation of metallic silver; such are lead, tin, cadmium, zinc, copper, mercury, and also bismuth, arsenic, and antimony.

Examination:

In the employment of argentic nitrate for surgical, ophthalmic, and similar purposes, it is desirable to overcome its brittle properties, and to impart thereto greater solidity, or to modify to some extent its action. This is attained by fusing the argentic nitrate with definite proportions of argentic chloride or potassium nitrate, and such admixtures are officinal in some pharmacopœias, *Argenti Nitras Fusus*, and *Argenti Nitras Dilutus*, U. S. P.; the former containing about 5 per cent. of argentic chloride, and the latter 50 per cent. of potassium nitrate. The *Argentum nitricum cum kali nitrico* of the Pharm. German. is a mixture obtained by fusing 1 part of argentic nitrate with 2 parts of potassium nitrate.

Such admixtures are indicated in the fused silver salt, by an alteration of its appearance, which is less translucent, whiter, and without the distinct radiate crystalline structure of pure argentic nitrate.

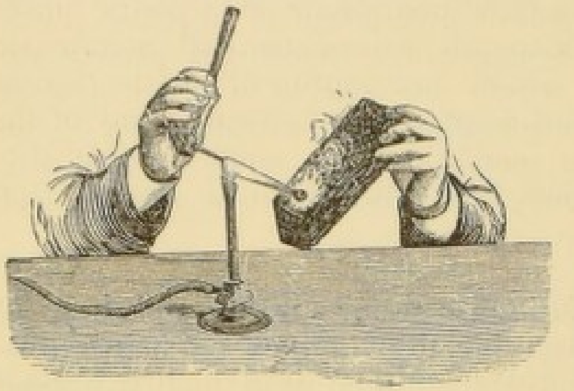
Among the methods of detecting such admixtures, the following are the readiest and most practicable ones:

Potassium Nitrate.—1. A concentrated aqueous solution of argentic nitrate is dropped into ten times its bulk of strong alcohol; if potassium nitrate be present, it will separate after a while in small, white granules, as it is far less soluble in alcohol. Sodium nitrate, which, however, on account of its hygroscopic character, is not adapted to this purpose, cannot be detected by this test, since it is more soluble in alcohol.

2. A small quantity of a dilute solution of argentic nitrate is completely precipitated with diluted hydrochloric acid; the liquid is then warmed, and must, in the case of pure argentic nitrate, when filtered, leave no fixed residue upon evaporation; such a residue would indicate alkaline nitrates or other impurities, the amount of which may be quantitatively estimated by repeated evaporation with a little dilute nitric acid, finally drying the residue at 100° C. (212° F.), and determining its weight, or by ascertaining the amount of dry argentic chloride which is yielded by a weighed amount of the salt.

3. A number of larger and smaller crystals are mixed and broken in a mortar; a small portion of the coarser powder, or fused argentic nitrate, if this be tested, is fused and completely reduced on charcoal before the blow-pipe (Fig. 97): a slight reticular metallic coating will remain behind, and some alkaline carbonate, if potassium or sodium nitrates were present; they will be recognized by the alkaline reaction, when moist, red litmus-paper is pressed upon the spot of the coal where the fusion took place.

FIG. 97.



Argentic chloride is indicated, as stated, by a white turbidity of the solution of argentic nitrate; its identity may be ascertained by its dissolving upon the addition of ammonia-water, but remaining insoluble in nitric acid.

Copper and *iron* may be detected by completely precipitating the aqueous solution of the salt with hydrochloric acid, and by subsequent approximate neutralization of the filtrate with ammonia-water; this solution is then tested with a few drops of a solution of potassium ferrocyanide; a red precipitate would indicate copper, a blue one, iron; copper may also be detected, or its presence confirmed, by dissolving a small quantity of the argentic nitrate in a little water, in a test-tube, and subsequently adding to the solution a few drops of ammonia-water; an ensuing blue coloration would indicate copper; a white turbidity, lead or zinc, which, in the case of zinc, disappears upon the addition of an excess of ammonia-water.

Lead and *bismuth*, as also foreign metals in general, may be detected by completely precipitating the silver from the aqueous solution of the argentic nitrate by means of hydrochloric acid, washing the precipitate well with water, subsequently testing the filtrate with hydrogen sulphide, and, after again filtering, if necessary, and supersaturating with ammonia-water, testing with ammonium sulphide; a coloration or precipitate in either case will indicate contamination with foreign metals. Lead may also be specially tested for by adding to a solution of 1 part of argentic nitrate in 10 parts of water, 4 times its volume of dilute sulphuric acid; a white precipitate will indicate the presence of lead.

Nitrous acid or *argentic nitrite*, traces of which are frequently met with in the fused argentic nitrate, and which are more considerable in amount in proportion to the extent of the admixture with potassium nitrate, will be indicated by a slight turbidity upon dissolving the salt in water, and readily recognized as follows: A dilute solution of the salt is completely precipitated by the addition of a slight excess of hydrochloric acid, rapidly filtered, and the filtrate added to a solution of potassium iodide, containing a little mucilage of starch; if nitrous acid be present, a blue coloration will be immediately produced.

Estimation:

The determination of the purity of crystallized argentic nitrate, as also the amount of the latter salt when associated with argentic chloride, potassium nitrate, or other substances which may be used as admixtures or for the purpose of adulteration, may be readily accomplished either gravimetrically or by the method of volumetric analysis.

I. *Gravimetric.*—One gram of the salt is dissolved in a small amount of water, the solution filtered, if necessary, and hydrochloric acid subsequently added until a precipitate ceases to be produced; the precipitate is collected upon a tared filter, thoroughly washed with water, and finally dried at 100° C. (212° F.) until of constant weight. If the salt be pure argentic nitrate, the precipitate of argentic chloride thus obtained will weigh 0.8441 gram; if it be *argenti nitras fusus*, it will weigh 0.801 gram, and if *argenti nitras dilutus*, 0.422 gram, respectively.

II. *Volumetric.*—About 0.5 gram of the salt is dissolved, in a beaker, in about 20 cubic centimeters of water, a few drops of a solution of potassium chromate added, and subsequently a decinormal solution of pure sodium chloride (containing 5.85 grams of the dry, crystallized salt in 1 liter) allowed to flow into the liquid from a burette until, with constant stirring, the red coloration of argentic chromate remains permanent.

One cubic centimeter of the decinormal sodium chloride solution corresponding to 0.017 gram of pure argentic nitrate, this number, when multiplied by the number of cubic centimeters employed, will indicate the amount of pure argentic nitrate in the specimen under examination.

ARGENTI OXIDUM.

ARGENTUM OXYDATUM.

Oxide of Silver. Argentic Oxide.

Ger. Silberoxyd; Fr. Oxyde d'argent; Sp. Oxido de plata.

Ag_2O; 231.4.

An olive-brown, amorphous, odorless powder, which, when heated at a temperature of from 60 to 80° C. (140–176° F.), becomes almost black; at 250° C. (482° F.) it begins to decompose, and at 300° C. (572° F.) it loses the whole of its oxygen, leaving behind spongy metallic silver; it is also gradually reduced by solar light.

Argentic oxide is sparingly soluble in water, one part requiring about 3000 parts for solution, but is freely dissolved by ammonia-water, as also by warm, concentrated nitric and sulphuric acids; it is insoluble, however, in the fixed alkaline hydrates. Its aqueous solution has an alkaline reaction and a metallic taste, and is rendered turbid by a small quantity of carbon dioxide, but becomes clear again upon the absorption of a larger quantity of the gas. When argentic oxide is triturated in a mortar with the sulphide of arsenic or antimony, finely divided sulphur, amorphous phosphorus, tannic acid, and many other readily oxidizable substances, ignition takes place.

The purity of argentic oxide is ascertained by its solubility in ammonia-water, and also in hot nitric acid, without effervescence, and by the fact that the latter solution, when completely precipitated with hydrochloric acid, gives a filtrate which leaves no residue upon evaporation, and yields no reaction with hydrogen sulphide, either in the acid solution, or on subsequent supersaturation with ammonia-water. One gram of argentic oxide when dissolved in nitric acid, the solution evaporated, diluted with water, if necessary, and subsequently completely precipitated by hydrochloric acid, yields a precipitate of argentic chloride, which, when washed and dried, should weigh 1.236 grams.

ARSENII BROMIDUM.

ARSENICUM BROMATUM.

Bromide of Arsenic. Arsenious Bromide. Arsenic Tribromide.

Ger. Arsenbromür; Fr. Bromure d'arsenic; Sp. Bromuro de arsénico.

$AsBr_3$; 314.3.

Colorless, prismatic crystals, which possess a peculiar (arsenical) odor, and deliquesce upon exposure to the air. The salt has a specific gravity of 3.66. It melts at from 20 to 25° C. (68–77° F.), boils at 220° C. (428° F.), and is completely volatilizable by heat. Arsenious bromide is miscible with a small amount of water, forming a clear solution, from which, upon standing, arsenic oxybromide, $As(OH)_2Br$, is separated; in contact with a larger amount of water, it is decomposed with the formation of arsenious and hydrobromic acids. Its aqueous solution, when saturated with hydrogen sulphide, yields a yellow precipitate of arsenic trisulphide; and when heated with diluted nitric acid, it is decomposed with the liberation of bromine, which dissolves, upon agitation with a few drops of chloroform or carbon bisulphide, with a yellowish or reddish-brown color.

ARSENII IODIDUM.

ARSENICUM IODATUM.

Iodide of Arsenic. Arsenious Iodide. Arsenic Triiodide.

Ger. Arsenjodür; Fr. Iodure d'arsenic; Sp. Ioduro de arsénico.

AsI_3; 454.7.

An orange-red or purple, crystalline solid, or bright red, shining, hexagonal tables, gradually losing iodine on exposure to the air, and possessing an iodine-like odor and taste. Its specific gravity is 4.39. When gently heated, the salt fuses, and may be sublimed without decomposition; when strongly heated, it is completely volatilized.

Arsenious iodide is soluble in 3.5 parts of water and in 10 parts of alcohol at 15° C. (59° F.), but is decomposed by boiling water into arsenious and hydriodic acids; it is also soluble in glycerin, ether, and carbon bisulphide, and crystallizes from the latter solutions upon evaporation unchanged. From its solution in a relatively small amount of water, upon standing, a compound consisting of arsenic trioxide with arsenic oxyiodide, $As(OH)_2I$, is separated, which crystallizes in bright yellow, shining, crystalline laminæ.

The aqueous solution of arsenious iodide is of a yellow color, and when saturated with hydrogen sulphide yields a bright yellow precipitate of arsenic trisulphide; when heated with diluted nitric acid, it is decomposed with the liberation of iodine, which dissolves, upon agitation with a few drops of chloroform or carbon bisulphide, with a reddish-violet or purple color.

ATROPINA.

ATROPINUM.

Atropine. Atropia.

Ger. Atropin; Fr. Atropine; Sp. Atropina.

$C_{17}H_{23}NO_3$; 289.

Colorless, silky, acicular crystals, or a yellowish-white crystalline powder, without odor, and of a bitter and acrid taste.

When carefully dried, the crystals melt at 112° C. (233.6° F.), and by very cautiously heating, in small amounts, may be partially sublimed; upon more strongly heating they become decomposed with the development of ammonia, swelling and emitting inflammable vapors, and leaving a carbonaceous residue, which is wholly dissipated at a red heat.

Atropine is soluble in 600 parts of water at 15° C. (59° F.), in 35 parts of boiling water, in 60 parts of ether, in 3 parts of chloroform, freely in alcohol and amylic alcohol, and is also soluble in glycerin, but is very sparingly soluble in carbon bisulphide. The aqueous solution possesses a purely bitter taste, without acridity, a strongly alkaline reaction, and powerfully dilates the pupil of the eye.

Atropine dissolves in concentrated nitric acid, imparting to it a yellowish color, and in cold concentrated sulphuric acid, without color, but, upon warming, the solution becomes reddish-brown, develops an odor resembling that of orange flowers, particularly upon the addition of a little water, and becomes finally black. The solution in cold concentrated sulphuric acid is not colored upon the addition of nitric acid (distinction from *morphine* and *brucine*), nor at once by solution of potassium bichromate (distinction from *strychnine*), but gradually assumes with the latter a green coloration, and, upon warming, the odor of oil of bitter almonds is evolved; the same odor is developed when, instead of potassium bichromate, potassium permanganate, manganese dioxide, or ammonium molybdate is employed. The aqueous solution of atropine or its salts yields precipitates with most of the ordinary alkaloidal reagents, but is not precipitated by picric acid (distinction from *daturine*), nor by platinic chloride, unless very concentrated (distinction from *hyoscyamine* and *belladonnine*); the latter is also distinguished by its amorphous character, and by its insolubility in a boiling solution of barium hydrate.

Atropine and its salts are decomposed and rendered inert by prolonged contact with potassium or sodium hydrate, and, when heated with either of the latter, vapors of ammonia are evolved. An aqueous solution of atropine or its salts also undergoes gradual decomposition at ordinary temperatures.

When atropine is heated at from 120 to 140° C. (248 to 284° F.) with concentrated hydrochloric acid, or with a concentrated solution of barium hydrate, it is resolved by assimilation of a molecule of water into a crystallizable base, *tropine*, $C_8H_{15}NO$, which is readily soluble in water, alcohol, and ether, and *tropic acid*, $C_9H_{10}O_3$ (phenylhydracylic acid,  $C_6H_5\text{–}CH\left\langle\begin{matrix}CH_2\text{–}OH\\ CO\text{–}OH\end{matrix}\right.$), which crystallizes in small colorless prisms, quite readily soluble in water, and freely in alcohol and ether.

$$\underbrace{C_{17}H_{23}NO_3}_{\text{Atropine.}} + H_2O = \underbrace{C_8H_{15}NO}_{\text{Tropine.}} + \underbrace{C_9H_{10}O_3}_{\text{Tropic acid.}}$$

Tropic acid, by further treatment with the above-mentioned reagents, is resolved by the loss of a molecule of water into *atropic* and *isatropic acids*, both of which have the composition $C_9H_8O_2$, and are therefore isomeric with cinnamic acid.

$$\underbrace{C_9H_{10}O_3}_{\text{Tropic acid.}} - H_2O = \underbrace{C_9H_8O_2}_{\substack{\text{Atropic acid.}\\ \text{Isatropic acid.}}}$$

Atropic acid, by oxidation with a solution of potassium bichromate in dilute sulphuric acid, is further converted into *benzoic acid*, with the evolution of carbon dioxide:

$$\underbrace{C_9H_8O_2}_{\text{Atropic acid.}} + 5O = H_2O + 2CO_2 + \underbrace{C_7H_6O_2}_{\text{Benzoic acid.}}$$

When melted with potassium hydrate, it yields *alphatoluylic acid*, $C_8H_8O_2$, together with formic acid; and, upon heating with fuming hydrochloric acid, it is converted into isatropic acid.

For the separation of atropine from other alkaloids, or when associated with complex organic mixtures, see page 108.

ATROPINÆ SULPHAS.

ATROPINUM SULFURICUM.

Sulphate of Atropine or Atropia. Atropine Sulphate.

Ger. Atropinsulfat; Fr. Sulfate d'atropine; Sp. Sulfato de atropina.

$(C_{17}H_{23}NO_3)_2.H_2SO_4$; 676.

A colorless, indistinctly crystalline powder, permanent in the air, without odor, but possessing an unpleasant, bitter taste. When heated to 180° C. (356° F.) it fuses, and when more strongly heated upon platinum-foil, it is decomposed with the evolution of acrid vapors, leaving a carbonaceous residue, which is finally wholly dissipated at a red heat. It gives the same reactions as atropine with concentrated nitric and sulphuric acids, and, in the latter solution, with potassium bichromate or permanganate, and other oxidizing agents.

Atropine sulphate is soluble in half its weight of water at 15° C. (59° F.), in 2.6 parts of alcohol, spec. grav. 0.835, in 0.3 part of absolute alcohol, and very freely soluble in boiling water and boiling alcohol; it is very sparingly soluble in amylic alcohol, ether, chloroform, and carbon bisulphide. Its aqueous solution is neutral in its action upon litmus, and yields with a solution of barium chloride a white precipitate of barium sulphate, insoluble in nitric acid.

From its concentrated aqueous solution, potassium or sodium hydrates, ammonia-water, and sodium carbonate precipitate the pure alkaloid, which is soluble in an excess of the solutions of the alkaline hydrates, as also in a large amount of water. In other respects, atropine sulphate shows the same behavior towards reagents as atropine, and, like the latter, when applied to the eye, even in very dilute solution, produces dilation of the pupil.

The aqueous solution of atropine sulphate, acidulated with sulphuric acid, should afford no precipitate upon the addition of a solution of picric acid; the formation of a precipitate with the latter reagent will indicate the presence of *daturine.*

AURI ET SODII CHLORIDUM.

AURO-NATRIUM CHLORATUM.

Chloride of Gold and Sodium. Sodium Chlor-aurate.

Ger. Natrium-goldchlorid; Fr. Chlorure d'or et de sodium;
Sp. Cloruro de oro y sodio.

$AuCl_3.NaCl + 2H_2O$; 396.8.

The double chloride of gold and sodium forms large yellowish-red rhombic tables or prisms, containing 2 molecules (9.04 per cent.) of water of crystallization. As officinal in the United States and German Pharmacopœias, however, a considerably larger amount of sodium chloride is employed than is required for the formation of a double salt of the above composition; the preparation consisting of a mixture of equal parts of the anhydrous chlorides of gold and sodium, corresponding to 32.4 per cent. of metallic gold, whereas the pure crystallized double salt contains 76.25 per cent. of auric chloride, or 49.49 per cent. of metallic gold. The officinal preparation, like the pure double salt, is of a yellow color, deliquescent upon exposure to the air, and, in contact with dust or other organic substances, becomes readily reduced. It is decomposed at red heat, leaving a residue of metallic gold; and imparts an intense, persistent yellow color to a non luminous flame.

Sodium chlor-aurate is freely soluble in water, forming a yellow solution of an acid reaction, and imparts to the skin a permanent red coloration; it suffers reduction in contact with many organic and inorganic bodies, and, when heated in a test-tube with a solution of oxalic acid, a light violet colored mirror of metallic gold is produced.

The solution of auric chloride, upon the addition of ammonia-water, yields a brownish-yellow precipitate of ammoniacal auric oxide or fulminating gold, $Au_2O_3(NH_3)_4$, which explodes most violently when in the dry state, either on percussion or when heated; the solution is not precipitated, however, by potassium or sodium hydrate, or their carbonates, in consequence of the combination of auric oxide with the alkali, and the formation of soluble alkaline aurates. The solution of auric chloride, when added to a solution of potassium iodide, assumes a dark-green color, and yields a green precipitate of auric iodide, AuI_3, which dissolves upon agitation in consequence of the formation of soluble potassium iod-aurate; upon the addition of an excess of the gold solution, however, a permanent precipitate is produced, which, after washing, may be dried, but is then quite readily decomposed with the evolution of iodine, and, upon standing, is converted into aurous oxide, Au_2O. Potassium bromide produces no precipitate in a solution of auric chloride, the auric bromide being readily soluble in water. With solution of argentic nitrate it yields a white, curdy precipitate of argentic chloride, insoluble in nitric acid, but soluble in ammonia-water.

Hydrogen sulphide produces in a cold solution of auric chloride a brownish-black precipitate of auric disulphide, Au_2S_2, which is soluble in solutions of the alkaline sulphides, and still more readily in a solution of potassium cyanide; from a hot solution of the chloride, a precipitate of metallic gold is produced.

Examination:

Free acid may be detected by the development of white fumes, when a glass rod, moistened with ammonia-water, is held over the surface of the salt.

The further examination of the chloride of gold and sodium should be directed to the estimation of the amount of contained gold. About 0.5 gram of the dry salt is accurately weighed, dissolved in about 50 cubic centimeters of water in a porcelain capsule, the solution acidulated with sulphuric acid, and subsequently gently heated for about two hours with a considerable excess of a clear solution of ferrous sulphate or oxalic acid. The gold is thereby completely reduced to the metallic state, according to the reactions expressed by the following equations:

$$2AuCl_3 + 6FeSO_4 = Au_2 + Fe_2Cl_6 + 2Fe_2(SO_4)_3.$$
$$2AuCl_3 + 3C_2H_2O_4 = Au_2 + 6HCl + 6CO_2.$$

The precipitated gold is finally collected on a filter, thoroughly washed with water, dried, ignited, and weighed. From the resulting weight, the percentage amount of pure gold contained in the preparation may be readily calculated.

If 0.5 gram of the officinal salt be employed for the test, the ignited residue should weigh not less than 0.162 gram, corresponding to 32.4 per cent. of metallic gold.

BARII CHLORIDUM.

BARYUM CHLORATUM. BARYTA MURIATICA.

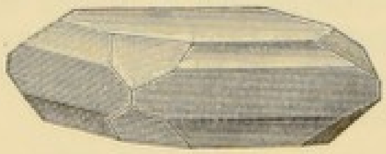
Chloride of Barium. Barium Chloride.

Ger. Chlorbaryum ; Fr. Chlorure de baryum ; Sp. Cloruro de bario.

$BaCl_2 + 2H_2O$; 243.6.

Colorless, shining, rhombic tables (Fig. 98), permanent in the air, and having a specific gravity of 3.05 at 4° C. (39.2° F.). They contain two molecules (14.75 per cent.) of water of crystallization, which are eliminated at a temperature of 113° C. (235.4° F.), forming a white powder, which fuses at a red heat, and imparts a yellowish-green color to the flame. By exposure to the air during the process of fusion, it loses a small amount of chlorine, with the formation of a little barium oxide, which imparts an alkaline reaction to the fused salt.

Fig. 98.



Barium chloride is soluble in 2.3 parts of water at 15° C. (59° F.), and in 1.3 parts of boiling water; it is insoluble in absolute or strong alcohol, but is sparingly dissolved by dilute alcohol, and in an amount proportionate to the quantity of water present. It is less soluble in diluted hydrochloric and nitric acids than in water, and is therefore partly precipitated from its aqueous solution, if not very dilute, upon the addition of concentrated hydrochloric or nitric acids, in the latter case with the formation of barium nitrate; the salt is, however, redissolved upon dilution with water. The aqueous solution has a bitter, nauseous, saline taste, is neutral in its action upon litmus, and yields copious white precipitates with sulphuric acid and sulphates, and with argentic nitrate, insoluble in diluted nitric acid; the latter precipitate being soluble in ammonia-water. With the soluble carbonates, phosphates, and chromates, precipitates of the respective barium salts are produced, all of which are soluble in hydrochloric and nitric acids.

Examination:

Aluminium may be detected, in the dilute aqueous solution, by a white turbidity on the addition of ammonia-water; a bluish coloration of the liquid would indicate *copper*.

Metals will be detected by a dark precipitate, or, if only traces of iron are present, by a dark-greenish coloration, upon the addition of ammonium sulphide to the aqueous solution; if a precipitate be formed, it is collected upon a filter, washed with water, dissolved in a few drops of warm nitric acid, and the solution supersaturated with ammonia-water; a blue coloration would confirm the presence of *copper;* a brown precipitate that of *iron.*

Calcium, *potassium*, and *sodium chlorides*, are detected, in the aqueous solution, by completely precipitating the barium with diluted sulphuric acid, and by subsequent examination of the filtrate in separate portions; *calcium* is recognized by a white precipitate when one of these portions is slightly supersaturated with ammonia-water, and tested with ammonium oxalate. *Potassium* and *sodium chlorides* will be indicated by a fixed residue upon complete evaporation of another part of the filtrate; they may be distinguished by the characteristic flame reactions, or by dissolving the residue in a few drops of water, and testing the solution with potassium antimoniate; a white turbidity would indicate sodium salt.

Strontium chloride is detected by agitating some of the powdered salt with about twenty times its weight of strong alcohol, filtering, and subsequently igniting the filtrate; the presence of strontium will be indicated by a red color of the flame, especially apparent toward the end of the combustion.

BENZINUM.

BENZINUM PETROLEI.

Benzin. Petroleum Benzin. Petroleum Ether.

Ger. Benzin; Fr. Benzine; Sp. Bensino.

A transparent, colorless, neutral, and highly inflammable liquid, possessing a characteristic odor, resembling that of petroleum. Its specific gravity varies from 0.670 to 0.675 at 15° C. (59° F.), and its boiling-point from 50 to 60° C. (122 to 140° F.).

Petroleum benzin, as indicated by the boiling-point, is not a definite body, but consists of a mixture of isomeric and homologous hydrocarbons of the paraffin series, among which hexane, C_6H_{14}, and heptane, C_7H_{16}, in their different isomeric modifications, are present in predominating amounts.

It is not miscible with water, and requires about six times its volume of alcohol, spec. grav. 0.835, for solution, but is miscible in all proportions with chloroform and ether; it possesses valuable properties as a solvent, dissolving fats, volatile oils, caoutchouc, and many resins, as also, to a certain extent, some of the alkaloids and other organic principles, but anhydrous carbolic acid is insoluble therein (distinction from benzol).

Examination:

Heavy hydrocarbons may be detected by a more or less viscid residue, when a small portion of the benzin is allowed to evaporate spontaneously on a watch-glass, or in a shallow glass or porcelain capsule.

Sulphur compounds and the *products of distillation of coal tar oils* may be detected by a brown coloration when a little of the benzin is mixed, in a test-tube, with one-fourth its volume of an alcoholic solution of ammonia, a few drops of solution of argentic nitrate subsequently added, and the mixture carefully heated for a few minutes to boiling; or, by a dark coloration of the liquid, attended with considerable elevation of temperature, when a small portion of the benzin is agitated with an equal volume of cold, concentrated sulphuric acid.

Sulphur compounds may be also detected by boiling a little of the benzin with a fragment of bright metallic sodium, decanting the clear liquid, and, after the careful addition of a little water to the residue, testing the aqueous liquid with sodium nitro-prusside; if sulphur compounds are present, a beautiful violet coloration will be produced.

Benzol, a hydrocarbon of the composition C_6H_6, obtained by the distillation of coal-tar oil, is the body to which the name benzin was first applied, and is consequently still, by the misapplication of names, frequently confused with petroleum benzin. It differs essentially from benzin in its chemical and many of its physical properties, solidifying at 0° C. (32° F.) to a mass of crystals, which have the form of rhombic pyramids, and yielding, with half its volume of alcohol, spec. grav. 0.835, a perfectly clear mixture. It may be readily detected by mixing, in a test-tube, 40 drops of concentrated sulphuric acid with 10 drops of pure nitric acid, subsequently adding to the mixture 5 drops of the benzin to be tested, and gently warming; if benzol is present, the characteristic odor of nitro-benzol (so-called artificial oil of bitter almonds) will be produced, which is rendered still more evident by subsequently pouring the liquid into a small porcelain capsule, diluting it with twice its volume of water, and allowing the nitrous acid, which is formed by the reaction, to evaporate.

BISMUTHI CITRAS.

BISMUTUM CITRICUM.

Citrate of Bismuth. Bismuthous Citrate.

Ger. Citronensaures Wismut; Fr. Citrate de bismuth; Sp. Citrato de bismuto.

$BiC_6H_5O_7$; 399.

A white, amorphous powder, without odor or taste, and permanent in the air. When heated with exsiccated sodium carbonate, on charcoal, before the blow-pipe, it yields brittle metallic grains, and, at the same time, a brownish-yellow incrustation of the coal is produced. When heated upon platinum foil, it is decomposed, with the separation of carbon, and the evolution of empyreumatic vapors, and, at a red heat, a fused mass remains, which, upon cooling, acquires a lemon-yellow color on the surface, and which is readily soluble in warm concentrated nitric acid; this solution, when dropped into a quantity of water, produces a white turbidity.

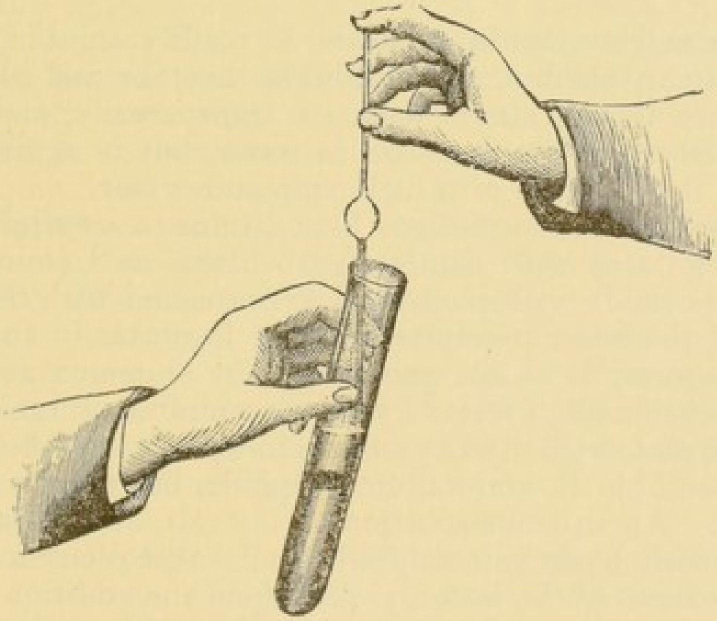
Bismuthous citrate is insoluble in water or alcohol, but is soluble in acids and in ammonia-water. The ammoniacal solution yields upon saturation with hydrogen sulphide a black precipitate of bismuth sulphide, and the filtrate therefrom, after being heated, to expel the excess of hydrogen sulphide, and the addition of a little lime-water or solution of calcium chloride, and again heating to boiling, yields a white precipitate of calcium citrate.

Examination:

Carbonates, *Chlorides*, and *Sulphates*.—A small portion of the bismuthous citrate is dissolved in dilute nitric acid; if effervescence ensues, *carbonates* are indicated. The dilute acid solution is then tested, in separate portions, with argentic nitrate and barium chloride, when an ensuing white precipitate will indicate *chlorides* or *sulphates* respectively.

Nitrates may be detected by dissolving a small portion of the salt in ammonia-water, completely precipitating the bismuth by hydrogen sulphide, filtering, heating to remove the excess of hydrogen sulphide, and to the clear liquid, contained in a test-tube, subsequently adding an equal volume of concentrated sulphuric acid, and afterward a solution of ferrous sulphate, so as to form two layers (Fig. 99); a violet or brown-colored zone at the line of contact of the two liquids will reveal the presence of nitrates.

Fig. 99.



BISMUTHI ET AMMONII CITRAS.

BISMUTUM ET AMMONIUM CITRICUM.

Citrate of Bismuth and Ammonium. Bismuth and Ammonium Citrate.

Ger. Citronensaures Wismut-Ammonium ; Fr. Citrate de bismuth et d'ammoniaque ; Sp. Citrato de bismuto y amoniaca.

$Bi(OH)_3,(NH_4)_3C_6H_5O_7$; 504.

Colorless, glossy, translucent scales, of a slightly acidulous and somewhat metallic taste. They contain, in acceptance of the correctness of the above formula, 46.43 per cent. of bismuth trioxide, Bi_2O_3, corresponding to 41.66 per cent. of metallic bismuth. When heated with exsiccated sodium carbonate, upon charcoal, before the blow-pipe, they yield brittle metallic grains, and, at the same time, a brownish-yellow incrustation of the coal is produced; when heated upon platinum-foil, they are decomposed, with the separation of carbon, and the evolution of moisture and of ammoniacal and empyreumatic vapors; and, at a red heat, a fused mass remains, which, upon cooling, acquires a lemon-yellow color on the surface, and which is readily soluble in warm concentrated nitric acid; this solution, when dropped into a quantity of water, produces a white turbidity. The salt, when heated with a solution of potassium or sodium hydrate, develops the odor of ammonia.

Bismuth and ammonium citrate is readily soluble in water, sparingly so in alcohol, and insoluble in ether and chloroform. By exposure to the air, it loses its transparency, and becomes gradually more or less insoluble in water, but is again rendered soluble by the addition of a little ammonia-water.

Its aqueous solution reddens blue litmus-paper slightly, gives white precipitates with dilute hydrochloric acid (soluble in an excess of the acid), with potassium hydrate, and with the alkaline carbonates, the latter precipitates being insoluble in an excess of the precipitants; it is not acted upon by ammonia-water; with potassium chromate, it forms a yellow precipitate, soluble in dilute nitric acid, and, with hydrogen sulphide, a brownish-black precipitate, insoluble in ammonium sulphide, but readily soluble in nitric acid. An aqueous solution of the salt, after complete precipitation with hydrogen sulphide, and subsequent warming to expel the excess of the latter, yields, upon the addition of a little lime-water or solution of calcium chloride, and heating to boiling, a white precipitate of calcium citrate.

Examination:

Chlorides and *sulphates* may be detected in the aqueous solution of the salt, acidulated with nitric acid, by an ensuing white precipitate, when tested, in separate portions, with argentic nitrate and barium chloride.

Nitrates may be detected in the aqueous solution of the salt by mixing it with an equal volume of concentrated sulphuric acid, and adding a solution of ferrous sulphate, so as to form two layers (Fig. 99, on page 271); a violet or brown colored zone at the line of contact of the two liquids will reveal the presence of nitrates.

BISMUTHI SUBCARBONAS.

BISMUTUM CARBONICUM.

Carbonate, Subcarbonate, or Oxy-carbonate of Bismuth. Basic Bismuthous Carbonate.

Ger. Basisches Wismutcarbonat; Fr. Sous-carbonate de bismuth; Sp. Subcarbonato de bismuto.

$2(BiO)_2CO_3.H_2O$; 1042.

A white, or pale yellowish-white, odorless and tasteless powder, permanent in the air, and which is blackened when in contact with hydrogen sulphide.

At 100° C. (212° F.) it loses water, and when more strongly heated it is readily converted into yellow bismuth trioxide, Bi_2O_3, with the elimination of carbonic acid gas: 100 parts of the salt thus yielding, upon ignition, 89.83 parts of bismuth trioxide, corresponding to a loss of 10.17 per cent. of water and carbonic acid gas. When heated with exsiccated sodium carbonate, on charcoal before the blow-pipe, it yields brittle globules of metallic bismuth and an incrustation on the coal, which is of an orange color when hot, and yellow when cold.

Basic bismuthous carbonate is insoluble in water, but slightly soluble in water saturated with carbonic acid gas; it is readily soluble, with effervescence, in acids, forming solutions which, when nearly neutralized by the bismuthous carbonate, produce white precipitates of very sparingly soluble basic salts when poured into a quantity of water, and yield upon the addition of alkaline hydrates a white precipitate of the hydroxide, which is insoluble in an excess of the precipitant.

Examination:

Nitrate may be detected, in a solution of the carbonate in cold diluted hydrochloric acid, by the addition of one or two drops of indigo solution, sufficient to impart to the liquid a slight bluish tinge, and subsequently heating to boiling; if decoloration of the liquid ensues, the presence of nitrate is indicated.

Insoluble admixtures may be detected by a residue, when 1 part of the salt is dissolved, by the aid of a gentle heat, in about 6 parts of a mixture of equal parts of concentrated nitric acid and water.

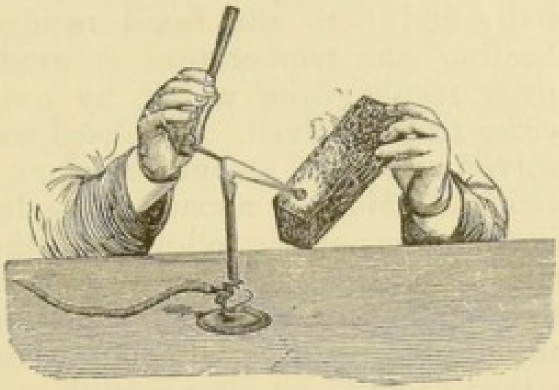
Metallic Impurities, *Chlorides*, and *Sulphates.*—The solution obtained in the preceding test is poured into 50 parts of water, filtered from the white precipitate thus produced, the filtrate concentrated by evaporation to 6 parts, and subsequently tested as follows: A portion of the liquid is mixed with 5 times its volume of diluted sulphuric acid, when a white cloudiness or precipitate will indicate the presence of *lead;* another portion is precipitated with an excess of ammonia-water, when an ensuing blue coloration of the liquid will reveal the presence of *copper;* a third portion of the liquid is diluted with five times its volume of water, and subsequently tested, in separate portions, with hydrochloric acid for *silver*, with argentic nitrate for *chlorides*, and with barium nitrate for *sulphates*, when a white turbidity or precipitate, insoluble in nitric acid, will indicate in either case the respective impurity.

Alkalies, *Alkaline Earths*, and *Zinc.*—A portion of the salt is dissolved, by the aid of a gentle heat, in diluted hydrochloric acid; after being allowed to cool, the liquid is filtered, subsequently saturated with hydrogen sulphide, and again filtered. The filtrate thus obtained should leave no residue upon evaporation. If a residue is obtained, it is dissolved in a little water, and tested with sodium carbonate, when an ensuing white precipitate will indicate salts of calcium, magnesium, or zinc. In order to distinguish the latter, the precipitate, if sufficient in amount, is collected and washed upon a filter, dissolved in a little dilute hydrochloric acid, ammonia-water in slight excess added, and subsequently tested with ammonium sulphide, when an ensuing white precipitate will indicate the presence of *zinc.* The filtrate from the latter is tested with ammonium carbonate, when a white precipitate will indicate *calcium*, and, after filtration and the addition of solution of sodium phosphate, an ensuing white, crystalline precipitate will reveal the presence of *magnesium.*

The presence or absence of alkalies or alkaline earths in bismuthous carbonate may also be ascertained, by boiling a portion of the salt for a few minutes with about ten times its weight of strong acetic acid: the liquid is then filtered, and completely precipitated with hydrogen sulphide; the filtrate must leave no fixed residue upon evaporation; if any such residue remains, alkalies or alkaline earths are indicated.

Calcium phosphates may be detected in the residue left by the evaporation of the liquid of the preceding test, by dissolving it in a little acetic acid, filtering, if necessary, and testing the solution, in separate portions, as follows: To a portion of the solution ammonium oxalate is added, when a white precipitate will indicate the presence of *calcium;* to another portion solution of ammonium molybdate is added, and the liquid heated to boiling, when a yellow crystalline precipitate will indicate the presence of *phosphates.* The presence of phosphates may be likewise determined in the solution, which

Fig. 100.



is first neutralized with ammonia-water as completely as possible, without causing precipitation, by the production of a lemon-yellow precipitate on the addition of ammoniated solution of argentic nitrate.

Ammonium salts may be detected by the odor of ammonia, and by white fumes from a glass rod moistened with acetic acid, and held over the orifice of the test-tube, when about 1 gram of the bismuthous carbonate is heated with 10 cubic centimeters of a strong solution of potassium or sodium hydrate.

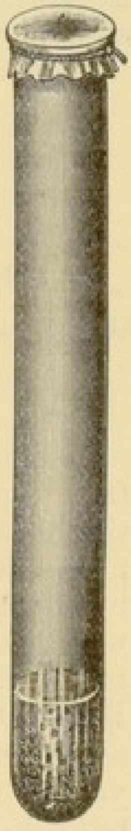
Arsenic, *Antimony*, and *Tin*.—The alkaline solution obtained in the preceding test, after thorough boiling, is diluted with water to the measure of about 50 cubic centimeters, filtered, the filtrate supersaturated with hydrochloric acid, and subsequently saturated with hydrogen sulphide; an ensuing yellow or orange-colored precipitate would indicate the above-mentioned impurities.

Arsenic will also be indicated, as a preliminary test, by the development of the characteristic garlic-like odor, when a little of the bismuthous salt is heated upon charcoal, before the blow-pipe (Fig. 100).

For the confirmation or more exact determination of the presence or absence of arsenic, one of the following tests should be applied:

I. About 1 gram of the bismuthous salt is boiled for some time with 10 cubic centimeters of a strong solution of potassium hydrate, which is free from chloride; after cooling, the clear alkaline solution is decanted into a test-tube, which should be filled to not more than one-fourth of its capacity, and containing about 0.5 gram of aluminium wire, cut in small pieces, or a little bright iron wire and a few fragments of metallic zinc; a cap of bibulous paper, moistened with a drop of a solution of argentic nitrate, is then placed over the mouth of the tube (Fig. 101), and the liquid gently warmed, when, if arsenic is present, hydrogen arsenide will be gradually developed, and produce a black stain upon the paper.

Fig. 101.



II. Three parts of the bismuthous salt are boiled for ten minutes with a solution of 3 parts of crystallized sodium carbonate (free from chloride) in 30 parts of water, the solution filtered, the filtrate evaporated to dryness, and the residue strongly heated;

after cooling, 2 parts of concentrated sulphuric acid are gradually added to the fused residue, and, after first cautiously heating, the temperature is gradually increased until a fused mass results, from which, by continued heating, yellow vapors cease to be evolved. The fused residue thus obtained is then dissolved in a small amount of water, and may be tested for arsenic, either in Marsh's apparatus, as described on page 33, or according to either of the following methods:

1. A portion of the solution is added to a solution of pure tinfoil or stannous chloride in concentrated hydrochloric acid, and the mixture gently warmed; a brown turbidity of the mixture, either at once or after a while, and a grayish-brown precipitate after subsiding, would indicate *arsenic.*

2. The remaining portion of the solution is added to dilute sulphuric acid, contained in a test-tube, together with a few fragments of pure metallic zinc or magnesium, not allowing the tube to be filled to more than one-fourth of its capacity; a cap of bibulous paper, moistened with a drop of a solution of argentic nitrate, having been placed over the mouth of the tube (Fig. 101), the mixture is allowed to repose for a short time, when, if arsenic is present, hydrogen arsenide will be developed, and produce a black stain upon the paper.

BISMUTHI SUBNITRAS.

BISMUTUM SUBNITRICUM. BISMUTUM ALBUM.

Subnitrate or Oxy-nitrate of Bismuth. Basic Bismuthous Nitrate.

Ger. Basisches Wismutnitrat; Fr. Sous-azotate de bismuth; Sp. Subnitrato de bismuto.

$$BiO(NO_3).H_2O = Bi(OH)_2NO_3;\ 306.$$

A heavy, white powder, which, according to its precipitation from hot or cold solutions, is either indistinctly crystalline, or in the form of microscopically minute crystalline scales; it reddens moistened blue litmus-paper, and becomes black in contact with hydrogen sulphide, but is not changed by exposure to light, except when containing certain impurities, as silver salts, organic matters, etc. At 100° C. (212° F.) it is converted into the compound $BiO(NO_3)_2(OH)_2$. When heated in a dry test-tube, it first emits moisture, and afterward reddish-yellow acid vapors, leaving a yellow residue, which, upon more strongly heating, melts to a reddish-brown mass, but, upon cooling, again assumes a yellow color. This residue is readily soluble in warm hydrochloric acid, forming a solution which, when poured into a quantity of water, produces a white precipitate, but, when mixed with strong alcohol, furnishes a perfectly clear mixture. Basic bismuthous nitrate, when dried at 120° C. (248° F.), loses from 3 to 5 per cent. of water, and, when dried at this temperature, yields upon ignition from 79 to 82 per cent. of oxide, Bi_2O_3; the variation being attributable to a lack of uniformity in the composition of the salt, as, according to the deviations in temperature, and proportions and strength of the solutions employed for its precipitation, a preparation varying in its chemical composition, as also in its physical properties, is obtained.

When heated with exsiccated sodium carbonate, on charcoal, before the blow-pipe, brittle globules of bismuth are obtained, and the charcoal becomes covered with a slight incrustation, which is of an orange color when hot, and yellow when cold. When mixed with a little potassium iodide and sulphur, and heated on charcoal, before the blow-pipe, a bright scarlet-red incrustation of bismuthous iodide is produced upon the coal.

Basic bismuthous nitrate is nearly insoluble in water; upon continued digestion, or by prolonged washing therewith, however, it suffers an alteration in its composition, in the latter case with the formation of the more basic salt, $BiONO_3 + BiO(OH)$, and is finally converted into the hydroxide. It is also insoluble in solutions of the alkaline hydrates, but by prolonged boiling with a concentrated solution of potassium or sodium hydrate, traces of bismuth are occasionally dissolved, as a probable result of the formation of bismuthic acid, and the alkaline solution then affords, upon saturation with hydrogen sulphide, a dark coloration or precipitate of bismuth trisulphide. Basic bismuthous nitrate is readily soluble in nitric and hydrochloric acids, and these solutions, when poured into a large amount of water, form white precipitates of basic bismuthous salts.

Examination:

Carbonates and *insoluble admixtures* are detected, the former by effervescence in the cold, the latter by remaining undissolved, when a portion of the salt is warmed with about ten times its weight of a mixture consisting of equal parts of concentrated nitric acid and water.

The examination for other admixtures or impurities is the same as described under bismuthous carbonate, on pages 274–275.

BISMUTHI VALERIANAS.

BISMUTUM VALERIANICUM.

Basic Valerianate of Bismuth. Basic Bismuthous Valerianate.

Ger. Basisches Wismutvalerianat; Fr. Valérianate de bismuth; Sp. Valerianato de bismuto.

A relatively heavy, white, amorphous powder, or, when contaminated with nitrate, of an indistinctly crystalline appearance, and possessing the odor of valerianic acid. When the salt is strongly heated in a dry test-tube, colorless, acid vapors are evolved, possessing the odor of valerianic acid, and which condense in the upper part of the tube to oil-like drops, while a dark grayish-colored residue, consisting of a mixture of bismuthous oxide with metallic bismuth, remains behind. This residue is incompletely dissolved by hydrochloric acid, but readily upon the subsequent addition of a few drops of nitric acid, and gently warming; the acid solution thus obtained is abundantly precipitated by the addition of a large amount of water, but forms with strong alcohol a perfectly clear mixture.

When heated with exsiccated sodium carbonate, or with a mixture of potassium iodide and sulphur, upon charcoal, before the blow-pipe, bismuthous valerianate affords the same reactions as bismuthous carbonate and nitrate (pages 273, 277). In contact with hydrogen sulphide it becomes blackened (distinction from zinc valerianate).

Bismuthous valerianate is insoluble in water and alcohol, but soluble in hydrochloric and nitric acids, separating an oily layer of valerianic acid, and forming solutions which produce white precipitates with a quantity of water.

Bismuthous valerianate is not a well-defined salt, and, in consequence of the facility with which it is decomposed, is of inconstant and variable composition. One part of the salt, when repeatedly moistened with nitric acid in a small tared porcelain crucible, and completely incinerated at a red heat, yields 0.68 to 0.75 (68 to 75 per cent.) part of bismuthous oxide, Bi_2O_3; thus corresponding approximately to a salt of the molecular composition $(BiO)C_5H_9O_2$, which, upon ignition, should yield 71.56 per cent. of oxide.

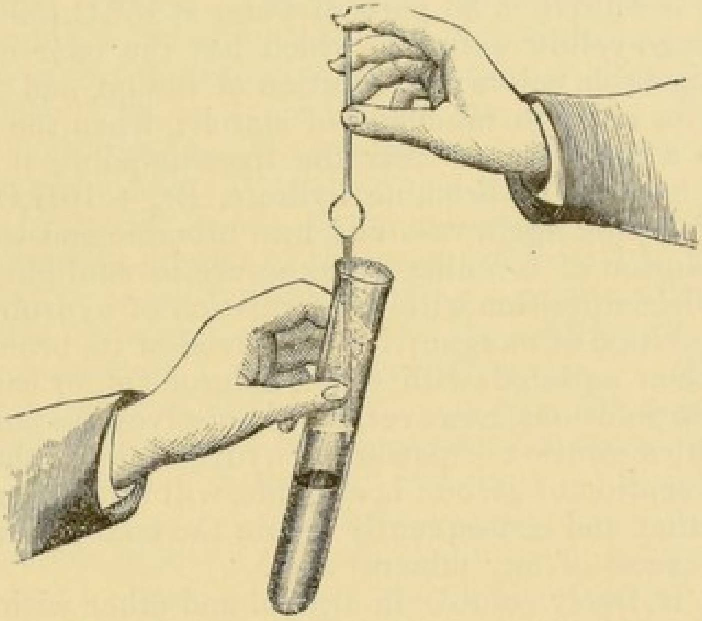
Examination:

The solution of bismuthous valerianate in acids, after dilution with water to an extent insufficient to cause the precipitation of the salt, should be passed through a moist double filter until a perfectly clear solution is obtained, in order to effect as completely as possible the separation of the valerianic acid before the application of the several tests.

Bismuthous nitrate or *carbonates* may be detected by dissolving a portion of the valerianate in cold concentrated hydrochloric acid; effervescence indicates carbonates, and, in this case, the solution of the salt diluted with a small amount of water, insufficient to cause its precipitation, is completely precipitated with hydrogen sulphide; the solution is then filtered, warmed in order to expel the excess of hydrogen sulphide, and the filtrate slightly supersaturated with sodium carbonate; a white precipitate would indicate salts of *calcium*, *magnesium*, or *zinc;* they may be discriminated by the same method as described on page 274.

Another part of the solution of the valerianate in hydrochloric acid is diluted with about four times its volume of water, and is faintly tinted with one drop of solution of indigo, and then gently warmed; if decoloration takes place, *nitrate* is indicated. The presence of nitrate may be also determined by dissolving a little of the valerianate in cold concentrated sulphuric acid, and adding to the liquid, in a test-tube, a concentrated solution of ferrous sulphate, so as to form two distinct layers (Fig. 102); a brownish or violet coloration at the line of contact of the two liquids will indicate contamination with nitrate.

FIG. 102.



The examination of bismuthous valerianate, *i. e.*, of its solutions in nitric or hydrochloric acid, for *chlorides* and *sulphates*, for *calcium phosphate* and salts of *calcium*, *magnesium*, and *zinc*, and for *metallic* impurities, is performed in the same way as with the corresponding solutions of bismuthous carbonate, described on pages 274–276.

BROMUM.

BROMINIUM.

Bromine.

Ger. Brom; Fr. Brome; Sp. Bromo.

Br; 79.8.

A heavy, dark brownish-red, very volatile liquid, of an intense and suffocating odor, somewhat resembling that of chlorine; its spec. grav. is 2.99 at 15° C. (59° F.).

Bromine solidifies at −24.5° C. (—12.1° F.), forming a dark-brown, brittle, crystalline mass, with a semi-metallic lustre, somewhat resembling that of iodine, which at —12° C. (+10.4° F.) still retains its solid condition; when containing water it solidifies at —7° C. (+19.4° F.). It is liquid and volatile at ordinary temperatures, and boils at 63° C. (145.4° F.), forming yellowish-red vapors of the spec. grav. 5.54 (compared with air), which strongly irritate the organs of respiration, and impart a green color to the flame.

Bromine is soluble in 33 parts of water at 15° C. (59° F.), yielding an orange-yellow solution, which has the odor of bromine, bleaches vegetable colors and solution of indigo, and imparts an orange-yellow color to mucilage of starch; when the solution is exposed to a temperature near the freezing-point, it forms red octahedral crystals of bromine hydrate, $Br_2 + 10H_2O$, which at 15° C. (59° F.) are again resolved into bromine and water. The aqueous solution of bromine, on exposure to sunlight, gradually undergoes decomposition with the formation of hydrobromic acid, and the evolution of oxygen; it is deprived of its bromine and of its color when agitated with ether, chloroform, or carbon bisulphide; these solutions, however, are themselves decolorized when agitated with a solution of potassium hydrate; but either of them, with the exception of carbon bisulphide, will form a new solution of the bromine, and consequently regain the color, upon the addition of an excess of any mineral acid.

Bromine is freely soluble in alcohol and ether with a reddish-brown color, and in chloroform, benzol, and carbon bisulphide, forming solutions of a yellowish-red color; it is also soluble in solutions of the alkaline hydrates, with the formation of bromide and bromate of the alkali, and, with an excess of alkali, yielding solutions which are colorless, or possess but a slight yellowish tinge:

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O.$$

In its chemical relations, bromine closely resembles chlorine, having a powerful affinity for hydrogen, though not quite so strong, and hence it acts with energy on many organic compounds, abstracting hydrogen with equivalent substitution.

Examination:

Water may be detected by the following method, which also admits of its quantitative estimation: To a weighed amount of the bromine, contained in a glass-stoppered bottle, about ten times its weight of water is added, and subsequently an accurately weighed amount of metallic mercury, equal to about twice the weight of bromine employed. The combined liquids are then shaken until complete decoloration ensues; thereupon the insoluble mixture of mercurous bromide and mercury is separated by filtration, dried at 100° C. (212° F.), and weighed. The difference between the combined weight of the amount of bromine and mercury employed and the weight of the obtained dried mixture, will indicate the presence, and represent the amount of contained water in the bromine.

Chlorine may be detected by adding to 3 grams of the bromine about ten times its weight of water, and subsequently water of ammonia, in small portions, until a perfectly colorless liquid is obtained. The liquid is then digested with an excess of barium carbonate, the solution filtered, evaporated to dryness, and the residue gently ignited. The ignited residue, which will contain all the bromine, together with any chlorine which may be present, in the form of barium bromide, or chloride, is then treated with absolute alcohol, when it should become entirely dissolved, or leave but a slight residue. The amount of insoluble residue, consisting of barium chloride, will bear a direct proportion to the amount of chlorine contained in the bromine, which, in the commercial product, is usually present to the extent of from 1 to 2 per cent.

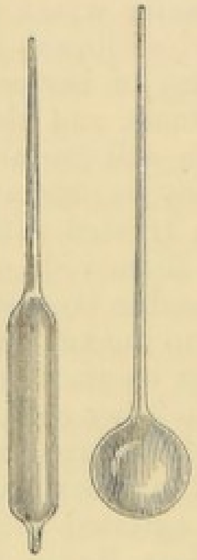
Iodine may be tested for by dissolving a portion of the bromine in forty times its weight of water, and the solution thus obtained, with the exception of a small reserved portion, is agitated with reduced iron or iron filings until a nearly colorless liquid is obtained, and the bromine is completely converted into ferrous bromide. The liquid is then filtered into a test-tube, a little mucilage of starch added, and subsequently a few drops of the reserved aqueous bromine solution carefully poured upon the surface; if iodine be present, a blue zone will appear at the line of contact of the two liquids. The presence of iodine may also be detected by the addition of an aqueous solution of the bromine to a solution of ammonium sulphide until no further separation of sulphur is produced, the liquid then evaporated upon the water-bath to dryness, the residue dissolved in water, filtered, a few drops of a dilute solution of ferric chloride added, and the mixture shaken with chloroform; if iodine be present, the chloroform will assume a violet color.

Bromoform will be recognized by the development of its characteristic odor, when a little of the bromine is added to a solution of potassium iodide, and the liberated iodine subsequently dissolved by means of a solution of sodium hyposulphite. When present to any considerable extent, it may be separated by fractional distillation; its boiling-point being at 150 to 152° C. (302 to 305.6° F.).

Cyanogen or its compounds may be detected by adding about 10 grams of the bromine to be tested, very gradually, and with constant stirring, to an equal weight of iron filings, previously mixed with 4 or 5 times their weight of water. The liquid, while still warm from the reaction, is filtered into a flask, which is afterward partially closed, and allowed to repose for one or two days; if cyanogen or its compounds are present, a precipitate of Prussian blue will be gradually deposited.

Estimation :

Fig. 103.



The quantitative estimation of free bromine, with a view to the determination of the amount of impurities present, may be most conveniently accomplished by the following volumetric method: About 0.3 gram of the bromine is accurately weighed in a small glass bulb (Fig. 103), which is afterwards opened under the surface of a solution of about 1 gram of potassium iodide in 10 cubic centimeters of water, and the liberated iodine estimated by means of a standard solution of sodium hyposulphite, page 94. From the amount of liberated iodine, the corresponding amount of bromine may be calculated by simple equivalent proportion; one atom of iodine (126.6) corresponding to one atom of bromine (79.8). Should the bromine, however, contain chlorine as an impurity, the latter will likewise liberate iodine from the potassium iodide, and thus preclude the direct calculation of the bromine. In the latter case, the calculation may be based upon the following consideration: If $A =$ the amount of liberated iodine, as determined by titration with a solution of sodium hyposulphite, and $B =$ the weight of employed bromine; then the amount of chlorine, X, which is contained in the bromine under examination, may be ascertained in accordance with the following formula:

$$X = \frac{A - 1.5875B}{2.0312}$$

and the amount of pure bromine is consequently $B - X$.

BRUCINA.

BRUCINUM.

Brucine. Brucia.

Ger. Brucin; Fr. Brucine; Sp. Brucina.

$C_{23}H_{26}N_2O_4 + 4H_2O$; 466.

Transparent, colorless, four-sided prisms, aggregations of stellate needles, or a crystalline powder, with a pearly lustre, and possessing a strongly bitter taste. Brucine contains 4 molecules (15.45 per cent.) of water of crystallization, and effloresces upon exposure to the air; it melts at 130° C. (266° F.), gradually losing its water of crystallization, and, upon further heating, may be partially sublimed without decomposition; when strongly heated upon platinum-foil, it is decomposed with the evolution of inflammable vapors, which burn with a bright sooty flame, and is finally completely dissipated.

Brucine is soluble in 320 parts of cold, and in 150 parts of boiling water, very freely soluble in alcohol, amylic alcohol, chloroform, and benzol, but is sparingly soluble in ether and petroleum benzin. It neutralizes the acids, forming crystallizable salts, which possess a bitter taste, and are readily soluble in water and alcohol, but insoluble in ether.

Brucine dissolves in moderately concentrated nitric acid with an intense blood-red color, which, however, soon changes to yellowish-red, and finally, upon warming, to yellow. If the acid solution be subsequently slightly warmed with a little water, again allowed to cool, and a few drops of solution of stannous chloride or ammonium sulphide added, the mixture assumes a beautiful violet color. The reaction is best obtained by the employment of but little nitric acid, and is not influenced by the presence of strychnine. If a solution of mercurous nitrate be slightly warmed in a shallow porcelain capsule on the water-bath, and an aqueous solutien of brucine added, a fine red coloration is gradually produced at the edges of the liquid, which, by the slow evaporation of the liquid to dryness, remains permanent. Brucine dissolves in concentrated sulphuric acid with a slight rose-red coloration, and the solution assumes, upon the addition of potassium bichromate, a transient reddish-brown color. If the brucine contains strychnine, traces of which are frequently present in the commercial alkaloid, its solution in sulphuric acid will afford, upon the addition of potassium bichromate, a rapidly fading blue-violet coloration. With concentrated sulphuric acid, which contains a trace of nitric acid, brucine affords an intensely red solution.

Chlorine-water colors an aqueous solution of a brucine salt first violet and then red, and, upon the subsequent addition of ammonia-water, a yellowish-brown color is produced. Aqueous solutions of brucine salts are precipitated by the alkaline hydrates and carbonates, as also by most of the commonly employed alkaloidal reagents, and yield crystalline precipitates with potassium chromate, sulphocyanide, and ferricyanide. By the action of oxidizing agents, brucine affords several interesting products of decomposition. Thus upon heating with dilute sulphuric acid and manganese dioxide, methylic alcohol and formic acid are produced, with the development of carbonic acid gas. By treatment with concentrated nitric acid, it assumes, as previously stated, an intense red color, and is resolved into water, nitric oxide, oxalic acid, methyl nitrite, and a crystallizable base, *cacoteline*.

$$\underbrace{C_{23}H_{26}N_2O_4}_{\text{Brucine.}}+5HNO_3=2H_2O+2NO+C_2H_2O_4+CH_3NO_2+\underbrace{C_{20}H_{22}N_4O_9}_{\text{Cacoteline.}}.$$

For the separation of brucine from other alkaloids, or when associated with complex organic mixtures, see page 108.

CADMII IODIDUM.

CADMIUM IODATUM.

Iodide of Cadmium. Cadmium Iodide.

Ger. Jodcadmium ; Fr. Iodure de cadmium ; Sp. Ioduro de cadmío.

CdI_2; 365.

Colorless, flat, micaceous crystals, or hexagonal tables, of a pearly lustre, permanent in the air, and having a specific gravity of 4.576.

When heated to about 316° C. (600.8° F.), the salt melts, forming an amber-colored fluid, and, at a dull red heat, is decomposed with the evolution of violet colored vapors of iodine.

Cadmium iodide is freely soluble in water: 100 parts of water dissolving, at 20° C. (68° F.), 92.6 parts, at 60° C. (140° F.), 107.5 parts, and at 100° C. (212° F.), 133.3 parts of the salt; it is also quite freely soluble in alcohol, and in a mixture of alcohol and ether. The aqueous solution has a slightly acid reaction upon litmus, and yields with hydrogen sulphide or ammonium sulphide a yellow precipitate, which is almost insoluble in an excess of the latter reagent (distinction from arsenic); with argentic nitrate it yields a pale yellow precipitate, insoluble in ammonia-water; with mercuric chloride a bright red precipitate; and with the alkaline hydrates and carbonates white precipitates, of which that with ammonia-water is soluble, the remainder insoluble in an excess of the precipitant. If to the aqueous solution of the salt a little chlorine-water be added, drop by drop, and subsequently a little mucilage of starch, the mixture will assume a deep blue color.

One hundred parts of cadmium iodide, when completely precipitated by argentic nitrate, yield a precipitate of argentic iodide, which, when thoroughly washed, and dried at 100° C. (212° F.), should weigh 128.55 parts.

Examination:

Metallic Impurities.—The aqueous solution of the salt, acidulated with hydrochloric acid, is completely precipitated by hydrogen sulphide, the resulting precipitate collected and washed upon a filter, and subsequently digested with ammonia-water, and again filtered; the latter filtrate, when supersaturated with hydrochloric acid, should afford no turbidity; an ensuing yellow coloration or precipitate will indicate the presence of *arsenic*. The filtrate from the original hydrogen sulphide precipitate is then supersaturated with ammonia-water; an ensuing white precipitate would indicate *zinc*, a black one, *iron*.

Chlorides may be detected by completely precipitating a small portion of the aqueous solution of the salt with argentic nitrate, collecting and washing the resulting precipitate upon a filter, and subsequently digesting it with ammonia-water, and filtering; the ammoniacal filtrate is then supersaturated with nitric acid, when an ensuing white curdy precipitate will indicate the presence of chloride.

CADMII SULPHAS.

CADMIUM SULFURICUM.

Sulphate of Cadmium. Cadmium Sulphate.

Ger. Schwefelsaures Cadmium ; Fr. Sulfate de cadmium ; Sp. Sulfato de cadmio.

$3CdSO_4.8H_2O$; 767.4.

Colorless, transparent, rhombic tables, having a specific gravity of about 3., and containing, for 3 molecules of the salt, 8 molecules (18.8 per cent.) of water of crystallization. They effloresce slightly by exposure to the air. lose 5 molecules of water upon drying at 100° C. (212° F.), and the remaining 3 molecules at a higher temperature.

Cadium sulphate is soluble in twice its weight of water at 17° C. (62.6° F.), but insoluble in alcohol. The solution has an acid reaction upon litmus, an astringent, acidulous, and slightly austere taste, and, when diluted with six times its volume of water, may be mixed with considerable amounts of alcohol without the separation of the salt, which finally takes place in the form of thick liquid drops.

The aqueous solution yields upon the addition of potassium or sodium hydrate, or ammonia-water, a white precipitate of cadmium hydroxide, which is insoluble in an excess of the first-named reagents, but soluble in an excess of ammonia-water; with alkaline carbonates it yields a white precipitate of cadmium carbonate, insoluble in an excess of the precipitant; and with hydrogen sulphide, a yellow precipitate of cadmium sulphide, which is soluble in moderately concentrated, warm sulphuric, hydrochloric and nitric acids, and to a slight extent in a solution of ammonium sulphide, but is insoluble in diluted acids and ammonia-water (distinction, in the latter instance, from arsenious sulphide).

Examination:

Arsenic may be detected by completely precipitating an acidulated solution of the salt with hydrogen sulphide, digesting the resulting precipitate with ammonia-water, filtering, and subsequently supersaturating the clear liquid with hydrochloric acid; the separation of a yellow precipitate will reveal the presence of arsenic. The acidulated solution of the salt, when completely precipitated by hydrogen sulphide, should yield a filtrate, which, upon evaporation to dryness, should leave no residue; if a residue remains, admixtures of other salts are indicated. In the latter case, the residue should be dissolved in dilute hydrochloric acid, and examined for metallic, earthy, and alkaline oxides by the systematic method of analysis as described on pages 56 to 61.

Estimation:

The quantitative estimation of cadmium may be readily accomplished by precipitating the carbonate from a boiling solution of a weighed quantity of the salt, by means of sodium carbonate; the precipitate is thoroughly washed, dried, and, by ignition at a red heat, converted into cadmium oxide, CdO, from the weight of which the corresponding amount of anhydrous or of crystallized cadmium sulphate may be calculated: 100 parts of cadmium oxide, CdO, corresponding to 162.69 parts of anhydrous sulphate, $CdSO_4$, or 200.31 parts of crystallized sulphate, $3CdSO_4.8H_2O$.

It may also be estimated by precipitation by hydrogen sulphide from an acidulated solution of its salt as cadmium sulphide, CdS, which, after washing, is dried at 100° C. (212° F.), and weighed. One hundred parts of cadmium sulphide correspond to 144.56 parts of anhydrous sulphate, $CdSO_4$, or 178 parts of crystallized sulphate, $3CdSO_4.8H_2O$.

CAFFEINA.

COFFEINUM.

Caffeine. Caffeia. Theine. Guaranine. Methyl-theobromine.

Ger. Caffeïn; Fr. Caféine; Sp. Cafeina.

$$C_8H_{10}N_4O_2 + H_2O = C_7H_7(CH_3)N_4O_2 + H_2O;\ 212.$$

Colorless, slender, and flexible, silky needles, containing one molecule (8.49 per cent.) of water of crystallization, which is lost by drying at 100° C. (212° F.). The crystals are odorless, neutral in their action upon litmus, and possess a slightly bitter taste. They melt at 234 to 235° C. (453.2 to 455° F.), although beginning to sublime at 180° C. (356° F.), and boil at 384° C. (723.2° F.); when slowly heated upon platinum foil, they are completely volatilized, without carbonizing.

Caffeine, when previously deprived of its water of crystallization, is soluble in 75 parts of water at 15° C. (59° F.), in 2 parts at 70° C. (158° F.), in 8 parts of chloroform, in 50 parts of ordinary alcohol, and in 520 parts of absolute alcohol, and is still less soluble in ether and carbon bisulphide. The aqueous solution is neutral in its action upon litmus, and possesses a slightly bitter taste; it is abundantly precipitated by tannic acid, the precipitate being readily re-dissolved upon warming, or upon the addition of an excess of the reagent, but is not precipitated by picric acid, nor by a dilute solution of potassio-mercuric iodide (distinction from most other alkaloids); it also remains unaltered, and does not assume a purple color, when it is exposed to the air, after the addition of a little ammonia-water (distinction from phlorizin).

Caffeine enters into combination with the stronger acids, without neutralizing them, with the formation of salts having an acid reaction, and which are readily decomposed; it also forms crystallizable compounds with some metallic salts. From its solution in the weaker acids, it crystallizes, upon evaporation, unchanged. With concentrated sulphuric and nitric acids, caffeine suffers no change of color in the cold (additional distinction from many alkaloids, and from salicin, which, with the former acid, produces a bright red coloration. When caffeine is added to chlorine-water, in a small porcelain capsule, and evaporated to dryness, a yellowish-red residue is obtained, which, upon the addition of a little ammonia-water, assumes a beautiful purplish-red color. The same reaction may be obtained by the employment of a little nitric acid, instead of chlorine-water, care being taken to avoid an excess of the acid; with the application of bromine-water, instead of chlorine, the coloration, upon the addition of ammonia, is more of a violet hue.

When boiled with an alcoholic solution of potassium hydrate, or with an aqueous solution of barium hydrate, caffeine is resolved, by the absorption of water and the elimination of carbonic acid gas, into an uncrystallizable base, *caffeidine*, $C_7H_{12}N_4O$, which is very readily soluble in water and alcohol, and whose sulphate crystallizes in long, colorless needles:

$$\underbrace{C_8H_{10}N_4O_2}_{\text{Caffeine.}} + H_2O = \underbrace{C_7H_{12}N_4O}_{\text{Caffeidine.}} + CO_2.$$

The decomposition of caffeine by barium hydrate is, however, not confined to the production of caffeidine, but methylamine, formic acid, and ammonia are simultaneously formed, and, by the long-continued action of the reagent, the caffeidine is itself decomposed into the above products and *sarkosine*, $C_3H_7NO_2$, with the evolution of carbonic acid gas.

CALCII BROMIDUM.

CALCIUM BROMATUM.

Bromide of Calcium. Calcium Bromide.

Ger. Bromcalcium; Fr. Brômure de calcium; Sp. Bromuro de cal.

$CaBr_2$; 199.6.

A white, granular salt, rapidly absorbing moisture on exposure to the air, and deliquescing to a syrupy liquid. Its specific gravity is 3.32. When heated to 680° C. (1256° F.) the salt undergoes igneous fusion, and, at a higher temperature, it is decomposed with the liberation of bromine.

Calcium bromide is soluble in 0.7 part of water and in 1 part of alcohol at 15° C. (59° F.), and very freely soluble in boiling water and boiling alcohol. Its aqueous solution is neutral in its action upon litmus, and possesses a pungent, saline, and bitter taste; it yields a white precipitate with ammonium oxalate, soluble in hydrochloric, but insoluble in acetic acid; and a white precipitate with argentic nitrate, which is sparingly soluble in ammonia-water. If a little chloroform or carbon bisulphide be added to a solution of the salt, and subsequently a little chlorine-water, drop by drop, and the whole agitated, the chloroform or carbon bisulphide will acquire a yellow or yellowish-brown color.

One gram of the dry salt, when completely precipitated by argentic nitrate, yields a precipitate of argentic bromide which, when washed, and dried at 100° C. (212° F.), should weigh 1.878 grams.

Examination:

Bromate may be detected by a yellow coloration when diluted sulphuric acid is dropped upon the salt; or by adding to an aqueous solution of the salt a few drops of diluted sulphuric acid, and subsequently a little chloroform or carbon bisulphide, and agitating the mixture; if bromate be present, the chloroform or carbon bisulphide will acquire a yellow or yellowish-brown color.

Iodide may be recognized in a solution of one part of the salt in about ten parts of water by the addition of a little mucilage of starch, and subsequently pouring a few drops of chlorine-water upon the surface of the liquid; a blue coloration at the line of contact of the two liquids will reveal the presence of iodide.

Chloride may be detected by completely precipitating a small portion of an aqueous solution of the salt with argentic nitrate, collecting the resulting precipitate upon a filter, washing it thoroughly with water, and subsequently digesting it with a concentrated solution of ammonium carbonate; the mixture is then filtered, and the filtrate supersaturated with nitric acid, when not more than a faint turbidity, insufficient to form a precipitate, should be produced; a white, curdy precipitate would reveal the presence of more than traces of chloride.

Sulphate may be detected in a solution of 1 part of the salt in about 20 parts of water by an ensuing white precipitate on the addition of a few drops of solution of barium chloride.

Magnesium salts may be recognized by first adding to an aqueous solution of the salt a little solution of ammonium chloride, and afterward solution of ammonium carbonate and ammonia-water until a precipitate ceases to be produced, and gently warming; the mixture is then filtered, and the filtrate tested with sodium phosphate, when an ensuing white, crystalline precipitate will reveal the presence of magnesium salt.

CALCII CARBONAS PRÆCIPITATUS.

CALCIUM CARBONICUM PRECIPITATUM. CALCARIA CARBONICA PRECIPITATA.

Precipitated Carbonate of Calcium. Precipitated Calcium Carbonate.

Ger. Kohlensaurer Kalk ; Fr. Carbonate de chaux ; Sp. Carbonato de cal.

$CaCO_3$; 100.

A white, light powder, without odor or taste, and permanent in the air. When obtained by precipitation from hot solutions, it is seen, when observed under the microscope, to consist of minute rhombic prisms, or, when precipitated from cold solutions, of minute rhombohedral crystals, although the crystalline form is frequently influenced by other substances which may be present in the solution. It displays a feebly alkaline reaction in contact with carefully prepared litmus; when exposed to a red heat, particularly when a current of air is passed over the surface, or, when heated upon charcoal before the blow-pipe, it loses carbonic acid gas, and is converted into calcium oxide, which possesses a strongly alkaline reaction.

Calcium carbonate is almost insoluble in water, 1000 parts of water, either cold or hot, dissolving but about 0.018 part, and is still less soluble in the presence of free ammonia or ammonium carbonate; but is more freely soluble in the presence of ammonium chloride or nitrate, with which, by mutual decomposition, a more readily soluble calcium salt is formed. It is also more freely soluble in water saturated with carbonic acid gas than in pure water; this solution reddens litmus, but changes the yellow color of turmeric-paper to brown; by boiling or exposure to the air, the carbonic acid is evolved, and the calcium carbonate partially deposited; the liquid still retaining, in 1000 parts, 0.034 part of calcium carbonate in solution, and this solution does not render lime-water turbid. It is readily soluble, with effervescence, in dilute hydrochloric, nitric, and acetic acids. The solution in acetic acid is precipitated by oxalic acid, but not by a solution of calcium sulphate (distinction from barium and strontium carbonates), nor by ammonia-water (evidence of the absence of aluminium and iron salts, and of phosphates), nor by potassium hydrate (distinction from magnesium carbonate). The solution should also afford no coloration or precipitate with hydrogen sulphide, either when containing an excess of acid, or upon subsequent supersaturation with ammonia-water (free from carbonate).

Examination:

If the calcium carbonate be agitated with a little water, and the mixture filtered, the filtrate should be perfectly neutral in its action upon litmus, and, with the exception of traces of dissolved carbonate, should leave no residue upon evaporation. Upon ignition, at a red heat, it should afford a perfectly white residue, possessing a strongly alkaline reaction, without the development of any empyreumatic odor.

An insufficient washing in the manufacture, or a fraudulent or accidental admixture of calcium sulphate, may be detected by agitating some of the carbonate with water, and by testing the filtrate, acidulated with one or two drops of nitric acid, in separate portions, with argentic nitrate for chloride, and with barium nitrate for sulphate.

Magnesium carbonate may be recognized, in addition to the above-mentioned test, by adding to a neutral solution of the salt in acetic acid, first solution of ammonium chloride and then ammonium carbonate and ammonia-water until a precipitate ceases to be produced, and gently warming; the mixture is then filtered, and the filtrate tested with sodium phosphate, when an ensuing white, crystalline precipitate will prove the presence of magnesium salt.

The crude varieties of calcium carbonate — chalk, prepared oyster-shells, and others derived from animal organisms—contain more or less of other bases (magnesium, iron, potassium, sodium, etc.) and acids (phosphoric, silicic, and sulphuric), and always, also, traces of organic substances; they do not afford a complete solution with dilute acetic or hydrochloric acid, and, although in every instance the acid solution should remain unaffected by hydrogen sulphide, yet upon subsequent supersaturation with ammonia-water a white or greenish turbidity is usually produced, dependent upon the presence of traces of phosphates. The estimation of the amount of carbonic acid contained in calcium carbonate may be accomplished by the method described for alkaline carbonates, on page 86.

CALCII CHLORIDUM.

CALCIUM CHLORATUM.

Chloride of Calcium. Calcium Chloride.

Ger. Chlorcalcium ; Fr. Chlorure de calcium ; Sp. Chloruro de calcio.

$CaCl_2$; 110.8.

A white, granular salt, or, as prepared by fusion, colorless, translucent, and friable masses; it may also be obtained by crystallization from its saturated solution in the form of large hexagonal prisms, having the composition $CaCl_2 + 6H_2O$. The crystals melt at 29° C. (84.2° F.) in their water of crystallization, and deliquesce rapidly by exposure to the air, forming a thick syrupy liquid. When heated to 200° C. (392° F.), they lose 4 molecules of water, leaving a white, porous, hygroscopic mass, and, upon more strongly heating, the anhydrous salt is obtained; the latter melts at a red heat, and, upon cooling, solidifies to a crystalline mass of the specific gravity 2.205, which, in contact with a small amount of water, produces a considerable elevation of temperature.

Calcium chloride is soluble in 1.5 parts of water and in 8 parts of alcohol at 15° C. (59° F.), very freely soluble in boiling water, and soluble in 1.5 parts of boiling alcohol; with alcohol it unites to form a crystallizable compound, having the composition $CaCl_2 + 4C_2H_6O$, which is decomposed by water with the separation of the alcohol; but is insoluble in ether. The aqueous solution of the salt possesses a sharp saline taste, and is neutral in its action upon litmus, unless the salt, by exposure to the heat of fusion, has undergone partial decomposition, with the loss of hydrochloric acid, and the formation of a little calcium oxide, when it will have an alkaline reaction; it yields white precipitates with the alkaline carbonates and phosphates, which are readily soluble in acetic acid, and, if the solution be not too dilute, a white crystalline precipitate with sulphuric acid, which is soluble in a large amount of water. The solution of the salt, even when very dilute, is likewise precipitated by oxalic acid and by argentic nitrate; both precipitates being insoluble in acetic acid, and that with the latter reagent also insoluble in nitric acid, but readily soluble in ammonia-water.

Anhydrous calcium chloride absorbs dry ammonia gas with great avidity, forming therewith a voluminous powder, having the composition $CaCl_2 + 8NH_3$; this is decomposed by exposure to the air, in contact with water, or on heating, with the loss of ammonia, and takes fire when thrown into chlorine gas.

If a concentrated solution of calcium chloride is boiled with slaked lime, and the solution filtered while hot, a basic salt separates out on cooling, in long, white, needle-shaped crystals, having the composition $ClCa{-}O{-}Ca(OH) + 7H_2O$.

Solutions of calcium chloride of various degrees of concentration are employed as baths for constant temperatures above 100° C. (212° F.), and the anhydrous salt, in consequence of its strong affinity for water, is largely employed as a desiccating agent, for drying gases, and for the removal of water from organic liquids. The crystallized salt, when dissolved in water, produces a considerable diminution of temperature, and, when mixed with snow, in the proportion of 1.3 parts to 1 part of the latter, the temperature sinks to —48° C. (—54.4° F.).

Examination:

Calcium sulphate may be detected by the incomplete solubility of the salt in alcohol, and may also be recognized in the aqueous solution of the salt by an ensuing white precipitate on the addition of solution of barium chloride.

Aluminium salts may be recognized in the aqueous solution, after the addition of a little ammonium chloride, by an ensuing white, flocculent precipitate on the addition of ammonia-water or ammonium sulphide; if the precipitate be brownish or black, it will indicate *iron*, which may also be recognized in the aqueous solution of the salt by a blue coloration or precipitate on the addition of a few drops of solution of potassium ferrocyanide.

Magnesium salts may be recognized by adding to the aqueous solution, first a little solution of ammonium chloride, and subsequently ammonium carbonate and ammonia-water until a precipitate ceases to be produced, and gently warming; the mixture is then filtered, and the filtrate tested with sodium phosphate, when an ensuing white, crystalline precipitate will reveal the presence of magnesium.

CALCII HYPOPHOSPHIS.

CALCIUM HYPOPHOSPHOROSUM. CALCIS HYPOPHOSPHIS.

Hypophosphite of Calcium. Calcium Hypophosphite.

Ger. Unterphosphorigsaurer Kalk ; Fr. Hypophosphite de chaux ;
Sp. Hipofósfito de cal.

$Ca(H_2PO_2)_2$; 170.

Small, colorless, transparent, four-sided prisms, or thin, flexible scales, or a white, crystalline powder, of a pearly lustre, permanent in the air, and containing no water of crystallization. When strongly heated in a dry test-tube, the salt decrepitates, emitting inflammable vapors of hydrogen phosphide, and a little water, and leaving a residue, amounting to about 80 per cent. of its weight; this residue, after cooling, appears yellowish-red, and consists of a mixture of calcium pyrophosphate and metaphosphate, together with a little red amorphous phosphorus, resulting from the decomposition of the hydrogen phosphide.

Calcium hypophosphite dissolves in six parts of cold water, and in about the same amount of boiling water, but is insoluble in alcohol (distinction from sodium hypophosphite); the aqueous solution has a slightly bitter taste, and, when largely diluted with water, suffers no change upon the addition of diluted sulphuric acid, nor with solutions of barium and calcium chlorides, nor of plumbic acetate (distinction from soluble phosphates and phosphites); it forms, however, white precipitates with the soluble carbonates, with oxalic acid and oxalates, and with argentic nitrate, which latter precipitate, in consequence of its rapid reduction to argentic phosphide and metallic silver, soon becomes black. When an aqueous solution of the salt, acidulated with hydrochloric acid, is added to an excess of solution of mercuric chloride, a white precipitate of mercurous chloride (calomel) is produced, and, on the further addition of the solution of hypophosphite, metallic mercury separates.

Examination:

The salt, when triturated with water, should not develop the alliaceous odor characteristic of hydrogen phosphide.

Calcium sulphate will be indicated by an insoluble residue when a portion of the salt is digested with about ten times its weight of cold water, and may also be recognized in the aqueous solution, acidulated with nitric acid, by an ensuing white precipitate on the addition of a few drops of solution of barium chloride.

Magnesium salts may be detected by first adding to an aqueous solution a little solution of ammonium chloride, and afterward solution of ammonium carbonate and ammonia-water until a precipitate ceases to be produced, and gently warming; the mixture is then filtered, and the filtrate tested with sodium phosphate, when an ensuing white, crystalline precipitate will reveal the presence of magnesium.

CALCII IODIDUM.

CALCIUM IODATUM.

Iodide of Calcium. Calcium Iodide.

Ger. Jodcalcium; Fr. Iodure de calcium; Sp. Ioduro de cal.

CaI_2; 293.2.

A white, granular salt, or lamellar masses of a pearly lustre, rapidly absorbing moisture on exposure to the air, and deliquescing to a syrupy liquid. When strongly heated, with access of air, it becomes decomposed, with the liberation of iodine, and leaving a residue of calcium oxide.

Calcium iodide is very freely soluble in both water and alcohol. Its aqueous solution is neutral in its action upon litmus, and possesses a pungent, saline, and bitter taste; it yields a white precipitate with ammonium oxalate, soluble in hydrochloric, but insoluble in acetic acid, and a yellowish precipitate with argentic nitrate, which is nearly insoluble in ammonia-water. If a little chloroform or carbon bisulphide be added to a solution of the salt, and subsequently a little chlorine-water, drop by drop, and the whole agitated, the chloroform or carbon bisulphide will acquire a red or violet color. One gram of the dry salt, when completely precipitated by argentic nitrate, yields a precipitate of argentic iodide which, when washed, and dried at 100° C. (212° F.), should weigh 1.59 grams.

Examination:

Iodate may be detected in the aqueous solution of the salt by a yellowish or brown coloration on the addition of a little acetic or tartaric acid; the solution will then also impart a blue color to mucilage of starch, and a red or violet tint to a few drops of chloroform or carbon bisulphide, when agitated therewith, if iodate be present.

Chlorides and *Bromides.*—To a small portion of the salt, dissolved in water, solution of argentic nitrate is added until a precipitate ceases to be produced. The resulting precipitate is collected upon a filter, washed with water, and subsequently digested with a strong solution of ammonium carbonate, and filtered; the filtrate is then slightly supersaturated with nitric acid, when an ensuing turbidity, or the formation of a white, curdy precipitate, will reveal the presence of chloride. The residue upon the filter is digested with a considerable excess of ammonia-water, filtered, and the filtrate slightly supersaturated with nitric acid, when not more than a faint turbidity should ensue; a white, curdy precipitate will reveal the presence of bromide.

Sulphate may be detected in a solution of 1 part of the salt in about 20 parts of water by an ensuing white precipitate on the addition of a few drops of solution of barium chloride.

Magnesium salts may be recognized by first adding to an aqueous solution of the salt a little solution of ammonium chloride, and afterward solution of ammonium carbonate and ammonia-water until a precipitate ceases to be produced, and gently warming; the mixture is then filtered, and the filtrate tested with sodium phosphate, when an ensuing white, crystalline precipitate will reveal the presence of magnesium.

CALCII PHOSPHAS PRÆCIPITATUS.

CALCIS PHOSPHAS. CALCIUM PHOSPHORICUM. CALCARIA PHOSPHORICA.

Precipitated Phosphate of Calcium. Tribasic Calcium Phosphate. Normal Calcium Orthophosphate.

Ger. Neutraler Phosphorsaurer Kalk; Fr. Phosphate de chaux précipité; Sp. Fosfato de cal.

$Ca_3(PO_4)_2$; 310.

A light, white, inodorous, and tasteless powder, which, when dried at 100° C. (212° F.), contains no water. and is perfectly amorphous. It is fusible, without decomposition, at an intense heat, and the powder, before or after ignition, assumes when moistened with a solution of argentic nitrate a straw-yellow color (distinction from acid calcium phosphate).

Neutral calcium phosphate is nearly insoluble in water, but upon long boiling therewith it is decomposed with the formation of an insoluble basic salt, $Ca_3(PO_4)_2 + Ca_2(PO_4)OH$, and a soluble acid salt which dissolves; it is more readily soluble in water saturated with carbonic acid gas, as also in solutions of sodium nitrate, sodium chloride, ammoniacal, and other salts, and is freely soluble in nitric, hydrochloric, and acetic acids.

An acid calcium phosphate (Monohydrogen Calcium Orthophosphate, $CaHPO_4 + 2H_2O$) is officinal in the German, Austrian, and Swiss Pharmacopœias. This salt is obtained as a crystalline powder, consisting of microscopically small, monoclinic tables or prisms, of an acid reaction, and containing two molecules (20.93 per cent.) of water of crystallization; when heated to from 150 to 200° C. (302 to 392° F.), it loses its water of crystallization, and, at a higher temperature, water of constitution is also eliminated, amounting in all to 26 per cent. of its weight. When moistened with a solution of argentic nitrate, it assumes a yellow color, which is not the case, however, after having been strongly heated upon platinum-foil, in consequence of its conversion into calcium pyrophosphate: $2CaHPO_4 = H_2O + Ca_2P_2O_7$. In its relation to solvents, the characters of acid calcium phosphate are similar to those of the normal salt, as above described, but it is not readily soluble in acetic acid.

Both varieties of calcium phosphate are readily and completely soluble in warm, diluted nitric acid, without effervescence. The solution, when heated with a few drops of a solution of ammonium molybdate, affords a yellow crystalline precipitate of ammonium phospho-molybdate (presence of phosphoric acid), and, after the addition of an excess of sodium acetate, yields a copious white precipitate on the addition of a solution of oxalic acid or ammonium oxalate (presence of calcium).

Examination:

Carbonates are indicated by effervescence when a little of the calcium phosphate is first thoroughly mixed with a little water, and concentrated nitric acid afterwards added.

Barium and *strontium salts* may be detected in the dilute nitric acid solution by a white precipitate on the addition of a solution of calcium sulphate.

Chlorides are detected in the dilute nitric acid solution by a white curdy precipitate on the addition of solution of argentic nitrate, which is soluble in ammonia-water, but insoluble in nitric acid.

Sulphates may be detected by agitating a little of the calcium phosphate with water for a few moments, filtering, and, after acidulating with a few drops of acetic acid, testing with solution of barium hydrate or nitrate; a white precipitate will reveal the presence of sulphates.

Magnesium Phosphate.—A portion of the salt is dissolved in hydrochloric acid, an excess of sodium acetate and a little solution of ferric chloride are added, and the mixture boiled and filtered; to the colorless filtrate a little ammonium chloride is added, and subsequently ammonium oxalate until a precipitate ceases to be produced; after standing for a few hours, the mixture is filtered, and to the filtrate solution of sodium phosphate and ammonia-water in slight excess are added, when an ensuing white crystalline precipitate will reveal the presence of magnesium.

Iron and *metallic salts* are detected by first saturating the solution of the calcium phosphate in dilute hydrochloric acid with hydrogen sulphide, and subsequently supersaturating the acid liquid with ammonia-water. The solution must remain perfectly unchanged with the first-named reagent, and the ensuing precipitate upon the addition of the latter should be perfectly white; a black coloration would indicate *iron*, which would likewise be detected in the dilute acid solution of the salt by a blue coloration or precipitate on the addition of a few drops of solution of potassium ferrocyanide.

CALX CHLORATA.

CALX CHLORINATA. CALCARIA CHLORATA. CALCIUM HYPOCHLOROSUM. CALCARIA HYPOCHLOROSA.

Chlorinated Lime. Bleaching-Powder. Calcium Hypochlorite.

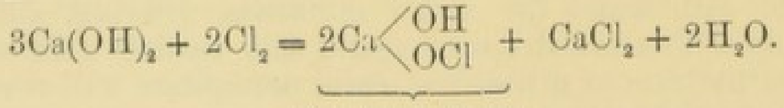
Ger. Chlorkalk; Fr Chlorure de chaux; Sp. Hipochlorito de cal.

A homogenous, dull-white, granular powder, possessing an alkaline reaction, the odor of hypochlorous acid rather than of chlorine, and becoming moist and gradually decomposing on exposure to the air.

In its composition, chlorinated lime is commonly regarded as a mixture of calcium hypochlorite and chloride, together with undecomposed hydrate, and its formation represented by the equation:

$$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O.$$

With reference, however, to the amount of available chlorine which can be obtained from a perfectly saturated product, it may be considered, with a much greater degree of probability, as consisting of a mixture of a basic salt (calcium hydroxy-chloride), with calcium chloride; and its formation expressed by the equation:



$$3Ca(OH)_2 + 2Cl_2 = \underbrace{2Ca\left\langle\begin{matrix}OH\\OCl\end{matrix}\right.}_{\text{Calcium hydroxy-chloride.}} + CaCl_2 + 2H_2O.$$

In contact with water, the calcium chloride dissolves, and the basic salt is decomposed, with the formation of calcium hypochlorite and hydrate, as follows:

$$2Ca\left\langle\begin{matrix}OH\\OCl\end{matrix}\right. = Ca\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + Ca\left\langle\begin{matrix}OCl\\OCl\end{matrix}\right..$$

When exposed to a gentle heat, chlorinated lime is converted, according to its composition and the temperature, into calcium chlorate and chloride, and, at a higher temperature, by decomposition of the chlorate, yields oxygen, and probably also some chlorine; by the action of sunlight, it is partially decomposed with the formation of calcium chlorate and chloride, and the liberation of oxygen. When well mixed with ten or more parts of water, it forms a creamy liquid, while its soluble constituents enter into solution, leaving behind calcium hydrate, and the insoluble impurities of the lime employed in the manufacture of bleaching-powder; the filtered solution is colorless, and of an acrid, nauseous taste, changes red litmus for a moment into blue, and decolorizes it almost at once, and completely; it emits the odor of chlorine with acids, and forms a white precipitate with sulphuric and oxalic acids.

By the decomposition of chlorinated lime with acids the entire amount of contained chlorine is available, as shown by the following equations:

$$(1)\ CaCl_2 + Ca(OCl)_2 + 4HCl = 2Cl_2 + 2CaCl_2 + 2H_2O.$$
$$(2)\ CaCl_2 + Ca(OCl)_2 + 2H_2SO_4 = 2Cl_2 + 2CaSO_4 + 2H_2O.$$

Chlorinated lime, exposed to the carbonic acid and moisture of the air, evolves hypochlorous acid, which, when free, readily breaks up into water, chlorine, and chloric acid; the latter is also soon resolved into oxygen, water, chlorine, and perchloric acid; a deliquescent residue, consisting of calcium hydrate, carbonate, and chloride, forms the final residual product. Upon this decomposition, or by the direct elimination of chlorine through the agency of stronger acids, depends the energetic chemical action of chlorinated lime as an oxidizing agent, which, therefore, is proportionate to the percentage of calcium hypochlorite, or, in other words, of the available chlorine, which, for most pharmaceutical and therapeutical purposes, should amount to 25, or, as the minimum, 20 per cent. In order to estimate this, and to determine the value of commercial bleaching-powder, several methods of testing are employed, among which the following two are simple and reliable:

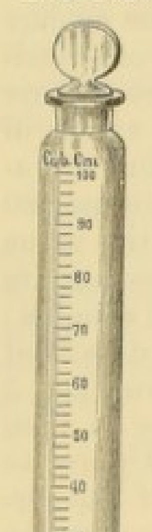
I. 1.96 parts of pure crystallized ferrous sulphate are dissolved in a capacious glass flask in a mixture of 20 parts of water and 5 parts of hydrochloric acid; 1 part of chlorinated lime is then thoroughly mixed, by trituration in a mortar, with 50 parts of water, and the mixture added at once to the solution of the ferrous salt. The flask being then tightly closed, it is actively agitated for a few minutes, and the mortar in which the chlorinated lime was triturated, subsequently rinsed with a little water, and this liquid added to the contents of the flask. After again agitating for a moment, the liquid should still retain the odor of chlorine, and, after filtration, when tested with a few drops of a solution of potassium ferridcyanide, should afford no blue coloration or precipitate.

This test, when employed with the above stated proportions of ferrous sulphate and chlorinated lime, will indicate a strength of the latter corresponding to at least 25 per cent. of available chlorine. With the employment of 1.57 parts of ferrous sulphate to 1 part of chlorinated lime, the application of the same test, which is based upon the oxidation of the ferrous to ferric salt through the agency of the liberated chlorine, will then indicate a strength of the chlorinated lime corresponding to at least 20 per cent. of available chlorine.

The United States Pharmacopœia directs that if 0.71 gram of chlorinated lime be mixed with a solution of 1.25 grams of potassium iodide in 120 cubic centimeters of water, and 9 grams of hydrochloric acid be then added, the resulting red-brown liquid should require for complete decoloration not less than 50 cubic centimeters of standard solution of sodium hyposulphite, corresponding to at least 25 per cent. of available chlorine.

II. The following method of estimation will afford an accurate result, when not alone the minimum, but the determination of the exact percentage amount of chlorine contained in the chlorinated lime is desired. One gram of the chlorinated lime is triturated in a mortar with a small portion of water until a uniform pasty mass is obtained, which is afterwards further diluted with water, and, together with the rinsings of the vessel, transferred to a graduated cylinder, provided with a glass-stopper (Fig. 104), and the liquid finally diluted to 100 cubic centimeters. The one per cent. solution thus obtained, after being thoroughly mixed by agitation, is allowed to repose until it becomes perfectly clear; 50 cubic centimeters of the clear liquid are then carefully drawn off by means of a pipette, and allowed to flow into a solution of 2 grams of potassium iodide in about 20 cubic centimeters of water, contained in a beaker. To the mixed solutions hydrochloric acid sufficient to render the mixture slightly acid is added, and the liberated iodine subsequently estimated by means of a standard solution of sodium hyposulphite, page 94. The strength of the sodium hyposulphite solution, or the amount of pure iodine corresponding to one cubic centimeter of the same, being known, the number of cubic centimeters required to produce decoloration of the liquid will indicate the amount of iodine liberated by the chlorine, and therefrom, by simple equivalent proportion (I, 127 = Cl, 35.5), the amount of chlorine contained in the number of cubic centi-

FIG. 104.



meters of the solution of chlorinated lime employed, from which the percentage strength of the chlorinated lime in active chlorine may be readily calculated.

In consequence of the facility with which chlorinated lime undergoes decomposition, particularly by exposure to the air and moisture, the amount of active chlorine contained in the commercial article is often found to vary from 10 to 35 per cent.

CALX SULPHURATA.

CALCIUM SULFURATUM.

Sulphurated Lime. Calcium Sulphide.

Ger. Schwefelkalk ; Fr. Sulfure de calcium ; Sp. Sulfuro de calcio.

Pure calcium monosulphide, CaS, forms a white or yellowish-white mass, which is very sparingly soluble in water, and in moist air develops the odor of hydrogen sulphide. As prepared by the reduction of calcium sulphate with carbon, or by the ignition of a mixture of caustic lime and sulphur (Calx Sulphurata, U. S. P.), a grayish or reddish-white mass is obtained, which is not a definite chemical compound, but consists of a mixture of calcium sulphide and polysulphides, with small and variable amounts of calcium sulphate, and carbonaceous matter or other impurities.

Calcium sulphide is dissolved to but a small extent by water, and, upon boiling therewith, is partially decomposed, with the formation of calcium hydrate and sulphydrate: $2CaS + 2H_2O = Ca(HS)_2 + Ca(OH)_2$. The solution is at first colorless, but, on exposure to the air, becomes decomposed, with the absorption of oxygen and carbonic acid gas, and acquires a yellowish color; it possesses an alkaline reaction, and the odor of hydrogen sulphide, which latter gas is abundantly developed therefrom upon the addition of an acid.

Calcium sulphide, when shaken with water, and the liquid filtered, should yield a solution which is not precipitated by solution of calcium sulphate, but affording upon the addition of solution of ammonium oxalate a white precipitate, soluble in hydrochloric, but insoluble in acetic acid. It should dissolve in dilute hydrochloric acid, with the abundant development of hydrogen sulphide, and without leaving a considerable insoluble residue.

The presence of at least 36 per cent. of pure calcium sulphide in sulphurated lime may be ascertained by gradually adding 1 gram of the salt to a boiling solution of 1.25 grams of cupric sulphate in 50 cubic centimeters of water; the mixture is then heated nearly to boiling for about ten minutes, and, when cold, filtered. The filtrate, when tested with one drop of test-solution of potassium ferrocyanide, should remain colorless.

CAMPHORA MONOBROMATA.

Monobromated Camphor. Camphor Monobromide.

Ger. Monobromcampher; Fr. Camphre monobromé; Sp. Monobromato de alcanfor.

$C_{10}H_{15}BrO$; 230.8.

Thin, colorless prisms, when crystallized from alcohol, or elongated, flat prisms, which are perfectly transparent and hard, when crystallized from petroleum benzin. It is permanent in the air; not affected by direct sunlight; slowly volatilized when boiled in water, and possesses an odor reminding of Borneo camphor, and a taste which is terebinthinate and scarcely bitter. It fuses at 65 C. (149° F.), and boils at 274° C. (525.2° F.), with partial decomposition; it does not sublime at ordinary temperatures, but sublimes abundantly at temperatures above its fusing-point, in the form of long, slender, colorless needles.

Monobromated camphor is almost insoluble in water, and sparingly soluble in glycerin, but freely in alcohol, although less so than ordinary camphor, and is readily dissolved by ether, chloroform, carbon bisulphide, warm petroleum benzin, and the volatile and fatty oils; it is also soluble in cold, concentrated sulphuric acid, and is precipitated unchanged upon the addition of water.

In alcoholic solution, in contact with sodium amalgam or argentic nitrate, it is converted into ordinary camphor; and, when boiled with a solution of argentic nitrate in dilute nitric acid, it is decomposed, with the formation of argentic bromide, corresponding in amount to 81.2 per cent. of the monobromated camphor employed.

CANTHARIDINUM.

Cantharidin.

Ger. Cantharidin; Fr. Cantharidine; Sp. Cantaridina.

$C_{10}H_{12}O_4$; 196.

Bright, colorless, rhombic prisms or laminæ (Fig. 105), permanent in the air. When heated to 210° C. (410° F.) they soften, and fuse at 218° C. (424.4° F.); at higher temperatures, by the cautious application of heat, they may be sublimed unchanged.

Fig. 105.

Cantharidin is soluble in 30,000 parts of cold, and half that amount of boiling, water, and sparingly soluble in cold alcohol and carbon bisulphide, but quite readily soluble in hot alcohol, and in chloroform, ether, acetic ether, benzol, and the volatile and fatty oils, particularly upon warming.

When digested for some time at about 100° C. (212° F.) with a dilute solution of potassium or sodium hydrate, it is converted, by assimilation of the elements of water, into *cantharidic acid*, $C_{10}H_{16}O_6$, or $C_5H_8O_3$, which combines with the alkali with the formation of well crystallizable salts. The aqueous solution of these salts possesses an alkaline reaction, and, upon the addition of a stronger acid, cantharidic acid is separated, but becomes, by the elimination of the absorbed elements of water, immediately resolved into cantharidin.

When heated with hydriodic acid of the spec. grav. 1.8, cantharidin is gradually converted into the crystallizable, monobasic *cantharic acid*, which has the same composition as cantharidin; it is soluble, however, in 120 parts of cold, and 12 parts of boiling, water, very soluble in alcohol, sparingly in ether, and does not produce vesication when its solution in glycerin is applied to the skin.

Cantharidin is an active poison, and, when applied to the skin, exerts powerful vesicating properties, which, for the want of any distinguishing chemical tests, may be employed as a means for its identification.

For the separation of cantharidin when associated with alkaloids or other organic principles, see page 106.

CARBONEI BISULPHIDUM.

CARBONEUM SULFURATUM. ALCOHOL SULFURIS.

Bisulphide of Carbon. Carbon Bisulphide.

Ger. Schwefelkohlenstoff; Fr. Sulfure de carbone; Sp. Bisulfuro de carbon.

CS_2; 76.

A transparent, colorless, very volatile liquid, of great refractive and dispersive power, of a pungent, somewhat aromatic taste, and a peculiar odor, which, when pure, slightly resembles that of chloroform. Its spec. grav. is 1.272 at 15° C. (59° F.), and it boils at 47° C. (116.6° F.), but does not solidify when exposed to a temperature of —110° C. (—166° F.). It is highly inflammable, taking fire in the air at 149° C. (300.2° F.), and burns with a blue flame, yielding, as the products of combustion, carbon dioxide and sulphur dioxide. Its vapor, when mixed with one-third of its volume of oxygen or atmospheric air, forms an explosive gas, which detonates with great violence in contact with flame; when mixed with nitric oxide, its vapor burns upon ignition with a very bright blue flame, which is particularly rich in chemically active rays.

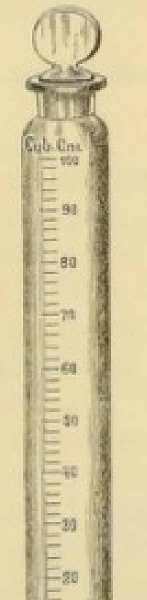
Carbon bisulphide is not dissolved to any appreciable extent by water, and sinks in that liquid; when agitated with iodine-water, it absorbs the minute quantity of iodine dissolved in the water, and acquires a faint, purple color.

Carbon bisulphide is remarkable and important on account of its extensive solvent powers; it is miscible, in all proportions, with absolute alcohol (the solubility decreasing with the decrease of strength of the alcohol), with ether, chloroform, benzol, essential and fatty oils; it dissolves readily and freely, among other substances, sulphur, phosphorus, bromine, iodine, iodoform, camphor, caoutchouc, gutta-percha, many resins, wax, paraffin, stearin, chloral hydrate, and many alkaloids which are soluble in ether and alcohol.

The vapor of carbon bisulphide is a powerful anti-putrescent, and retards fermentation, but is also an active poison when inhaled in large quantity, and is capable of producing very serious effects when inhaled for a considerable time, even in very small amount. By exposure to sunlight, carbon bisulphide becomes partially decomposed, acquiring a disagreeable odor and a yellowish color; it then contains sulphur in solution, and reddish-brown flocks of polymeric carbon monosulphide $(CS)_x$ are separated. When preserved under water, it also acquires a yellowish color, with the formation of small amounts of carbonic and sulphuric acids, and, when heated with water in a sealed tube, at 150° C. (302° F.), it is further decomposed with the formation of hydrogen sulphide.

Carbon bisulphide may be recognized, even in very minute quantities, by warming it in a closed flask with concentrated ammonia-water, or by mixing it with a little ammoniacal alcohol and gently heating; these liquids furnish, upon evaporation on the water-bath, a residue consisting of ammonium sulphocyanide, which, when dissolved in a little water, and a drop of solution of ferric chloride added, yields the characteristic blood-red color of ferric sulphocyanide.

FIG. 106.



Examination:

The odor of carbon bisulphide should not be repulsive, nor fetid; it should not cause a dark turbidity or precipitate in a solution of plumbic acetate, when agitated with it (absence of hydrogen sulphide), nor change the color of moist litmus-paper (absence of sulphurous acid), and, when allowed to evaporate spontaneously upon a watch-glass, should leave no residue (absence of free sulphur, or other impurities).

An admixture of ethyl or methyl alcohol may readily be detected by the lesser specific gravity of the liquid, by its impaired property of dissolving fatty oils, and by its diminution in volume when shaken, in a graduated cylinder (Fig. 106), with an equal volume of water or glycerin.

CERII OXALAS.

CERIUM OXALICUM.

Oxalate of Cerium. Cerium Oxalate.

Ger. Ceroxalat ; Fr. Oxalate de cérium ; Sp. Oxalato de cerium.

$Ce_2(C_2O_4)_3 + 9H_2O$; 708.

A white, granular powder, without odor or taste, containing 9 molecules (22.88 per cent.) of water, and permanent in the air; it is almost insoluble in water, alcohol, ether, chloroform, and solutions of potassium or sodium hydrate, but soluble in hydrochloric and sulphuric acids. Exposed to heat, the salt is decomposed, and at a dull red heat is completely converted into ceroso-ceric oxide, Ce_3O_4, which is of a dark-red color when hot, yellowish-white when cold (a brown color would indicate the presence of didymium), and soluble without effervescence in boiling hydrochloric acid; this solution gives, with an excess of a saturated solution of potassium sulphate, a crystalline precipitate of potassium-cerous sulphate, $3K_2SO_4 + Ce_2(SO_4)_3$.

Cerium oxalate, when heated with a solution of potassium hydrate, filtered, and the filtrate neutralized with acetic acid, affords upon the addition of a solution of calcium chloride a white precipitate of calcium oxalate, which is insoluble in acetic, but readily and completely soluble in hydrochloric acid.

Examination:

Earthy carbonates are indicated by effervescence of the salt with hydrochloric acid.

Soluble salts may be readily detected by digesting the cerium oxalate with water, filtering, and evaporating the filtrate to dryness; any considerable residue, upon evaporation, will reveal the presence of such impurities.

Alumina or *aluminium salts* may be detected by boiling the oxalate of cerium with a strong solution of potassium hydrate, filtering, and adding an excess of solution of ammonium chloride, when a white, flocculent precipitate of aluminium hydrate will be formed, if such be present.

Other impurities, such as metallic oxides, insoluble earthy phosphates, foreign oxalates, etc., may be sought for, when indicated, according to the systematic methods of analysis, as described on pages 51 to 61.

CHINOIDINUM.

Chinoidin. Quinoidin.

Ger. Chinoïdin ; Fr. Quinoidine ; Sp. Quinoidina.

A brittle, resin-like mass, of a deep brown color, a glossy, conchoidal fracture, and a peculiar aromatic odor, and consisting principally of diquinidine, $C_{40}H_{48}N_4O_3$, accompanied by varying amounts of quinicine, $C_{20}H_{24}N_2O_2$, cinchonicine, $C_{20}H_{24}N_2O$, and other amorphous bases; it becomes soft and tough at a moderate temperature, and melts like a resin when warmed; at a stronger heat, it burns away, and leaves, upon incineration, a white ash, which should not amount to more than 0.7 per cent. of its weight.

Chinoidin is almost insoluble in water, and only partly soluble in ether, benzol, and in glycerin, but freely soluble in diluted acids, in alcohol, and in chloroform, forming dark brown solutions of an aromatic, bitter taste and odor; the alcoholic and ethereal solutions are precipitated by water, and the acid aqueous solution becomes green when first mixed with sufficient chlorine-water to decolorize it, and subsequently with an excess of ammonia-water.

Examination:

Gum-Resins.—A small portion of the triturated chinoidin is agitated, in a test-tube, with about 20 times its weight of water; the mixture is then heated to boiling, with constant agitation; when cool, the water must be nearly colorless, and remain so upon the addition of a few drops of a concentrated solution of potassium hydrate, and subsequent heating; if a brown coloration takes place, in either of these tests, gum-resins (aloes) or other soluble admixtures (liquorice, glucose, dextrin, etc.) are indicated.

Resins may be detected in the chinoidin remaining undissolved in the preceding test, by dissolving it, with the aid of heat, in diluted sulphuric acid; a complete or almost complete solution must take place, otherwise an admixture of resins, insoluble in diluted acids, is indicated.

As a confirmatory test for gum-resins, liquorice, glucose, etc., a few drops of the obtained solution may be allowed to fall into alcohol; they must form a clear solution; an ensuing turbidity would establish the presence of such admixtures.

Inorganic admixtures are indicated by an insoluble residue when the chinoidin is dissolved in alcohol, or by a residue left upon ignition.*

Copper may be specially sought for in the residue left upon

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* In consequence of the slow combustion of the substance, its complete ignition may be facilitated by the addition of a few drops of nitric acid to the carbonaceous residue left upon heating, and again strongly heating, when the organic matter will become completely removed.

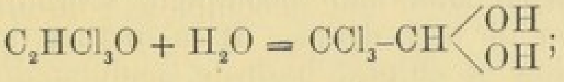
ignition, by dissolving it in a few drops of warm hydrochloric acid, and, after dilution with water, testing the solution in separate portions, with a drop of solution of potassium ferrocyanide, and with an excess of ammonia-water; a reddish-brown turbidity with the first-named reagent, and a blue coloration of the liquid with the latter, will determine the presence of copper.

CHLORAL.

CHLORALI HYDRAS. CHLORALUM HYDRATUM.

Chloral. Hydrate of Chloral. Chloral Hydrate.

Ger. Chloralhydrat; Fr. Hydrate de chloral; Sp. Hidrato de cloral.



$$C_2HCl_3O + H_2O = CCl_3\text{–}CH\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix};\ 165.2.$$

Colorless, semi-transparent, needle shaped crystals, or crystalline plates, belonging to the monoclinic system, and possessing a peculiar ethereal odor and pungent taste. Exposed in a dry test-tube to a gentle heat, by dipping the tube into hot water, chloral hydrate fuses at 58° C. (136.4° F.), forming a clear, colorless liquid of the spec. grav. 1.575, which, at 46° C. (114.8° F.), again solidifies; at 78° C. (172.4° F.), it is resolved into chloral, which boils at 99° C. (210.2° F.), and water, and, at a higher temperature, is wholly volatilized, without the evolution of inflammable vapors.

Chloral hydrate is soluble in about half its weight of cold water, and freely in both alcohol and ether, but only sparingly soluble in *cold* chloroform, in carbon bisulphide, in benzol, benzin, and in fixed and volatile oils. Its aqueous solution possesses a faintly acid reaction, but, when slightly acidulated with diluted nitric acid, no change, or but a faint opalescence, should be produced upon the addition of solution of argentic nitrate; upon the subsequent addition of a little ammonia-water, however, and heating the mixture, decomposition takes place with effervescence, and with the formation of argentic chloride and metallic silver, the latter coating the walls of the tube. When the aqueous solution is acidulated with diluted sulphuric acid, and faintly tinged with a few drops of solution of potassium permanganate, no decoloration should take place within a few hours. The alcoholic solution of chloral hydrate, in distinction from the aqueous, should not affect the color of moistened blue litmus-paper, and should also afford no turbidity upon the addition of a solution of argentic nitrate.

Concentrated sulphuric, nitric, and hydrochloric acids dissolve chloral hydrate with decomposition, but without color, and without the evolution of colored vapors. Solutions of the alkaline hydrates decompose it, when heated, into soluble formiates and chloroform. Ammonium sulphide dissolves chloral hydrate, with the evolution of heat, forming a turbid, reddish-brown liquid; the same reagent produces, in concentrated as well as in diluted solutions of chloral hydrate, a yellow coloration, which becomes dark brown, forming, with the separation of sulphur, a reddish-brown compound, gradually when cold, immediately upon warming.

Chloral hydrate liquefies when mixed with carbolic acid or with camphor, without decomposition, and is separated again by the subsequent addition of water.

Examination:

Decomposition of chloral hydrate is indicated by the emission of vapors and by a pungent odor upon opening the vial, by the reddening of moistened blue litmus-paper when immersed in it, as also by a yellowish color and incomplete solubility in water, with the formation of oily drops. It is further indicated, in the aqueous solution of chloral hydrate, acidulated with a few drops of diluted nitric acid, by a white precipitate with argentic nitrate, and in another portion, acidulated with sulphuric acid, by decoloration of solution of potassium permanganate.

Chloral alcoholate, $C_2HCl_3O + C_2H_6O = \left(CCl_3{-}CH\left\langle\begin{smallmatrix}O{-}C_2H_5\\ OH\end{smallmatrix}\right.\right)$, is distinguished from the hydrate by the evolution, upon strongly heating, of inflammable vapors, which burn with a yellowish, smoky flame; by the property of being readily and freely soluble in *cold* chloroform, in carbon bisulphide, or in oil of turpentine, but less soluble in *cold* water than is the hydrate; and by its yielding a reddish-brown or brown solution with warm concentrated sulphuric acid, and by the evolution of red nitrous vapors with concentrated nitric acid.

An admixture of the alcoholate with the hydrate may be detected by dissolving a portion of the salt in about 10 times its weight of water, in a test-tube, adding sufficient of a solution of iodinized potassium iodide to impart a dark brown coloration, and subsequently a solution of potassium hydrate, in small portions, until the liquid is nearly decolorized and retains but a slight yellowish tint; the mixture is then gently warmed, by immersing the test-tube for a short time in hot water, and subsequently allowed to cool; if chloral alcoholate is present, small yellow crystals of iodoform (Fig. 107) will be separated, which may be recognized by their odor, and their appearance under the microscope, whilst the liquid, in consequence of the separated chloroform, will assume a milk-like turbidity.

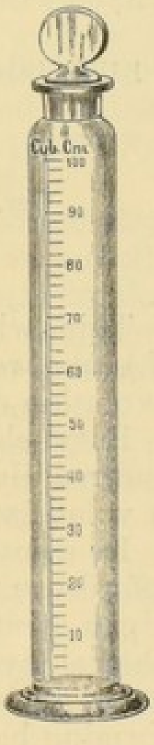
Fig. 107.

The following methods of approximate estimation of the purity of chloral hydrate depend upon the volumetric determination of the quantity of chloroform produced by the decomposition of a known quantity of chloral hydrate, or upon the determination of the amount of normal alkali which is required for the complete decomposition of the salt into chloroform and an alkaline formiate:

$$\underbrace{C_2HCl_3O + H_2O}_{\text{Chloral hydrate.}} + NaHO = H_2O + \underbrace{NaCHO_2}_{\text{Sodium formiate.}} + \underbrace{CHCl_3}_{\text{Chloroform.}}$$

I. Fifty parts of the chloral hydrate are dissolved in about an equal weight of water in a graduated glass tube or cylinder, divided into 100 parts (Fig. 108); a warm solution of potassium or sodium hydrate (containing about 20 parts of potassium hydrate, or 15 parts of sodium hydrate) is then added, and, finally, sufficient water to make the entire liquid measure 100 parts. The cylinder is then closed, agitated for a short time, and allowed to repose, when the fluid will soon separate into two layers, a lower one of chloroform, and an upper layer, consisting of an alkaline solution of potassium or sodium formiate.

FIG. 108.



If the sample was pure hydrate, the chloroform should measure not less than 24.06 parts, corresponding to 36.10 parts by weight, or 72.2 per cent. of the chloral hydrate employed; if it was chloral alcoholate, the chloroform will measure 20.53 parts, corresponding to 30.88 parts by weight, or 61.75 per cent. of the chloral alcoholate.

An admixture of the alcoholate with the hydrate will, therefore, be indicated, proportionately, by the decrease of the quantity of chloroform, ranging, in the above test, between 24.06 and 20.53 parts by volume, and 36.10 and 30.88 parts by weight.

II. About 3 grams of chloral hydrate are accurately weighed, and dissolved, in a beaker, in about 10 cubic centimeters of water; the solution being then gently warmed, about 25 cubic centimeters of a normal solution of potassium or sodium hydrate (page 87) are allowed to flow in from a burette, when the chloral hydrate will become completely decomposed into chloroform and potassium or sodium formiate. To the cooled liquid a few drops of a neutral solution of litmus are then added, and the excess of alkali (18.12 cubic centimeters of normal alkali are theoretically required for the decomposition of 3 grams of chloral hydrate) inversely titrated by means of a normal solution of oxalic acid, page 82. The number of cubic centimeters of the normal acid which are required for the exact neutralization of the liquid, subtracted from the number of cubic centimeters of normal alkali originally employed, will indicate the amount of alkali required for the decomposition of the chloral hydrate, and therefrom the purity of the salt may be readily determined; one cubic centimeter of normal alkali corresponding to 0.1655 gram of pure chloral hydrate.

If the chloral hydrate contains alcoholate, the number of cubic centimeters of alkali required to effect the decomposition of the salt will be less, and in proportion to the extent of the admixture; 3 grams of chloral alcoholate requiring for its decomposition 15.50 cubic centimeters of normal alkali.

CHLORALUM BUTYLICUM.

BUTYLO-CHLORALUM HYDRATUM. CROTONO-CHLORALUM HYDRATUM.

Butyl-chloral Hydrate. Croton-chloral Hydrate.

Ger. Butylchloralhydrat; Fr. Hydrate de chloral butylique;
Sp. Hidrato de cloral-croton.

$C_4H_5Cl_3O + H_2O$; 190.2.

Thin, white scales, of a silky lustre, fusing at 78° C. (172.4° F.), and readily volatilizing above that temperature, with the evolution of irritating vapors.

Butyl-chloral hydrate is soluble in about 20 parts of cold water, and readily soluble in boiling water, in alcohol, and in glycerin; it volatilizes freely with the vapors of boiling water.

Its solution should be neutral in its action upon litmus, and affords no turbidity when tested with solution of argentic nitrate. Upon gently heating with concentrated sulphuric acid, butyl-chloral hydrate should remain colorless, and form oily drops of colorless butyl chloral. It is decomposed by alkaline hydrates, forming bichlorallylene ($C_3H_2Cl_2$), and alkaline formiate and chloride.

CHLOROFORMUM.

CHLOROFORMIUM.

Chloroform.

Ger. Chloroform; Fr. Chloroforme; Sp. Cloroformo.

$CHCl_3$; 119.2.

A dense, colorless, volatile, and limpid liquid, of an agreeable, ethereal, aromatic odor, and sweetish taste; it does not act upon litmus, and is not readily inflammable, but, when a wick is saturated with chloroform, and ignited, it burns with a greenish flame, emitting pungent vapors which contain hydrochloric acid. It is very volatile at common temperatures, producing, by rapid evaporation, great cold, and leaving neither a residue, nor a film of moisture, nor any unpleasant odor, when wholly evaporated by the warmth of the hand, by causing the chloroform to flow to and fro, in a porcelain capsule. It boils at 62° C. (143.6° F.).

Chloroform sinks in water, being but slightly soluble, one part requiring about 200 parts of water for solution. The spec. grav. of pure chloroform is 1.502 at 15° C. (59° F.); in this state of purity, it is subject to rapid decomposition by the combined action of atmospheric oxygen and of solar light; it is, however, protected against this deterioration by a slight percentage of ethylic alcohol, which is, therefore, retained in the preparation of medicinal chloroform, or subsequently added thereto in amounts of from one to two per cent., whereby its specific gravity is decreased from 1.4854 to 1.4705 at 15° C. (59° F.), and its boiling-point, despite the higher boiling-point of pure alcohol, reduced in the first instance, from 60.2 to 61.6° C. (140.3 to 141.8° F.), and, in the latter, from 59 to 61.2° C. (138.2 to 142.1° F.).

Chloroform is miscible, in all proportions, with absolute alcohol, with ether, benzol, carbon bisulphide, and fixed and volatile oils, and is an extensive solvent for resins, caoutchouc, gutta-percha, camphor, paraffin, etc.; it also dissolves iodine, bromine, and, more or less completely, most vegetable alkaloids, which latter it almost completely withdraws from their aqueous, alkaline solutions.

Chloroform is not miscible with glycerin, and is insoluble in the concentrated mineral acids; when shaken with them, even at an elevated temperature, it undergoes no perceptible change; nor is it acted upon at ordinary temperatures by aqueous solutions of the alkaline hydrates, iodides, or bromides, nor by argentic nitrate.

When heated with an alcoholic solution of potassium or sodium hydrate, it is decomposed, with the formation of alkaline chloride and formiate:

$$CHCl_3 + 4NaHO = 2H_2O + 3NaCl + NaCHO_2.$$

On the subsequent addition of a little water, and the evaporation of the chloroform and alcohol, the liquid, when exactly neutralized by dilute sulphuric acid, will yield a white precipitate upon the addition of a solution of argentic nitrate; if the filtrate therefrom be then gently warmed, a reduction of the argentic nitrate will take place, and a silver mirror obtained on the sides of the tube. When heated to 180° C. (356° F.) with an aqueous or alcoholic solution of ammonia, it is resolved into ammonium chloride and cyanide; and, in the presence of a little potassium hydrate, the decomposition takes place below 100° C. (212° F.):

$$CHCl_3 + NH_3 + 4KHO = 4H_2O + 3KCl + KCN.$$

The liquid, upon the subsequent addition of a few drops of a solution of a ferrous and ferric salt, and supersaturation with hydrochloric acid, will yield a precipitate of Prussian blue.

When chloroform, or its aqueous or alcoholic solution, is gently heated with an alcoholic solution of sodium hydrate, and a few drops of aniline, vapors of phenyl-isocyanide (phenylcarbylamin), C_6H_5–NC, are evolved, which possess an exceedingly penetrating and unpleasant odor, and produce insensibility when inhaled.

$$CHCl_3 + 3NaHO + C_6H_5(NH_2) = C_6H_5\text{–}NC + 3NaCl + 3H_2O.$$

When chloroform, or its aqueous solution, is warmed with an alkaline solution of cupric tartrate (Fehling's solution), a separation of red cuprous oxide is produced, in consequence of the formation of a trace of sodium formiate.

Examination of Commercial Impure and of Purified Chloroform:

As a *preliminary test* for the indication of a partial decomposition of chloroform, a test-tube may be rinsed with ammonia-water, and, subsequently, one or two drops of the chloroform allowed to fall to the bottom of the tube; the appearance of white fumes would indicate such decomposition. In another test-tube equal volumes of the chloroform and of water, the latter slightly blued with neutral litmus-solution, are shaken together; a decoloration or a red appearance of the water, after subsiding, would likewise show decomposition.

The result of these tests should also be negative, if the chloroform has been previously exposed, in a white glass bottle, to direct sunlight, for about ten hours.

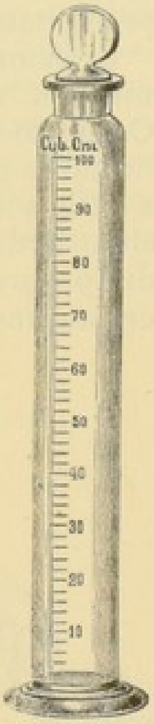
When shaken with half its volume of concentrated sulphuric acid in a bottle closed by a glass stopper, no coloration should be produced, either at once or upon standing; a dark coloration of either liquid will indicate a partial decomposition of the chloroform, attended by the liberation of chlorine, which, combining with the ethylic or other alcohols which may be present, gives rise to the formation of chlorinated ethers, which impart a brown color to the sulphuric acid.

Chlorine and *Hydrochloric Acid.*—Two volumes of chloroform are shaken in a graduated cylinder (Fig. 109) with one volume of water. A perceptible diminution of the volume of the chloroform, after subsiding, would indicate an objectionable percentage of alcohol. The supernatant water must neither appear turbid, nor redden blue litmus-paper, nor afford a precipitate when tested with a dilute solution of argentic nitrate. An acid reaction upon litmus, and the occurrence of a precipitate with the latter reagent, would indicate free *chlorine* or *hydrochloric acid.*

Chlorine may also be detected by adding the chloroform, drop by drop, to a solution of potassium iodide (free from iodate) in a test-tube. When agitated, the chloroform, after subsiding, will appear rose-colored, and the aqueous solution yellow, if even traces of free chlorine be contained in the chloroform; when this is the case, and the addition of chloroform, in drops, is continued, each drop, falling through the aqueous solution, will assume a slight purplish tint.

Ethylene dichloride (Dutch liquid), $C_2H_4Cl_2$, will be indicated by its lower specific gravity (1.247 at 18° C. = 64.4° F.), and higher boiling-point (85° C. = 185° F.), as also by the following test: A little fused potassium hydrate is dissolved, in a dry test-tube, in some absolute alcohol; after complete solution is effected, and the impurities have subsided, the clear liquid is decanted into a dry test-tube, and a little chloroform added. No reaction will take place in the clear fluid unless the chloroform contains Dutch liquid, in which case an elevation of temperature will appear perceptible by a small thermometer immersed in the liquid; a slight evolution of gas from the liquid will also occur, and a crystalline precipitate of potassium chloride will be gradually produced.

FIG. 109.



Alcohol.—Since medicinal chloroform, as stated above, contains about one or two per cent. of alcohol, an examination for an admixture of alcohol by one of the following sensitive tests would obviously be a *contradictio in adjecto.* The specific gravity, the volumetric test in the preceding examination, and the property of chloroform to form a perfectly clear and transparent mixture with sweet oil of almonds, which it will not do if it contains more than five or six per cent. of alcohol, afford sufficient evidence of the quality of chloroform in this respect. A chloroform which has a specific gravity of less than 1.4705 at 15° C. (59° F.), and which renders oil of almonds turbid, and causes a perceptible rise of temperature when actively shaken, in a dry test-tube, with an equal volume of concentrated sulphuric acid, cannot be considered as being of medicinal strength.

Tests for the Detection of Alcohol in Chloroform.

1. Strong sulphuric acid, to which a little potassium bichromate has been added, when shaken with an equal bulk of chloroform, will turn green, if the latter contains alcohol.

2. Two volumes of chloroform and one volume of concentrated sulphuric acid are mixed in a bottle closed with a glass stopper; after repeated agitation, the bottle is set aside for a few hours; the liquid is then carefully diluted with about an equal bulk of water, the supernatant aqueous liquid is decanted into a beaker, and so much of a mixture of pure barium carbonate in water is added, with constant stirring with a glass rod, as completely to

neutralize the acid, so that, after gentle warming, the cooled liquid does not change blue litmus-paper; it is then passed through a moist filter, and the filtrate tested with diluted sulphuric acid. If the chloroform contained traces of alcohol, this would have given rise to the formation of ethyl-sulphuric acid (sulphovinic acid), and subsequently to soluble barium ethyl-sulphate, contained in the filtered solution, and which is precipitated by sulphuric acid as barium sulphate. Consequently, the occurrence of a white precipitate will be evidence of the presence of alcohol.

3. A mixture of two volumes of the chloroform with five volumes of water is warmed in a test-tube to about from 30 to 40° C. (86 to 104° F.); after active agitation for a few minutes, the liquid is passed through a moist filter, and to the filtrate is added a little solution of iodinized potassium iodide; a solution of potassium hydrate is then gradually added until the color of the liquid disappears. After twelve hours' standing in a conical glass, a crystalline deposit of iodoform (Fig. 110) will have taken place if alcohol be present; the crystals may be recognized under the microscope, when the liquid is carefully removed by means of a small pipette (Fig. 111), and the deposit transferred to a glass slip.

FIG. 110.

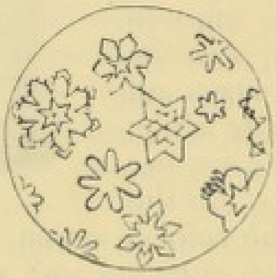


FIG. 111.

CHRYSAROBINUM.

Chrysarobin.

Ger. Chrysarobin; Fr. Chrysarobine; Sp. Crisarobin.

A pale, orange-yellow, crystalline powder, without odor or taste, and permanent in the air. When heated to 162° C. (323.6° F.), it melts, and, at a higher temperature, may be partially sublimed; when strongly heated on platinum-foil, it emits yellow vapors with the separation of carbon, and is finally completely dissipated.

Chrysarobin is almost insoluble in water, and sparingly soluble in alcohol, but is quite readily soluble in ether, chloroform, benzol, and the fixed and volatile oils; it is also soluble in solutions of the alkaline hydrates, with a yellowish-red or reddish-yellow color, which is changed to red by passing air through the liquid. When shaken with ammonia-water, chrysarobin assumes, after some hours, a fine carmine-red color. It dissolves in cold concentrated sulphuric acid, with a deep blood-red color, and on pouring the solution into water it is again separated unchanged. If a little of the powder be strewn upon a drop of fuming nitric acid, and the red solution exposed in a thin layer to the action of the air, it then assumes in contact with ammonia a violet color.

CINCHONIDINA.

CINCHONIDINUM.

Cinchonidine. Cinchonidia.

Ger. Cinchonidin; Fr. Cinchonidine; Sp. Cinconidina.

$C_{19}H_{22}N_2O$; 294.

Colorless, hard, shining prisms, odorless, possessing a bitter taste, although less intense than that of quinine, and an alkaline reaction. They contain no water of crystallization, and fuse at 206.5° C. (403.7° F.); when strongly heated upon platinum-foil, they become decomposed and charred, and are finally completely dissipated.

Cinchonidine is soluble in 1680 parts of water at 10° C. (50° F.), in 19.7 parts of 80 per cent. alcohol, and in 76.4 parts of ether; it dissolves readily in diluted acids with the formation of neutral and acid salts, which are mostly well crystallizable, more freely soluble in water than the corresponding salts of quinine, and quite readily soluble in alcohol, but very sparingly soluble in ether.

In contact with concentrated nitric or sulphuric acid, cinchonidine suffers no change of color (distinction from brucine, morphine, salicin, etc.), and its solution in the latter acid does not afford a purple coloration in contact with a crystal of potassium bichromate (distinction from strychnine).

When dissolved in water, acidulated with diluted sulphuric acid, the solution displays no fluorescence, and, upon the addition of a little chlorine-water, and subsequently of ammonia, no green coloration is produced (distinction from quinine and quinidine). It is distinguished from cinchonine by its greater solubility in ether, the latter requiring at 17° C. (62.6° F.) 370 parts of ether for solution.

In the absence of any specially characteristic chemical test for cinchonidine, its identity as a cinchona alkaloid may be determined, in connection with the described physical characters, by its property of affording, when mixed with a little sugar, and heated in a perfectly dry test-tube, a bright-red tarry sublimate, which, as far as at present known, is only produced by the dry distillation of cinchona barks or their alkaloids, when in contact with some indifferent organic substance, such as sugar.

When cinchonidine is dissolved in water, acidulated with dilute sulphuric acid, it responds to the tests for a solution of cinchonidine sulphate, as described under the latter, on page 314.

CINCHONIDINÆ SULPHAS.

CINCHONIDINUM SULFURICUM.

Sulphate of Cinchonidine or Cinchonidia. Cinchonidine Sulphate.

Ger. Schwefelsaures Cinchonidin; Fr. Sulfate de cinchonidine; Sp. Sulfato de cinconidina.

$$(C_{19}H_{22}N_2O)_2.H_2SO_4 + 3H_2O;\ 740.$$

Colorless, silky, lustrous needles, or thin quadrangular prisms, without odor, but possessing a very bitter taste, and feebly alkaline reaction. They contain about three molecules (7.30 per cent.) of water of crystallization when crystallized from a concentrated aqueous solution, or six molecules (13.60 per cent.) when crystallized from a dilute aqueous solution. When heated to 100° C. (212° F.) the salt loses its water of crystallization, and when strongly heated upon platinum-foil it is decomposed and charred, and finally completely dissipated.

Cinchonidine sulphate is soluble in 100 parts of water and in 71 parts of alcohol at 15° C. (59° F.), in 4 parts of boiling water and in 12 parts of boiling alcohol, freely soluble in acidulated water, and soluble in 1000 parts of chloroform; but nearly insoluble in ether and benzol. The aqueous solution possesses a bitter taste, and is precipitated by the general alkaloidal reagents: potassio-mercuric iodide, platinic chloride, tannic acid, etc., and upon the addition of solutions of the alkaline hydrates, carbonates, or bicarbonates, a white precipitate of cinchonidine is produced, which is nearly insoluble in an excess of the precipitant, but soluble in about 76 times its weight of ether, and, upon standing, becomes crystalline; with solution of barium chloride it yields a white precipitate of barium sulphate, insoluble in hydrochloric acid.

In contact with concentrated nitric or sulphuric acid, cinchonidine sulphate suffers no change of color (distinction from brucine, morphine, salicin, etc.), and its solution in the latter acid does not afford a purple coloration in contact with a crystal of potassium bichromate (distinction from strychnine).

The solution of cinchonidine sulphate in water, acidulated with sulphuric acid, displays no fluorescence, and, upon the addition of a little chlorine-water, and subsequently of ammonia, no green coloration is produced (distinction from the sulphates of quinine and quinidine). It is distinguished from cinchonine sulphate by the solubility of the latter in 60 parts of chloroform, whereas cinchonidine sulphate, as previously stated, requires 1000 parts of chloroform for solution.

A cold saturated solution of cinchonidine sulphate affords, upon the addition of a solution of potassium and sodium tartrate (Rochelle salt), in slight excess, a white crystalline precipitate of cinchonidine tartrate, $(C_{19}H_{22}N_2O)_2.C_4H_6O_6 + 2H_2O$, which requires 1265 parts of water for solution, and is quite insoluble in an excess of the reagent.

Examination:

Moisture, or the verification of the proper amount of water of crystallization, may be determined by exposing one gram of the salt to the temperature of 100° C. (212° F.), until the weight remains constant; when thus dried the residue should weigh not less than 0.92 gram, indicating an amount of water corresponding to between three and four molecules.

Cinchonine and *Quinidine Sulphates*.—In addition to the above described points of distinction, the presence of any appreciable amount of cinchonine or quinidine sulphates may be readily detected by the following test: 0.5 gram of the cinchonidine sulphate is digested with 20 cubic centimeters of cold distilled water, 0.5 gram of potassium sodium tartrate added, the mixture macerated, with frequent agitation, for one hour, at 15° C. (59° F.), then filtered, and one drop of ammonia-water added to the filtrate, when not more than a slight turbidity should occur; a white precipitate would indicate the presence of more than 0.5 per cent. of cinchonine sulphate, or of more than 1.5 per cent. of quinidine sulphate.

CINCHONINA.

CINCHONINUM.

Cinchonine. Cinchonia.

Ger. Cinchonin; Fr. Cinchonine; Sp. Cinconina.

$C_{19}H_{22}N_2O$; 294.

Colorless, transparent, monoclinic prisms or needles, without odor, and at first nearly tasteless, but developing a bitter after taste, and possessing an alkaline reaction. They contain no water of crystallization, and are permanent in the air. When heated to 220° C. (428° F.) they begin to volatilize, and when heated in a current of hydrogen or ammonia gas, they may be sublimed, without decomposition, in long needles; they melt at about 250° C. (482° F.), but assume a brown color, and become thereby partially decomposed; when more strongly heated, upon platinum-foil, they become charred, and are finally completely dissipated.

Cinchonine is very sparingly soluble in cold water, one part requiring at 17° C. (62.6° F.) 3700 parts for solution, and is not much more soluble in solutions of the alkalies or in boiling water, requiring of the latter about 2500 parts for solution; it is soluble in 110 parts of alcohol at 15° C. (59° F.), in 28 parts of boiling alcohol, in 370 parts of ether, and in 350 parts of chloroform. It dissolves readily in dilute mineral acids, with the formation of neutral or acid salts, which are mostly well crystallizable, and possess a persistent, strongly bitter taste.

In contact with concentrated nitric or sulphuric acid, cinchonine suffers no change of color (distinction from brucine, morphine, salicin, etc.), and its solution in the latter acid does not afford a purple coloration in contact with a crystal of potassium bichromate (distinction from strychnine).

The aqueous solution of cinchonine possesses an alkaline reaction and a bitter taste. When cinchonine is dissolved in water, acidulated with dilute sulphuric acid, the solution displays no fluorescence, and, upon the addition of a little chlorine-water, and subsequently of ammonia, no green coloration is produced (distinction from quinine and quinidine). It is distinguished from cinchonidine by the solubility of the latter in 76 parts of ether, whereas cinchonine, as stated above, requires 370 parts for solution.

In the absence of any specially characteristic chemical test for cinchonine, its identity may be determined, in connection with the above described physical characters, by its property, common to all cinchona alkaloids, of affording, when mixed with a little sugar, and heated in a perfectly dry test-tube, a bright-red tarry sublimate, which, as far as at present known, is only produced by the dry distillation of cinchona barks, or the alkaloids contained therein, when in contact with some indifferent organic substance, such as the above-mentioned carbohydrate.

When cinchonine is dissolved in water, acidulated with dilute sulphuric acid, it responds to the tests for a solution of cinchonine sulphate, as described under the latter, on page 317.

CINCHONINÆ SULPHAS.

CINCHONINUM SEU CINCHONIUM SULFURICUM.

Sulphate of Cinchonine or Cinchonia. Cinchonine Sulphate.

Ger. Schwefelsaures Cinchonin; Fr. Sulfate de cinchonine; Sp. Sulfato de cinconina.

$(C_{19}H_{22}N_2O)_2.H_2SO_4+2H_2O$; 722.

Transparent and colorless, hard, shining prisms of the monoclinic system, possessing no odor, but a very bitter taste, and a slightly alkaline reaction. They contain two molecules (4.98 per cent.) of water of crystallization, which are lost by drying at 100° C. (212° F.). When heated to about 240° C. (464° F.), the salt melts with partial sublimation, and when strongly heated, upon platinum foil, it fuses to a red, resinoid mass, becomes charred, and is finally completely dissipated.

Cinchonine sulphate is soluble in about 70 parts of water and in 6 parts of alcohol at 15° C. (59° F.), in 14 parts of boiling water, in 1.5 parts of boiling alcohol, and in about 60 parts of chloroform, but is insoluble in ether or benzol; it dissolves readily in dilute sulphuric acid, with the formation of an acid sulphate, or mono-cinchonine sulphate, $C_{19}H_{22}N_2O.H_2SO_4+4H_2O$, which is difficultly crystallizable, and soluble in half its weight of water, but requires 100 parts of absolute alcohol for solution.

The aqueous solution of cinchonine sulphate possesses a very bitter taste, and exhibits no fluorescence; it is precipitated by the general alkaloidal reagents: potassio-mercuric iodide, platinic chloride, tannic acid, etc., and upon the addition of solutions of the alkaline hydrates, carbonates, or bicarbonates, a white precipitate of cinchonine is produced, which is but very sparingly soluble in an excess of the precipitant; with potassium ferrocyanide a white amorphous precipitate is produced, which, upon warming, is soluble in an excess of the reagent, and is separated in a crystalline form upon cooling; with solution of barium chloride it yields a white precipitate of barium sulphate, insoluble in hydrochloric acid.

In contact with concentrated nitric or sulphuric acid, cinchonine sulphate suffers no change of color (distinction from brucine, morphine, salicin, etc.), and its solution in the latter acid does not afford a purple coloration in contact with a crystal of potassium bichromate (distinction from strychnine).

Cinchonine sulphate is distinguished from the sulphates of quinine and quinidine, by its greater solubility in water, by the absence of any fluorescence of its solution in dilute sulphuric acid, and by the latter solution, upon the addition of a little chlorine-water and subsequently of ammonia, affording no green coloration; it is also distinguished therefrom by the very sparing solubility of the pure alkaloid, when precipitated from a solution of its salt by ammonia-water, and subsequently shaken with ether. It is distinguished from cinchonidine sulphate by the latter requiring 1000 parts of chloroform for solution, whereas anhydrous cinchonine sulphate is soluble in 60 parts of chloroform; and, on the other hand, free cinchonidine is soluble in 76 parts of ether, whereas pure cinchonine requires 370 parts of ether for solution.

CODEINA.

CODEINUM.

Codeine. Codeia.

Ger. Codein; Fr. Codéine; Sp. Codeina.

$C_{18}H_{21}NO_3 + H_2O$; 317.

Colorless, transparent, octahedral crystals, belonging to the rhombic system, and containing one molecule (5.68 per cent.) of water of crystallization, which is lost by drying at 120° C. (248° F.). When crystallized from anhydrous ether or carbon bisulphide, it forms small, colorless crystals, containing no water of crystallization, but likewise belonging to the rhombic system.

Codeine, when previously deprived of its water of crystallization, melts at 150° C. (302° F.), and solidifies upon cooling in a crystalline form; when strongly heated upon platinum foil, it is decomposed with the evolution of inflammable vapors, and is finally completely dissipated. It is soluble in 80 parts of water at 15° C. (59° F.), and in 17 parts of boiling water, in 6 parts of ether, in 10 parts of benzol, and freely soluble in alcohol, amylic alcohol, chloroform, and carbon bisulphide, but very sparingly soluble in petroleum benzin; when heated with less water than is required for solution, or when dropped into boiling water, it sinks to the bottom, and melts in the form of an oily liquid. It is also readily soluble in dilute acids, with the formation of well crystallizable salts, which are soluble in water and alcohol, but nearly insoluble in ether, and possess a strongly bitter taste.

The aqueous solution of codeine has a very bitter taste and strongly alkaline reaction, precipitating from neutral solutions of the salts of lead, iron, copper, cobalt, and nickel, their respective hydrates; and is itself precipitated by the ordinary alkaloidal reagents: potassio-mercuric iodide, iodinized potassium iodide, tannic acid, platinic chloride, etc., as also from its saturated solution by concentrated solutions of potassium or sodium hydrate, but remains unchanged upon the addition of ammonia-water, in which liquid it is nearly as soluble as in pure water.

When a cold saturated aqueous solution of codeine is carefully neutralized with dilute sulphuric acid, it affords no coloration with a neutral solution of ferric chloride, and does not reduce iodine from a solution of iodic acid (distinction from morphine); neither does it afford any coloration, or but a slight brownish one, upon the gradual addition of concentrated sulphuric acid, and subsequent addition of a trace of potassium bichromate (distinction from strychnine).

Nitric acid, of the spec. grav. 1.200, dissolves codeine with a yellow color, without becoming red (additional evidence of the absence of morphine). With concentrated sulphuric acid it forms a colorless solution, which, upon warming, assumes a green or bluish coloration, and, after being allowed to cool, yields, upon the addition of a drop of nitric acid, a blood-red color. With concentrated sulphuric acid, containing a trace of ferric oxide in solution, it affords a deep blue color, which, upon warming, changes to violet or red. When dissolved in concentrated sulphuric acid, and one or two drops of a concentrated solution of cane-sugar are added, and gently warmed, a fine purplish-red coloration is produced. With concentrated sulphuric acid, containing a little ammonium molybdate, it affords a green solution, soon changing to blue, and gradually becoming yellow. It dissolves in chlorine-water, forming a colorless solution, which, upon the addition of ammonia, becomes yellowish-red.

When equal parts of codeine and iodine are dissolved separately in the smallest possible quantity of alcohol, and the solutions mixed, small, deep violet-colored crystals of *codeine tri-iodide*, $C_{18}H_{21}NO_3.I_3$, are separated upon standing; they possess an almost metallic lustre, are insoluble in water and ether, but dissolve with a reddish-brown color in alcohol.

When heated with concentrated hydrochloric acid, in a sealed tube, codeine is resolved into methyl chloride and *apomorphine hydrochlorate:*

$$\underbrace{C_{18}H_{21}NO_3}_{\text{Codeine.}} + 2HCl = H_2O + CH_3Cl + \underbrace{C_{17}H_{17}NO_2.HCl.}_{\text{Apomorphine hydrochlorate.}}$$

With glacial acetic acid or acetic anhydride, codeine is readily converted into *aceytl-codeine:*

$$\underbrace{C_{18}H_{21}NO_3}_{\text{Codine.}} + C_2H_4O_2 = H_2O + \underbrace{C_{18}H_{20}(C_2H_3O)NO_3.}_{\text{Acetyl-codeine.}}$$

Codeine hydrochlorate, when heated for a short time at 180° C. (356° F.) with a concentrated solution of zinc chloride, is converted into *apocodeine hydrochlorate:*

$$\underbrace{C_{18}H_{21}NO_3.HCl}_{\text{Codeine hydrochlorate.}} = H_2O + \underbrace{C_{18}H_{19}NO_2.HCl.}_{\text{Apocodeine hydrochlorate.}}$$

Codeine in its composition and chemical characters may be regarded as methyl-morphine, $C_{17}H_{18}(CH_3)NO_3$. It is distinguished from morphine by its ready solubility in ether and chloroform, and greater solubility in water, as also by affording no precipitate with solution of mercuric chloride, by not reducing iodine from a solution of iodic acid, and other special tests; it is distinguished from narcotine in not being precipitated by ammonia-water from an aqueous solution of its salts, and by not being absorbed by chloroform from an acid solution of its salts, as also by the special chemical tests and reactions.

The above described characteristics of codeine are sufficient to ascertain its identity and purity. Fraudulent admixtures, like sugar-crystals, or crystallized inorganic salts, are at once indicated by their ready solubility in cold water, and by their insolubility in alcohol and ether, and the latter also by a fixed residue upon incineration on platinum-foil.

For the separation of codeine from other alkaloids, or when associated with complex organic mixtures, see page 108.

COLCHICINA.

COLCHICINUM.

Colchicine.

Ger. Colchicin; Fr. Colchicine; Sp. Colchicina.

$C_{17}H_{23}NO_6$; 337.

An amorphous, yellow, or yellowish-white mass or powder, possessing a feebly aromatic odor, a very slight alkaline reaction, and a persistent, strongly bitter taste. It melts at 145° C. (293° F.), acquiring thereby a brown color, and solidifies on cooling, to a transparent brittle mass; when heated upon platinum-foil, it melts and burns away, with intumescence, leaving no residue, or but slight traces of ash.

Colchicine is freely soluble in water, alcohol, and chloroform, but very sparingly soluble in ether. Its aqueous solution has a bright yellow color, which becomes more intense upon the addition of alkalies or mineral acids, and a very bitter, but not an acrid taste; it is precipitated by tannic acid, phospho-molybdic acid, and iodinized potassium iodide, and assumes with ferric chloride a dark green coloration; but with potassio-mercuric iodide, potassio-cadmic iodide, and picric acid, no precipitate or but a faint turbidity is produced, until after the addition of a mineral acid; with chlorine-water, a yellow precipitate is produced, which dissolves in ammonia-water with an orange-yellow color.

Colchicine, when added to concentrated sulphuric acid, in a dry test-tube, agglomerates, and, upon agitation, dissolves with an intense yellow color; upon the subsequent addition of a drop of nitric acid, a dark-brown zone is produced, which gradually changes to violet, and becomes finally yellow; the reaction being more distinct and the violet coloration more permanent when, instead of nitric acid, a little potassium nitrate is employed.

When brought in contact with a few drops of very concentrated nitric acid, in a small porcelain capsule, a violet or bluish-violet coloration is produced, which soon changes to a brownish-red; upon the subsequent addition of a little water, a bright yellow solution is obtained, which, upon supersaturation with an alkali, assumes a fine orange-yellow or orange-red color. With moderately concentrated nitric acid, colchicine produces simply a yellow coloration, but if a little concentrated sulphuric acid be subsequently carefully added, a transitory, but pure violet coloration will be produced at the point of contact of the two liquids.

Colchicine, by long-continued exposure to the air, or upon warming, is converted, through the loss of water and ammonia, into an amorphous, dark-brown, resinous body, very sparingly soluble in water, *colchicoresin*, $C_{51}H_{60}N_2O_{15}$.

$$\underbrace{3(C_{17}H_{23}NO_6)}_{\text{Colchicine.}} = \underbrace{C_{51}H_{60}N_2O_{15}}_{\text{Colchicoresin.}} + NH_3 + 3H_2O.$$

By the action of dilute mineral acids in the cold, or more quickly upon heating, colchicine is converted into crystallizable *colchiceine*, associated with small and varying amounts of an amorphous, dark-brown, resinous product, insoluble in water and ether, *beta-colchicoresin*, $C_{34}H_{39}NO_{10}$.

$$\underbrace{C_{17}H_{23}NO_6}_{\text{Colchicine.}} = \underbrace{C_{17}H_{21}NO_5}_{\text{Colchiceine.}} + H_2O.$$

Colchiceine, $C_{17}H_{21}NO_5 + 2H_2O$, crystallizes in small, colorless, rhombic tables or prisms, which melt at 150° C. (302° F.), and solidify upon cooling to an amorphous, yellow, brittle mass; it possesses a taste less bitter than that of colchicine, and a slightly acid reaction.

Colchiceine is sparingly soluble in cold, more readily in hot, water, and freely soluble in alcohol, chloroform, and solutions of the alkalies, but is difficultly soluble in ether; its alcoholic solution deviates the plane of polarization to the left, and possesses a slight acid reaction. When heated for some time with water, at a temperature of 100° C. (212° F.), it is converted into a yellowish-brown, uncrystallizable mass, and is apparently thereby inversely converted into colchicine. Its aqueous solution assumes a yellow color upon the addition of mineral acids, and, upon boiling therewith, is decomposed, with the separation of a brownish resin; it is not precipitated by tannic acid, except upon standing, and affords no precipitate with potassio-mercuric iodide or picric acid, even upon the addition of an acid, but, like colchicine, assumes a bright green color upon the addition of a dilute solution of ferric chloride.

Colchiceine combines with bases to form salts, which are amorphous, and, with the exception of the potassium and sodium compounds, insoluble in water, but readily soluble in alcohol and chloroform.

Colchicine is a very indifferent substance, being capable of combining with proportionately few, and apparently with no acid bodies, to form a definite chemical compound, and possesses but few properties which are common to the group of organic bases. It is prominently distinguished from most alkaloids by being absorbed from its acid solutions by ether, chloroform, and amylic alcohol, and may thus be readily separated from them, or from other complex organic principles with which it may be associated, as described on page 106.

CONIINA.

CONIINUM.

Coniine. Conia.

Ger. Coniin; Fr. Conicine; Sp. Conicina.

$$C_8H_{15}N = C_8H_{14}{=}NH;\ 125.$$

A colorless, transparent, oily-looking, volatile fluid, becoming brown and darker upon exposure to warmth and air; it has a strong, penetrating odor, resembling that of a combination of the odors of tobacco and mice; its taste is acrid, somewhat like that of oil of tobacco, and it is exceedingly poisonous. When dropped upon paper, coniine produces, like an essential oil, only a transient stain, which by a gentle warmth entirely disappears. It burns with a bright, smoky flame, and, when heated upon platinum-foil, is entirely dissipated.

The spec. grav. of coniine is 0.846 at 12.5° C. (54.5° F.); when dropped upon water, it floats (distinction from nicotine). In an atmosphere free from oxygen, it boils at 170° C. (338° F.) without decomposition.

Coniine combines at 2° C. (35.6° F.) with one-fifth of its weight of water, forming a clear solution, which, however, becomes turbid by elevation of temperature, and assumes a cloudy appearance when a glass vessel containing it is heated by the warmth of the hand (additional distinction from nicotine). It is but sparingly soluble in water, one part requiring at 17° C. (62.6° F.) 100 parts of water for solution; the saturated solution has a strongly alkaline reaction, becomes turbid when warmed, turns brown when exposed to the air, and gradually deposits a brown resinous mass; it forms precipitates with tannic acid, potassio-mercuric iodide, iodinized potassium iodide, mercuric chloride, and picric acid, as also with chlorine, bromine, and iodine-water, but not with platinic chloride.

Coniine dissolves readily in water acidulated with hydrochloric acid, and is miscible with alcohol, amylic alcohol, ether, and aceton, as also with the fixed and volatile oils, but is sparingly soluble in chloroform and petroleum benzin; it decomposes carbon bisulphide, particularly upon warming, the solution assuming a yellow color, with the separation of sulphur.

When coniine is carefully neutralized with hydrochloric acid, and the resulting salt dissolved in alcohol, it affords upon the addition of platinic chloride a precipitate of the double salt $(C_8H_{15}N.HCl)_2PtCl_4$, which is very freely soluble in water, but may be crystallized from alcohol.

Coniine readily dissolves sulphur, with the formation of a reddish-yellow liquid, as also argentic oxide and chloride, and resembles ammonia in its behavior towards solutions of the salts of aluminium and the heavy metals; it precipitates the hydrates or oxides from solutions of the salts of aluminium, tin, mercury, copper, silver, lead, zinc, iron, and manganese, but the precipitate produced in solutions of cupric salts is insoluble in an excess of coniine (distinction from ammonia).

Coniine neutralizes diluted acids completely with the formation of neutral salts, which are mostly difficultly crystallizable and deliquescent, readily soluble in water, alcohol, and in a mixture of ether and alcohol, but not in pure ether. Although odorless in their dry condition, the aqueous solutions of salts of coniine are very prone to decomposition, soon becoming discolored, even at ordinary temperatures, and evolving the odor of coniine.

Coniine produces white fumes with the vapors of nitric, hydrochloric, and acetic acids, and is rapidly decomposed in contact with the concentrated mineral acids. With concentrated sulphuric acid, it assumes a purplish-red color, which gradually changes to olive-green. With a very small amount of concentrated nitric acid, a blood-red coloration is produced; upon the addition of large amounts of the acid, a violent reaction ensues, with the evolution of nitrous acid vapors. In contact with dry chromic anhydride, coniine becomes instantly inflamed.

When coniine, dissolved in a little ether, is allowed to evaporate in a small porcelain capsule, by swaying it to and fro, and the residue, distributed over the interior surface of the capsule, is brought in contact with dry hydrochloric acid gas, a purplish-red, and finally an indigo-blue coloration is produced.

The alkaline hydrates do not act upon coniine, with the exception of decreasing its solubility in water.

Examination:

An admixture of *volatile* or *fixed oils*, or of *ammonia* (which may also have resulted from the gradual decomposition of the coniine), may be detected by mixing one drop of coniine with 10 drops of water, upon a watch-glass or in a test-tube, and by the subsequent addition of one drop of strong hydrochloric acid; the coniine should readily and wholly dissolve to a clear homogeneous liquid; any turbidity or oily appearance would indicate such an admixture. If, now, a few drops of a solution of platinic chloride are added, a yellow crystalline precipitate will be produced if ammonia is present. The presence of ammonia may also be detected by mixing 2 parts of coniine with 1 part of water, and subsequently carefullly neutralizing the mixture with oxalic acid; after standing for some hours, crystals of ammonium oxalate will separate from the solution if ammonia be present, and the filtrate will afford an additional amount of the salt upon the addition of a mixture of one part of ether and three parts of alcohol; pure coniine oxalate is soluble in the latter liquid as also in strong alcohol.

Nicotine will be indicated by a higher specific gravity (1.027 at 15° C. = 59° F.), as also by its property of mixing with water in all proportions, forming clear solutions, which do not become turbid upon warming, nor upon the addition of chlorine-water, or in contact with bromine vapor, but afford a crystalline precipitate upon the addition of a solution of platinic chloride.

The separation of coniine from many other alkaloids or from complex organic matters, may be effected by its property of being absorbed by ether from an alkaline solution, as described on page 108; and may usually be readily recognized by its characteristic odor, and the above-described physical and chemical properties. It should, however, in toxicological research, be carefully identified as distinct from the class of bodies called *ptomaines* or *septicine*, which are produced by the spontaneous decomposition of animal matter, and which have received brief notice on pages 104 and 105.

CREASOTUM.

CREOSOTUM. KREOSOTUM.

Creasote. Wood-Tar Creasote.

Ger. Kreosot; Fr. Créosote; Sp. Creosota.

A distinction has to be made with commercial creasote between the creasote obtained from wood-tar and that derived from coal-tar; the latter is principally a mixture of impure phenol, cresol, and similar homologous phenols, or only an impure carbolic acid, and exhibits the properties and reactions of carbolic acid (*see* page 139), whereas wood-tar creasote, although not a substance of definite or constant composition, contains as its essential constituents, *cresol*, $C_6H_4(CH_3)OH$, in its different isomeric modifications, *phlorol*, $C_6H_3(CH_3)_2OH$ or $C_6H_4(C_2H_5)OH$, *guaiacol*, $C_6H_4(OCH_3)OH$, and *creosol*, $C_6H_3(OCH_3)(CH_3)OH$.

Wood-tar creasote is a colorless or pale yellow, transparent, somewhat oily and strongly refractive liquid, of a peculiar, persistent odor, resembling that of smoked meat, and of a caustic, pungent taste; it is neutral in its action upon litmus, and does not decompose by exposure to the air and light, but absorbs moisture, and becomes in time yellowish or reddish. It is combustible, and burns with a sooty flame.

The specific gravity of wood-tar creasote is 1.035 to 1.085 at 12° C. (53.6° F.), and its boiling-point at about 203° C. (397.4° F.), but it does not crystallize, nor solidify, when its temperature is reduced to —27° C. = —16.6° F. (distinction from coal-tar creasote).

Wood tar creasote is but sparingly soluble in water; when mixed with from 120 to 150 parts of hot water, it affords a clear solution, which, however, becomes turbid on cooling, and gradually, after the separation of the excess of creasote, again clear. It is miscible with absolute alcohol, ether, chloroform, benzol, glacial acetic acid, carbon bisulphide, and with fixed and volatile oils, and some varieties form a clear mixture with anhydrous glycerin, while others do not. It is also readily soluble in moderately concentrated or strong solutions of potassium or sodium hydrate, but sparingly soluble in ammonia-water; when mixed with a little ether, it affords, upon the addition of a concentrated alcoholic solution of potassium hydrate, a crystallizable compound of potassium creosolate, $KC_8H_9O_2 + H_2O$ ($C_6H_3(OCH_3)CH_3OK + H_2O$), which is soluble in water; it is decomposed by heating with an alcoholic solution of potassium or sodium hydrate. as also by contact with cold, concentrated sulphuric or nitric acid.

Wood-tar creasote dissolves phosphorus, sulphur, many resins, camphor, and fats; it does not coagulate albumen nor collodion (distinction from carbolic acid), and is a powerful antiseptic and antiputrescent.

A freshly prepared, clear, aqueous solution of wood-tar creasote assumes, upon the addition of a drop of a dilute solution of ferric chloride, a bright blue color, which, however, in distinction to the coloration produced by carbolic acid, changes immediately to gray, and, upon the addition of alcohol, to green.

Examination:

Carbolic acid, or *coal-tar creasote*, in their physical properties and behavior towards reagents, have many similarities with wood-tar creasote, so that they may be either mistaken for, or employed as an adulterant of, the latter. The two classes of bodies may be very readily distinguished when in their pure condition, but the reverse is the case when the one is mixed or contaminated with the other, whereby the characteristic reactions of each are more or less concealed. The examination of wood-tar creasote for its purity, and for the determination of the absence of any considerable proportion of carbolic acid, or coal-tar creasote, may, however, be directed to the following tests. Wood-tar creasote should require not less than 120 parts of cold water for solution, and should boil at a temperature not below 200° C. (392° F.). It should not dissolve when shaken with five times its weight of stronger ammonia-water.

When one part of wood-tar creasote, and one part of stronger ammonia-water, are heated with one thousand parts of water, the solution, after cooling, should afford, in contact with the vapor of bromine, and subsequent agitation, no blue coloration, even after standing for several hours. This test will serve to detect the presence of carbolic acid in wood-tar creasote, in amounts of not less than 2.5 per cent.

The following distinctions between the two bodies may be also observed:

Wood-tar creasote remains liquid when cooled in a mixture of broken ice and common salt; coal-tar creasote and carbolic acid either solidify or deposit crystals at such temperatures.

Wood-tar creasote, when mixed and shaken with collodion, produces a clear liquid; carbolic acid and coal-tar creasote form a kind of jelly.

The admixture of *volatile* or *fixed oils* and *oily impurities* may be detected when one part of the creasote is agitated with three parts of strong acetic acid; a clear solution must take place; a residual oily layer or oily appearance would indicate such admixtures.

CUPRI ACETAS.

CUPRUM ACETICUM.

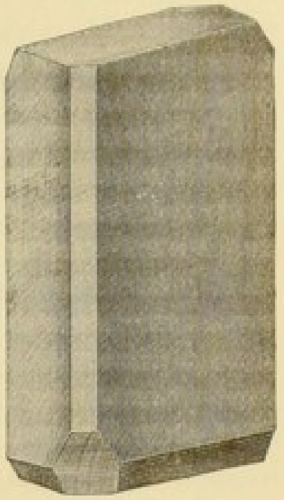
Acetate of Copper. Cupric Acetate.

Ger. Essigsaures Kupferoxyd; Fr. Acetate neutre de cuivre; Sp. Acetato de cobre.

$$Cu(C_2H_3O_2)_2 + H_2O;\ 199.2.$$

Deep green, prismatic crystals, belonging to the monoclinic system (Fig. 112), having a specific gravity of 1.914, and slightly efflorescent on exposure to the air. They contain one molecule (9.03 per cent.) of water of crystallization, which, together with traces of acetic acid, is lost by drying at 140° C. (284° F.); at 240 to 260° C. (464 to 500° F.) acetic acid and aceton are evolved, and at 270° C. (518° F.) white, woolly flakes of cuprous acetate, $Cu_2(C_2H_3O_2)_2$, begin to sublime, together with the evolution of carbonic acid and inflammable gases, whilst a residue, consisting, for the most part, of metallic copper and its oxides, remains. When strongly heated upon platinum foil, the crystals glimmer with a greenish-colored flame, and when triturated, or gently warmed in a test-tube, with concentrated sulphuric acid, the odor of acetic acid is evolved.

FIG. 112.



Cupric acetate is soluble in 15 parts of water and in 135 parts of alcohol at 15° C. (59° F.), in 5 parts of boiling water, and in 14 parts of boiling alcohol, spec. grav. 0.830, but is insoluble in ether; its solutions have a bluish-green color, a nauseous, styptic taste, and assume, when much diluted with water, an azure-blue color upon the addition of an excess of ammonia-water or solution of ammonium carbonate, the cold solution remaining clear upon the subsequent addition of a solution of potassium hydrate, but, upon heating therewith, the entire amount of copper is precipitated as black, hydrated cupric oxide.

When cupric acetate is dissolved to saturation in dilute acetic acid, at 60° C. (140° F.), the cold solution affords large prismatic crystals of a salt having the composition $Cu(C_2H_3O_2)_2+5H_2O$; at 30° C. (86° F.) this salt is resolved into a crystalline powder of the ordinary acetate, with the elimination of water.

Examination:

Alkalies and *alkaline earths* may be detected by completely precipitating the aqueous solution of cupric acetate, acidulated with hydrochloric acid, by hydrogen sulphide; the filtrate should leave no residue upon evaporation, and should yield no precipitate upon the addition of a solution of sodium carbonate in excess; in the latter instance confirming also the absence of *aluminium*, *zinc*, and *iron*.

Metallic impurities may be detected by completely precipitating a boiling aqueous solution of the salt with potassium or sodium hydrate; the filtrate should afford no coloration or precipitate when saturated with hydrogen sulphide; a dark coloration or precipitate would indicate *lead*, a white precipitate, *zinc*.

Carbonic, *sulphuric*, and *hydrochloric acids* may be detected by dissolving a little of the salt in dilute nitric acid; effervescence will indicate *carbonates;* the clear solution is then tested in separate portions, with barium chloride for sulphuric acid, and with argentic nitrate for hydrochloric acid; a white precipitate in either case will reveal the presence of such impurities.

Arsenic, the presence of which may be due to an accidental admixture with *Schweinfurth green* (a mixture of cupric acetate with arsenite), or *Scheele's green* (cupric arsenite), may be detected by dissolving a little of the salt in diluted sulphuric acid, and testing in Marsh's apparatus, as described on page 33; or, by the repeated evaporation of the cupric acetate to dryness with ammonia-water, and finally extracting the residue with hot water, as long as it thereby affords a colorless liquid upon filtration; the filtered solution, which will then contain the arsenic, if present, in the form of arsenic acid, will respond to the well-known tests of the latter.

Cupri Subacetas.—*Aerugo* or *verdigris* is a mixture of several basic cupric acetates with various impurities; it occurs in masses of a pale-green or bluish color, or in bluish crystalline scales or needles, which, upon gently heating, or by exposure to the air, assume, in consequence of the loss of water, a green color. When heated upon charcoal before the blow-pipe, it becomes decomposed, with the evolution of inflammable vapors, leaving a residue of metallic copper. When heated in a test-tube, with concentrated sulphuric acid, it emits acetic-acid vapors. Water resolves verdigris into a more freely soluble, less basic acetate, and an insoluble, more strongly basic salt; the decomposition takes place more quickly upon gently warming, and may be represented essentially by the following equation:

$$3[Cu(C_2H_3O_2)_2 + Cu(OH)_2] = [Cu(C_2H_3O_2)_2 + Cu(OH)_2] + [Cu(C_2H_3O_2)_2 + 2Cu(OH)_2].$$

Verdigris is soluble in diluted acetic, hydrochloric, nitric, and sulphuric acids, and in an excess of ammonia-water or solution of ammonium carbonate; the insoluble residue consists mainly of impurities, among which calcium carbonate (crude chalk) is recognized by effervescence of the verdigris with acids. For further examination, its solution in diluted hydrochloric acid is completely precipitated by hydrogen sulphide; the filtrate should leave no residue upon evaporation, nor afford a precipitate when supersaturated with sodium carbonate; a residue and a brown precipitate would indicate *alkaline salts* or *earthy admixtures*, or *iron*.

CUPRI OXIDUM.

CUPRUM OXYDATUM.

Black Oxide of Copper. Cupric Oxide.

Ger. Kupferoxyd; Fr. Bioxyde de cuivre; Sp. Oxido de cobre.

CuO; 79.2.

A dense, black powder, when prepared by the ignition of cupric nitrate; or a less dense, bluish-black, soft powder, when obtained by the ignition of cupric carbonate or by precipitation. It remains unaltered when heated to redness, is insoluble in water and alcohol, but slightly soluble in saliva and in the gastric juice, and readily soluble in acids; its solutions have a blue or greenish-blue color, and they assume, when so much diluted as to appear almost colorless, an azure-blue color upon the addition of ammonia-water, and a brownish-red color with potassium ferrocyanide.

When heated upon charcoal, before the blow-pipe, cupric oxide is readily reduced to metallic copper. It has a strong affinity for moisture, and should therefore be preserved in tightly closed vessels.

Cupric oxide, when prepared by precipitation, is readily and completely soluble in a warm solution of ammonium chloride (distinction from ferric oxide).

Examination:

Cupric nitrate is recognized, in the oxide, by the evolution of acid nitrous vapors, when heated, in a test-tube, either dry, or with concentrated sulphuric acid; if they are not distinctly recognized by the odor, they are by their action upon moist blue litmus-paper, when held in the orifice of the tube.

Metallic Impurities.—A portion of the oxide is dissolved in warm concentrated hydrochloric acid, the solution diluted with water, and the copper completely precipitated by hydrogen sulphide; the liquid, rapidly filtered from the precipitate of cupric sulphide, should leave no residue upon evaporation, and yield no precipitate upon supersaturation with sodium carbonate; an ensuing precipitate would indicate metallic (ferric) or earthy oxides.

Carbonic, *hydrochloric*, and *sulphuric acids* may be detected by dissolving a little of the cupric oxide in nitric acid; effervescence will indicate *carbonates;* the clear solution is then diluted with water, and tested in separate portions, with barium chloride for sulphuric acid, and with argentic nitrate for hydrochloric acid; an ensuing white precipitate in either case will reveal the presence of such impurities.

CUPRI SULPHAS.

CUPRUM SULFURICUM.

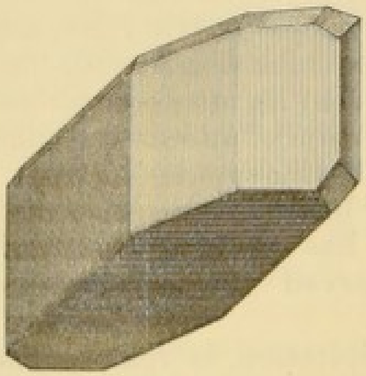
Sulphate of Copper. Cupric Sulphate. Blue Vitriol.

Ger. Schwefelsaures Kupferoxyd; Fr. Sulfate de cuivre; Sp. Sulfato de cobre.

$CuSO_4 + 5H_2O$; 249.2.

Large, transparent crystals, of a deep blue color, belonging to the triclinic system (Fig. 113), and having a specific gravity of 2.277. They contain five molecules (36.08 per cent.) of water of crystallization, effloresce slightly upon the surface by exposure to a very dry atmosphere, and lose four molecules (28.9 per cent.) of water when heated for some time to 100° C. (212° F.), leaving a salt of the composition $CuSO_4 + H_2O$, in the form of a bluish-white powder; at a temperature of from 220 to 240° C. (428 to 464° F.) the remaining molecule of water is eliminated, and at a white heat the salt is decomposed, with the evolution of sulphur trioxide, sulphur dioxide, and oxygen, leaving a residue of black cupric oxide. The anhydrous salt is colorless, but absorbs moisture with great avidity, assuming again a blue color.

FIG. 113.



Cupric sulphate is soluble in 2.6 parts of water at 15° C. (59° F.), and in 0.55 part of boiling water, but is insoluble in absolute alcohol and ether, and very sparingly soluble in dilute alcohol. Its solution has an acid reaction, a strong metallic, styptic taste, and, when diluted with so much water as to make it appear almost colorless, reassumes a blue color upon the addition of ammonia-water; it gives a white precipitate with barium chloride, a reddish-brown one with potassium ferrocyanide, and a green one with arsenious and arsenic acids upon subsequent exact neutralization of the liquid with ammonia-water.

Examination:

Ferrous sulphate is recognized by dissolving the sulphate in diluted ammonia-water, or, in solutions, by adding an excess of ammonia-water; the ferrous hydrate is precipitated together with the cupric hydrate, without, however, being redissolved by an excess of the reagent.

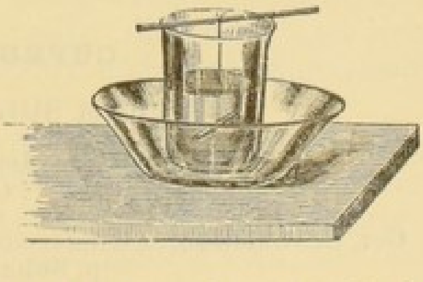
Traces of iron may be detected by mixing an aqueous solution of the salt with twice its volume of chlorine-water, and by the subsequent addition of ammonia-water; the precipitate, formed by the first addition of the ammonia-water, will be dissolved by a sufficient addition of the reagent, yielding a complete violet-blue solution. This is then filtered, and, when all the liquid has passed through the filter, the latter is washed with a little dilute ammonia-water; a brown coating, remaining upon the filter, would indicate traces of iron salts.

Aluminium, Magnesium, Zinc, Potassium, and Sodium Sulphates.—A small portion of the cupric sulphate, taken from a number of triturated crystals, is dissolved in about ten times its weight of water, the solution acidulated with hydrochloric acid, and the copper completely precipitated by hydrogen sulphide; the liquid is then rapidly filtered from the precipitate of cupric sulphide, and the filtrate evaporated to dryness, when no residue should remain; if a residue is thus obtained, it is dissolved in a little water, the solution acidulated with a few drops of hydrochloric acid, and ammonia-water, in considerable excess, subsequently added; a white flocculent precipitate, insoluble in an excess of ammonia-water, will indicate *aluminium;* the liquid filtered from the latter precipitate, if such be obtained, is then tested in separate portions with ammonium sulphide and with sodium phosphate; a white precipitate with the first reagent would indicate *zinc*, a white crystalline precipitate with the latter reagent, *magnesium*. If neither of these be present, the above obtained residue should be tested for *potassium* and *sodium* sulphates, which may be recognized by the violet or bright yellow coloration imparted to the non-luminous flame.

Estimation of Commercial Crude Cupric Sulphate:

The following is a simple and ready method of ascertaining the percentage of cupric sulphate contained in crude blue vitriol, some inferior kinds of which are largely crystallized together with ferrous sulphate: About ten grams of the salt, taken from a portion of the mixed and triturated crystals, are dissolved, in a small tared glass capsule or beaker, in ten times their weight of water; when necessary, the solution is filtered, and the filter washed with a small portion of water; the filtrate is returned to the beaker, is acidulated with about five grams of concentrated hydrochloric acid, and then a piece of a thin zinc rod, about one inch long, is suspended in the solution by a very thin platinum-wire (Fig. 114); the beaker is then allowed to stand perfectly quiet for twenty-four hours. After that time, the copper will have precipitated as a bright, spongy mass, around the zinc rod. In order to ascertain if the precipitation has been complete, a few drops of the solution are taken by a glass rod or a pipette, and dropped into a little ammonia-water, or tested with a solution of potassium ferrocyanide, or with water saturated with hydrogen sulphide: they will

FIG. 114.



produce a blue coloration in the first instance, and a reddish-brown or brown turbidity with the latter reagents, if any copper is left in solution. The copper is then carefully and completely removed from the zinc rod by means of a camel's-hair brush, and, if necessary, the apparatus is allowed, after the addition of a little diluted hydrochloric acid, to stand for twenty-four hours more; then, when the copper is completely abstracted from the solution, it is brushed down into the liquid, and washed from the zinc by means of a wash-bottle; the zinc is now removed, a little diluted hydrochloric acid added, and the copper allowed to deposit; when this has taken place, the supernatant liquid is carefully removed by decantation, or by means of a pipette, and water is added and removed in the same manner as soon as the copper has subsided; this washing is repeated several times, until the water ceases to redden litmus-paper, the copper being finally washed with strong alcohol. Then the beaker with the copper is completely dried at a temperature of 100° C. (212° F.), and is finally weighed. The weight gives the quantity of metallic copper, and, multiplied by 2.542, the corresponding quantity of crystallized cupric sulphate, contained in ten grams, or the amount of the blue vitriol employed.

TABLE *of the percentage strength of solutions of crystallized Cupric Sulphate* ($CuSO_4+5H_2O$) *of different specific gravities.*

Temperature 15° C. (59° F.).

Per cent. of $CuSO_4+5H_2O$.	Specific gravity.	Per cent. of $CuSO_4+5H_2O$.	Specific gravity.	Per cent. of $CuSO_4+5H_2O$.	Specific gravity.
1	1.007	9	1.062	17	1.121
2	1.013	10	1.069	18	1.129
3	1.020	11	1.076	19	1.137
4	1.027	12	1.084	20	1.144
5	1.033	13	1.091	21	1.152
6	1.040	14	1.099	22	1.160
7	1.048	15	1.106	23	1.169
8	1.055	16	1.114	24	1.177

CUPRUM AMMONIATUM.

CUPRUM SULFURICUM AMMONIATUM.

Ammoniated Copper. Ammonio-Sulphate of Copper. Ammoniated Cupric Sulphate.

Ger. Schwefelsaures Kupfer-ammonium; Fr. Sulfate de cuivre ammoniacal; Sp. Sulfato de cobre ammoniacal.

$$CuSO_4 + 4NH_3 + H_2O;\ 245.2.$$

A deep azure-blue, crystalline powder, or long, thin, transparent prisms of the rhombic system, and possessing an ammoniacal odor. The crystals, upon exposure to the air, lose ammonia and water, and are gradually transformed into ammonium sulphate and basic cupric salphate; when gently heated to 150° C. (302° F.), they are converted into a powder of an apple-green color, having the composition $CuSO_4 + 2NH_3$.

Ammoniated cupric sulphate is soluble in about two parts of cold water, affording a fine blue solution; incomplete solubility indicates partial decomposition. When the solution is diluted largely with water, it becomes turbid, and separates basic cupric sulphate, which, however, is redissolved upon the addition of ammonia-water or of acids, whilst ammonium sulphate remains in solution.

The salt may be examined, by determining the loss of weight occasioned by ignition at a gentle heat, which should amount to 35.1 per cent.; the residue, consisting of cupric sulphate, when dissolved in water, should respond to the tests of purity for the latter salt, as described on pages 330–331.

CURARINA.

CURARINUM.

Curarine. Curaria.

Ger. Curarin; Fr. Curarine; Sp. Curarina.

$C_{36}H_{35}N$; 481?

Colorless, four-sided prisms, which are very hygroscopic, and possess a slightly alkaline reaction, and an intensely bitter taste. When gently heated they are decomposed, with the evolution of ammoniacal vapors, and when strongly heated, on platinum-foil, they are completely dissipated.

Curarine is soluble in all proportions in alcohol and water, sparingly soluble in amylic alcohol and chloroform, and quite insoluble in anhydrous ether, benzol, and carbon bisulphide. It neutralizes acids with the formation of salts, which, however, are mostly uncrystallizable, or crystallize with difficulty, and are quite unstable; the chromate is amorphous, and is characterized by its very sparing solubility in water.

An aqueous solution of curarine, when carefully neutralized with acetic acid, is precipitated by tannic acid, potassio-mercuric iodide, auric and platinic chlorides, and most alkaloidal reagents; it affords a copious yellow precipitate with picric acid, and an orange-yellow precipitate with potassium chromate.

Curarine dissolves in concentrated sulphuric acid with a pale violet color, which gradually changes to a dirty-red, and after some hours assumes a rose-red color. If, to the solution in sulphuric acid, a crystal of potassium bichromate be added, a bluish-violet coloration will be produced at the points of contact, but which differs from the similar reaction of strychnine, produced under the same circumstances, by its greater permanence. With concentrated sulphuric acid, containing a trace of nitric acid, it produces at first a brownish-violet, and finally a pure violet coloration.

Curarine is distinguished from most alkaloids from the fact of its not being absorbed, either from an acid or an alkaline solution, by ether, petroleum benzin, chloroform, or amylic alcohol. Its identification and purity may be established by the consideration of the above-described behavior towards reagents and solvents; and its freedom from inorganic matter by the absence of any non-volatile residue, when strongly heated upon platinum-foil.

For the separation of curarine from other alkaloids, or for its isolation when associated with other complex organic principles, see page 111.

DIGITALINUM.

Digitalin.

Ger. Digitalin ; Fr. Digitaline ; Sp. Digitalina.

Commercial digitalin varies somewhat in its physical and chemical properties, in consequence of different modes of preparation and different grades of purity, and consists usually of a complicated mixture of several distinct principles, with their products of decomposition.

German digitalin, which is mostly used in the United States, forms yellowish-white or yellowish-brown porous scales, or a yellowish powder, inodorous, and of an intensely bitter taste; heated upon platinum-foil, it burns off slowly, with intumescence. It is soluble in water, forming a turbid, neutral liquid, which froths upon agitation; it is also soluble in alcohol, partly so in chloroform, and insoluble in ether. Its aqueous solution, when slightly acidulated with hydrochloric acid, becomes first turbid, and a flocculent white precipitate soon ensues, especially upon gentle warming. When the liquid, after several hours, is filtered off, and supersaturated with sodium carbonate, it turns blue upon the addition of one drop of dilute solution of cupric sulphate, and, when set aside, in a warm place, deposits, after a while, red cuprous oxide.

When about two drops of the aqueous solution of digitalin are mixed, in a test-tube, with four or five drops of strong hydrochloric or sulphuric acid, the liquid remains at first clear, but, when immersed in boiling water, it turns successively yellow, yellowish-green, and then yellowish-brown, and a precipitate is formed, which, upon addition of water to the liquid, appears white, with a slightly greenish tint; the supernatant liquid shows the same color. After some time, this tint disappears, and the precipitate as well as the liquid becomes colorless. When the same test is performed with a dilute solution of sugar and with hydrochloric acid, a similar reaction takes place, but without the formation of any precipitate.

German digitalin, or the *digitalin of Walz*, is decomposed by boiling with dilute hydrochloric or sulphuric acids, into sugar and *digitaletin*, the latter, by loss of water, being partially converted into *paradigitaletin*, and also, by further decomposition, into sugar and *digitaliretin.*

Digitalin prepared by the process of Homolle and Quevenne, or *French digitalin*, consists, according to the authors, of a mixture of digitalin, digitaline, and digitalose, and forms either a yellowish-white powder, or a white, porous, mammillated mass, or small scales, almost insoluble in cold and warm water and in ether, but readily soluble in alcohol and in acids; it is also soluble in chloroform. If not already purified by solution in chloroform, and subsequent evaporation, as it now occurs in commerce, this digitalin, when treated with chloroform, leaves an insoluble residue, and the solution yields, upon evaporation, a crystallizable digitalin. Its solution in hydrochloric acid is of a faint-yellowish color, but soon changes to green; upon dilution with water, it is decolorized, and digitalin separates in a resinous state. Its solution in nitric acid is at first colorless, but becomes yellow and remains so after subsequent dilution with water. Sulphuric acid dissolves it with a green color, disappearing upon dilution with water. Moistened with sulphuric acid and afterward exposed to the vapor of bromine, it assumes a violet color.

The crystallizable digitalin, or the *digitalein* of *Nativelle*, is obtained from its solution in chloroform in fine, colorless, shining needles, intensely bitter, and, as claimed, of a far greater physiological action; it gives an intense emerald-green coloration with hydrochloric acid, is almost insoluble in benzol and in pure ether, only sparingly soluble in water, soluble in 12 parts of alcohol, and abundantly soluble in chloroform.

This crystallizable digitalin of Nativelle, however, is, according to recent researches, not a simple body, but consists largely of two distinct principles, to which the names of *digitoxin* and *paradigitogenin* have been applied.

Digitoxin, $C_{31}H_{13}O_7$, forms perfectly colorless scales or needle-shaped crystals, insoluble in water, to which it does not even impart its intensely bitter taste, as displayed in the alcoholic solution, and likewise insoluble in benzin and carbon bisulphide; it is sparingly soluble in ether, more abundantly in chloroform, and freely soluble in alcohol, either cold or warm. It is not a glucoside, but is very prone to decomposition by acids, either dilute or strong, and is a powerful poison. When warmed with concentrated hydrochloric acid, it assumes the yellow or greenish hue observed with commercial digitalin; and when decomposed by dilute acids in alcoholic solution, it is converted into *toxiresin*, an uncrystallizable, yellowish substance, readily soluble in ether.

The commercial digitalin has been likewise resolved into three distinct substances, viz., *digitonin*, *digitalin*, and *digitalein*. *Digitonin*, $C_{31}H_{52}O_{17}$, is closely related in its composition and properties to saponin; when boiled with dilute sulphuric acid it yields two glucosidal principles, *digitoresin* and *digitonein*, either of which, by prolonged boiling in alcoholic solution with dilute sulphuric acid, is converted into a crystallizable substance, *digitogenin*, which dissolves in warm concentrated sulphuric acid with a yellowish color, and displays a magnificent green fluorescence; from digitonin a crystallizable principle, *paradigitogenin*, is obtained by the slow fermentation of its solution, which is closely allied to digitogenin, but differs from the latter by assuming a brown color in contact with cold concentrated sulphuric acid. *Digitalin* $C_5H_8O_2$ (Schmiedeberg), forms small, soft, colorless grains, soluble in alcohol, alcohol containing chloroform, and in dilute acetic acid, but is sparingly dissolved by ether or chloroform, and still less by water, even when boiling. It is a very active and poisonous substance, and is the prominent constituent of several kinds of commercial "digitalin," especially that of Homolle and Quevenne. It is a glucoside, and is resolved by the action of acids into glucose and *digitaliresin;* the latter is also a powerful poison, and is capable of being further decomposed into sugar and another body, not yet thoroughly examined. *Digitalein* (Schmiedeberg) bears some resemblance to the digitalin of the same author, but differs therefrom by being freely soluble in water, and forming, like digitonin, a frothing solution; it differs also from digitonin by being readily soluble in absolute alcohol.

Commercial digitalin may be recognized by the following reactions: It is precipitated from its aqueous solution, if not too dilute, by tannic acid; and when a very small portion of it is dissolved in a capsule with concentrated sulphuric acid, and a trace of bromine-water subsequently brought into the liquid, a violet-red coloration is produced. When a trace of digitalin, together with a little purified ox-gall, is dissolved in a little water, in a capsule, a small amount of concentrated sulphuric acid added, and subsequently warmed at from 60 to 80° C. (140 to 176° F.), the solution gradually assumes a fine red color.

Digitalin is further characterized by its property of being absorbed from an acid solution by ether, and much more readily and completely by chloroform. It may thus be separated from most of the alkaloids, and from other complex organic principles with which it may be associated, as described on page 106.

ELATERINUM.

Elaterin.

Ger. Elaterin; Fr. Elatérine; Sp. Elaterina.

$C_{20}H_{28}O_5$; 348.

Small, colorless, shining, hexagonal scales or prisms, without odor, of an extremely bitter, somewhat acrid, taste, and neutral in their action upon litmus. They melt at 200° C. (392° F.), assuming thereby a yellow color, and solidify again upon cooling to a yellowish, amorphous mass; when more strongly heated, upon platinum-foil, they are decomposed, and finally completely dissipated.

Elaterin is insoluble in water or glycerin, soluble in 125 parts of alcohol at 15° C. (59° F.), in 2 parts of boiling alcohol, in 290 parts of ether, and readily soluble in amylic alcohol, carbon bisulphide, and chloroform; it is also soluble in concentrated aqueous solutions of the alkaline hydrates and in ammonia-water, being thereby converted into an acid body, devoid of drastic properties, and which may be separated by supersaturating the solution with a mineral acid.

With cold, concentrated sulphuric acid, elaterin assumes a yellow color, gradually changing to red; when evaporated to dryness with hydrochloric acid, the residue also assumes, with concentrated sulphuric acid, a fine red color. When a few crystals of elaterin are placed in a small porcelain capsule, and a few drops of the liquefied crystals of pure carbolic acid are added, the elaterin is readily dissolved without the production of color; if, however, two or three drops of concentrated sulphuric acid are now allowed to flow into the mixture, an intense and beautiful carmine-red color is developed, changing at first to orange, and, after some time, to scarlet; the color is discharged by alkalies.

Elaterin is not decomposed by boiling with dilute acids (distinction from glucosides); its alcoholic solutions are neutral, and are not precipitated by tannic acid, nor by solutions of metallic salts (distinction from the alkaloids).

EMETINA.

EMETINUM.

Emetine. Emetia.

Ger. Emetin ; Fr. Emétine ; Sp. Emetina.

$C_{28}H_{40}N_2O_5$; 484.

Colorless, hard, needle-shaped or tabular crystals, or a whitish or yellowish-white, inodorous powder, possessing a slightly bitter and acrid taste. The crystals melt at 62 to 65° C. (143.6 to 149° F.). When strongly heated upon platinum-foil, emetine burns with a sooty flame, and is finally completely dissipated.

Crystallized emetine is soluble in about 100 parts of water, more readily soluble in alcohol, ether, chloroform, and diluted acids; it has a strong alkaline reaction, and neutralizes acids with the formation of salts, among which the hydrochlorate has been obtained in a crystalline form, whilst the nitrate, although amorphous, is characterized by its very sparing solubility in water. The aqueous solutions of the salts of emetine, even when quite dilute, are precipitated by tannic acid, potassio-mercuric iodide, platinic and auric chlorides, and most alkaloidal reagents; and with solutions of the alkaline hydrates, carbonates, and bicarbonates, amorphous precipitates of emetine are produced, insoluble in an excess of the precipitant.

Concentrated sulphuric acid dissolves emetine with a green coloration, which soon changes to yellow; with concentrated sulpuric acid containing ammonium molybdate in solution, it forms a red solution, which, however, soon changes to yellowish-green, and, finally, to green. An aqueous solution of emetine assumes, with a few drops of a freshly prepared saturated solution of chlorinated lime, and the subsequent addition of one or two drops of hydrochloric or strong acetic acid, a bright orange or lemon-yellow coloration. If a few drops of hydrochloric acid are poured upon a little potassium chlorate, in a test-tube, and a drop of a solution of emetine is added, an orange-red color, changing to violet, is produced.

Emetine is further more particularly characterized by its strongly emetic properties; it is distinguished from veratrine, which likewise exerts a violent emetic action, by the behavior of the latter towards concentrated sulphuric or hydrochloric acid, and other special tests.

Emetine is absorbed by ether from its alkaline solution, and may thus be separated from many other alkaloids, or from complex organic principles with which it may be associated, in a form sufficiently pure to admit of its subsequent identification, as described on page 108.

FERRI ARSENIAS.

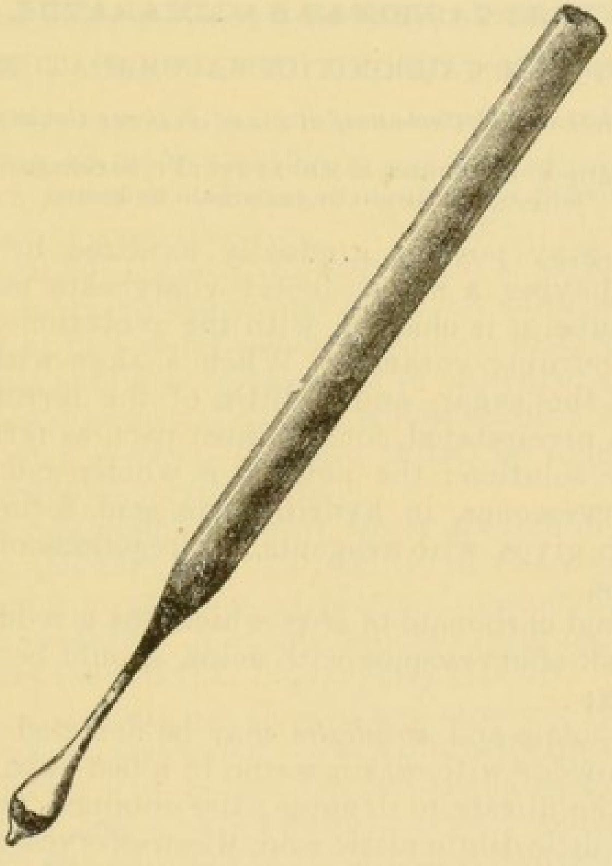
FERRUM ARSENICUM.

Arseniate of Iron. Ferroso-ferric Arseniate.

Ger. Arsensaures Eisonoxyd-oxydul; Fr. Arséniate de fer; Sp. Arseniato de hierro.

When freshly prepared, an amorphous white powder, consisting of ferrous arseniate, but which, owing to the absorption of oxygen and the consequent formation of ferroso-ferric arseniate, quickly assumes a green or greenish-blue color. When heated in a dry test-tube, it first emits aqueous vapor, and afterwards affords a crystalline sublimate of arsenious acid, whilst a dark-colored semi-fused mass remains; when heated upon charcoal, before the blow-pipe, the characteristic alliaceous or arsenical odor is evolved; and when heated in a dry narrow glass tube, Fig. 115, with about six times its weight of a mixture of equal parts of exsiccated sodium carbonate and potassium cyanide, a bright mirror of metallic arsenic is produced.

Fig. 115.



Ferroso-ferric arseniate is insoluble in water, but readily soluble in warm hydrochloric acid, forming a yellow solution, which, when largely diluted with water, yields a blue coloration with both potassium ferrocyanide and ferricyanide, and, upon saturation with hydrogen sulphide, particularly upon warming, affords a yellow precipitate of arsenic trisulphide. When boiled in a solution of sodium carbonate, it yields a filtrate which, when exactly neutralized with nitric acid, gives a reddish-brown precipitate with argentic nitrate, and a white crystalline one with magnesium mixture.

Examination:

A small portion of the powder is shaken with a little tepid water, and the filtrate tested by evaporation on platinum-foil, as also with barium chloride; no fixed residue should remain in the first instance, nor should a white precipitate be produced with the latter reagent, as thereby an insufficient washing of the ferroso-ferric arseniate would be indicated.

FERRI CABBONAS SACCHARATUS.

FERRUM CARBONICUM SACCHARATUM.

Saccharated Carbonate of Iron, or Ferrous Carbonate.

Ger. Zuckerhaltiges, kohlensaures Eisenoxydul; Fr. Saccharure de carbonate de fer; Sp. Sacarato de carbonato de hierro.

A greenish-gray powder, gradually oxidized by exposure to the air, and having a sweet, feebly chalybeate taste. Heated in a dry test-tube, it is charred, with the evolution of the vapors and odor of burning caramel. When shaken with cold water, this dissolves the sugar, and a little of the ferrous carbonate, which may be precipitated, for the most part, as ferrous hydrate, by boiling the solution; the powder is wholly and readily soluble, with effervescence, in hydrochloric acid, forming a yellow solution which gives, with reagents, the reactions of both ferrous and ferric salts.

A saccharated carbonate of iron which has a reddish color, and affords no brisk effervescence with acids, should be rejected.

Examination:

Sodium carbonate and *sulphates* may be detected by shaking a little of the powder with warm water, in a test-tube, filtering, and evaporating the filtrate to dryness; the obtained residue is then dissolved in a little dilute nitric acid, when effervescence will indicate *soluble carbonates*, and the resulting diluted solution, when tested with barium chloride, will afford a white precipitate if *sulphates* are present, both of which impurities would indicate an insufficient washing of the preparation.

Copper and Zinc.—The portion remaining undissolved upon the filter, after extraction with water, as in the preceding test, is digested, in a test-tube, with a little solution of ammonium carbonate, for about one hour. The liquid is then filtered; a bluish color of the filtrate would indicate the presence of *copper*, and the formation of a white precipitate upon the addition of a few drops of ammonium sulphide, that of *zinc*.

If 8 grams of the saccharated carbonate of iron be dissolved in water with an excess of hydrochloric acid, and the solution mixed with 33 cubic centimeters of standard solution of potassium bichromate (page 91), the mixture should still afford a blue color or precipitate on the addition of solution of potassium ferricyanide, indicating the presence of at least 15 per cent. of ferrous carbonate.

FERRI CHLORIDUM.

FERRI PERCHLORIDUM. FERRUM SESQUI-CHLORATUM.

Chloride of Iron. Perchloride of Iron. Ferric Chloride.

Ger. Eisenchlorid; Fr. Perchlorure de fer; Sp. Percloruro de hierro.

$Fe_2Cl_6+12H_2O$; 540.2: or $Fe_2Cl_6+6H_2O$; 432.2.

Orange-yellow, crystalline masses, having a radiate structure, and containing 12 molecules (39.93 per cent.) of water, or large, brownish-red, rhombic tables, containing 6 molecules (24.94 per cent.) of water of crystallization. The normal chloride, Fe_2Cl_6 + $12H_2O$, melts at 36° C. (96.8° F.) to a liquid of a deep brownish-red color; upon more strongly heating, it becomes partially decomposed, losing at first water and hydrochloric acid, whilst a portion of the chloride sublimes in the form of anhydrous, brown, iridescent plates or hexagonal tables, which exhibit a red color by transmitted, and a green metallic lustre by reflected light, and leaving a residue of ferric oxide.

Ferric chloride is deliquescent, freely soluble in water, alcohol, and glycerin, and also, but less readily, in ether and chloroform; it is abstracted from its aqueous solution by ether, and also, to a less extent, by chloroform. A strong aqueous solution, of a spec. grav. of 1.405, forms the officinal *Liquor ferri chloridi*. This, as well as the solution of the salt, has an acid and strongly styptic taste, and an acid reaction on test-paper; when diluted with water, they give a blue precipitate with potassium ferrocyanide, a white one with argentic nitrate, and a bulky reddish-brown precipitate of ferric hydrate, upon the addition of the alkaline hydrates in excess.

Examination:

Ferric chloride should yield a complete and clear solution with water and with alcohol; if a reddish, insoluble residue remains, the chloride has undergone partial decomposition.

Ferrous chloride is detected, in the largely diluted solution, by the formation of a blue precipitate with potasssium ferricyanide.

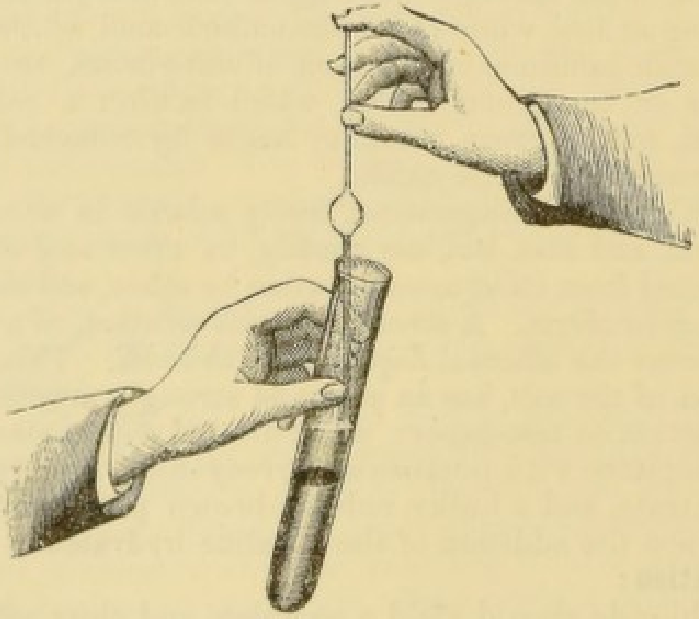
Fixed Impurities, other Metallic Chlorides, and Nitric and Sulphuric Acids.—A small portion of the ferric chloride is dissolved in about ten times its weight of water, the solution heated to boiling, and ammonia-water, in slight excess, subsequently added, until the iron is completely precipitated, or until a little of the clear solution no longer affords a blue coloration upon the addition of a solution of potassium ferrocyanide. The liquid is then filtered, and subsequently tested in separate portions as follows:

Fixed impurities will be recognized by evaporating a portion of the liquid to dryness, and strongly heating the residue upon platinum-foil.

Copper and Zinc.—The presence of copper will be indicated by a blue color of the ammoniacal solution, and, if present, the solution should be slightly acidulated with hydrochloric acid, and subsequently saturated with hydrogen sulphide, when the copper will be completely precipitated as brownish-black cupric sulphide; after the removal of the latter by filtration, the solution is again supersaturated with ammonia-water, and tested with ammonium sulphide, when a white precipitate will indicate the presence of zinc.

Sulphuric acid will be indicated by a white precipitate when a portion of the diluted solution, slightly acidulated with hydrochloric acid, is tested with barium chloride.

FIG. 116.



Nitric acid may be detected by slightly acidulating a portion of the diluted solution with sulphuric acid, and by testing it, in two portions, with solution of indigo and solution of potassium permanganate; a decoloration of the faintly colored solutions, upon gently warming, would indicate nitric acid.

The presence of nitric acid may be confirmed by mixing a portion of the solution, previously neutralized with sulphuric acid, with a strong solution of ferrous sulphate, and by the subsequent careful addition of concentrated sulphuric acid, so as to form two layers (Fig. 116); a brown coloration at the line of contact of the two liquids will ensue, if nitric acid or oxides of nitrogen be present.

FERRI CITRAS.

FERRUM CITRICUM OXYDATUM.

Citrate of Iron. Ferric Citrate.

Ger. Citronensaures Eisenoxyd; Fr. Citrate de fer; Sp. Citrato de hierro.

$Fe_2(C_6H_5O_7)_2 + 6H_2O$; 597.8.

Thin, transparent scales, of a garnet-red color, permanent in the air; when heated on platinum-foil, they are charred without fusing, and without the evolution of an ammoniacal odor (distinction from ammonio-ferric citrate); when completely incinerated, aided, if necessary, by the addition of a few drops of nitric acid, red ferric oxide, Fe_2O_3, amounting to 26.76 per cent. of the original weight, is left, which, when cool, should have no alkaline reaction upon moist turmeric or litmus paper (distinction from potassio-ferric tartrate).

Ferric citrate is slowly but completely soluble in cold, and readily in hot, water, and insoluble in alcohol; its aqueous solution has a yellow color, a mild chalybeate taste, and an acid reaction upon litmus; it is not precipitated by ammonia-water, but is rendered darker in color, and affords a precipitate of ferric hydrate when heated with a solution of potassium hydrate; when largely diluted with water, and slightly acidulated with hydrochloric acid, it yields a deep blue color upon the addition of a few drops of solution of potassium ferrocyanide.

Examination:

Ferric citrate when shaken with cold concentrated sulphuric acid should not impart any color to the latter, even after several hours, and should produce no effervescence when added to a cold solution of sodium carbonate.

Ammonium salts, or an admixture of ammonio-ferric citrate, may be detected by the odor of ammonia, when a little of the ferric citrate is heated, in a test-tube, with a concentrated solution of potassium hydrate.

Ferric tartrate may be detected by completely precipitating a warm solution of ferric citrate with potassium hydrate, and testing the colorless filtrate by slightly supersaturating a portion of it with acetic acid; when the solution is very dilute, it is first reduced by evaporation, and, when cold, tested with a few drops of a concentrated alcoholic solution of potassium acetate; a white crystalline precipitate, occurring at once or after some time, would indicate tartrate. Another portion of the filtrate is precipitated with calcium chloride, and filtered; the filtrate, when heated to boiling, should yield a white, granular precipitate of calcium citrate, which redissolves on cooling, being confirmatory evidence of the identity of a citrate.

FERRI ET AMMONII CHLORIDUM.

AMMONIUM CHLORATUM FERRATUM. AMMONIUM MURIATICUM MARTIATUM.

Ammonio-Chloride of Iron. Ammonio-Ferric Chloride.

Ger. Eisensalmiak; Fr. Chlorure de fer et d'ammoniaque; Sp. Cloruro de hierro y de amoniaco.

An orange-yellow, crystalline powder, somewhat deliquescent, readily soluble in water or glycerin, and to some extent in alcohol, forming a yellow, transparent solution, which has an acid reaction upon litmus. Its aqueous solution gives a copious rust-brown precipitate with alkaline hydrates, and, when very dilute, a deep-blue one with potassium ferrocyanide, and a white, curdy one with argentic nitrate; when heated with a concentrated solution of potassium hydrate, it develops the odor of ammonia, and deposits ferric hydrate.

Examination:

One part of the salt should afford a complete and transparent solution with five parts of water; a reddish-brown insoluble residue would indicate decomposition of the ferric chloride by exposure to too strong a heat while drying the salt. The solution thus obtained should not afford a blue coloration upon the addition of two drops of a freshly prepared solution of potassium ferricyanide (absence of ferrous salt).

Zinc and Copper.—The warm diluted aqueous solution is completely precipitated by the addition of ammonia-water in slight excess, and subsequently filtered; a blue coloration of the liquid will reveal the presence of *copper;* if the latter be absent, the filtrate may then be directly tested with ammonium sulphide, when a white precipitate will indicate the presence of *zinc;* if, however, copper be present, the ammoniacal liquid is first slightly supersaturated with hydrochloric acid, and the copper completely precipitated by hydrogen sulphide, when the liquid, after filtration, will afford upon the addition of ammonia-water a white precipitate, if zinc be present.

FERRI ET AMMONII CITRAS.

FERRUM ET AMMONIUM CITRICUM. FERRUM CITRICUM AMMONIATUM.

Citrate of Iron and Ammonium. Ammonio-ferric Citrate.

Ger. Citronensaures Eisenoxyd-Ammonium ; Fr. Citrate de fer et d'ammoniaque ; Sp. Citrato de hierro amoniacal.

Thin, transparent, garnet-red scales, of a slightly sweetish and astringent taste; they evolve, when heated, water and ammonia, and, when completely incinerated upon platinum-foil, leave behind about 25 per cent. of ferric oxide, which should not change the color of moistened red litmus-paper (evidence of the absence of potassio-ferric salts). Heated with a concentrated solution of potassium hydrate, ammonia is evolved (distinction from ferric citrate), and ferric hydrate is deposited.

Ammonio-ferric citrate is readily soluble in water, glycerin, and diluted alcohol, but not in strong alcohol or ether; its aqueous solution is neutral or has a slightly alkaline reaction, remains unaltered, or is but slightly darkened in color on the addition of ammonia water, and is not affected by solution of potassium ferrocyanide until after the addition of a mineral acid, when a deep blue color or precipitate is produced.

Examination:

Ammonio-ferric tartrate may be recognized, as an incidental or fraudulent admixture or substitution, by completely precipitating a not too dilute aqueous solution of the salt with potassium hydrate; the liquid is heated nearly to boiling, and, when cool, filtered; one portion of the colorless filtrate is examined by slight supersaturation with acetic acid, and by the subsequent addition of a little alcoholic solution of potassium acetate, and allowing the liquid to stand for some hours; the formation of a white, crystalline deposit would indicate *tartrate*.

Another portion of the filtrate is precipitated with calcium chloride, filtered, and the filtrate heated to boiling. A white precipitate of calcium citrate, disappearing again on cooling, will bear evidence of the identity of a citrate.

FERRI ET AMMONII SULPHAS.

FERRUM ET AMMONIUM SULFURICUM. FERRUM SULFURICUM OXYDATUM AMMONIATUM.

Sulphate of Iron and Ammonium. Iron Alum. Ammonio-Ferric Sulphate.

Ger. Schwefelsaures Eisenoxyd-Ammonium (Eisen-ammonium-alaun); Fr. Sulfate de fer et d'ammoniaque; Sp. Sulfato de hierro ammoniacal.

$$Fe_2(NH_4)_2(SO_4)_4 + 24H_2O.$$

Pale-violet, octahedral crystals (Fig. 86, page 213), containing 24 molecules (44.8 per cent.) of water of crystallization, and efflorescing by exposure to the air.

Exposed to heat, they undergo aqueous fusion, lose the water of crystallization, swell up, and leave a pale-brown residue. When the crystals, or an aqueous solution of the salt, is heated with a concentrated solution of potassium hydrate, ammonia is evolved, which may be recognized by its odor, and a precipitate of ferric hydrate is produced.

Ammonio-ferric sulphate is soluble in 3 parts of water at 15° C. (59° F.), and in 0.8 part of boiling water; it is less soluble in glycerin, and insoluble in alcohol, ether, and chloroform. Its aqueous solution has a slightly acid reaction, a sour, astringent taste, and becomes partially decomposed on boiling, with the separation of an insoluble, yellowish-brown, basic salt; it yields a blue precipitate with potassium ferrocyanide, a brown one with the alkaline hydrates, and a white one, insoluble in acids, with barium nitrate or chloride.

When the solution of ammonio-ferric sulphate is completely precipitated with potassium hydrate, and the filtrate slightly supersaturated with hydrochloric acid, it should not afford a white, gelatinous precipitate upon the subsequent addition of an excess of ammonia-water (absence of aluminium); the solution of the salt, when completely precipitated by ammonia-water, should afford a filtrate, which, upon evaporation to dryness and subsequent ignition, should leave no permanent residue, nor impart a violet color to the non-luminous flame (absence of potassium salts).

FERRI ET AMMONII TARTRAS.

FERRUM ET AMMONIUM TARTARICUM. FERRUM TARTARICUM AMMONIATUM.

Tartrate of Iron and Ammonium. Ammonio-Ferric Tartrate.

Ger. Weinsaures Eisenoxyd-Ammonium; Fr. Tartrate de fer et d'ammoniaque; Sp. Tartrato de hierro ammoniacal.

Transparent, deep-red scales, of a sweet taste, and of a rust-brown color when reduced to powder; when heated in a test-tube, the salt emits vapors of water and ammonia, and, when completely incinerated, by exposure to a red heat, it leaves a residue of ferric oxide amounting to about 25 per cent. of its weight. Heated with potassium hydrate, it evolves the odor of ammonia, and deposits ferric hydrate.

Ammonio-ferric tartrate is slowly but freely soluble in water and in glycerin, but insoluble in alcohol and ether; its solution is neutral or slightly alkaline, remains unaltered, or is but slightly darkened in color on the addition of ammonia-water, and, when cold, is not precipitated by the fixed alkaline hydrates or carbonates, but is so upon boiling it with either of these reagents. Its solution is not rendered blue by potassium ferrocyanide, unless acidulated with a few drops of a mineral acid. When completely precipitated by potassium hydrate, the filtrate, if not too dilute, gradually yields, after supersaturation with acetic acid, a white, crystalline deposit of acid potassium tartrate, but should afford no precipitate with hydrogen sulphide.

The aqueous solution of ammonio ferric tartrate, when acidulated with a few drops of hydrochloric acid, should afford upon saturation with hydrogen sulphide but a white turbidity of sulphur; a dark turbidity would indicate other metals (copper); if required, the nature of the precipitate of the sulphides may be ascertained, and the metals contained therein recognized, by the method described on pages 52–56.

FERRI ET POTASSII TARTRAS.

FERRUM ET POTASSIUM TARTARICUM. TARTARUS FERRATUS.

Tartrate of Iron and Potassium. Potassio-Ferric Tartrate.

Ger. Weinsaures Eisenoxyd-Kalium; Fr. Tartrate de fer et de potasse;
Sp. Tartrato de hierro y potasa.

Transparent, ruby-red scales, of a sweetish and slightly astringent taste; when heated, they emit at first the odor of burnt sugar, and leave, upon incineration at a red heat, a residue which, when cold, changes the color of moistened red litmus-paper to blue, and effervesces when moistened with a drop of hydrochloric acid.

Potassio-ferric tartrate is freely soluble in water and in glycerin, but scarcely in alcohol; its solution is neutral or slightly alkaline, remains unaltered or is but slightly darkened in color on the addition of ammonia-water, and, at ordinary temperatures, gives no precipitate with the fixed alkaline hydrates or carbonates, but, upon boiling, a reddish-brown precipitate of ferric hydrate is produced; with potassium ferrocyanide it affords no reaction until after the addition of a mineral acid, when the solution, even when very dilute, assumes a deep blue color. If the iron be completely precipitated from the solution by boiling with a solution of potassium hydrate, and the filtrate slightly supersaturated with acetic acid, it gives, on cooling, if not too dilute, a crystalline deposit of acid potassium tartrate, but should afford no precipitate with hydrogen sulphide. The aqueous solution of potassio-ferric tartrate, when acidulated with a few drops of hydrochloric acid, should afford upon saturation with hydrogen sulphide but a white turbidity of sulphur; a dark turbidity would indicate other metals (copper); if required, the nature of the precipitate of the sulphides may be ascertained, and the metals contained therein recognized, by the method described on pages 52–56. When heated with a solution of potassium hydrate, potassio-ferric tartrate should not develop the odor of ammonia (distinction from ammonio-ferric tartrate).

FERRI ET QUININÆ CITRAS.

FERRUM ET CHININUM CITRICUM. CHININUM FERRO-CITRICUM.

Citrate of Iron and Quinine or Quinia. Quinine Ferric Citrate.

Ger. Chininhaltiges Citronensaures Eisenoxyd; Fr. Citrate de fer et de quinine; Sp. Citrato de hierro y quinina.

Thin, transparent scales, varying in their color from a yellowish-brown, with a tint of green, to a reddish-brown, according to the thickness of the scales. When strongly heated, they are decomposed with the evolution of white fumes, and leave, upon incineration, a residue of ferric oxide, which should not change moistened red litmus-paper (evidence of the absence of alkaline citrates).

Quinine ferric citrate is slowly but freely soluble in cold, and readily in hot, water, but insoluble in alcohol and ether; its solution is neutral or slightly acid, and has a bitter, mild, chalybeate taste; it gives, at ordinary temperatures, a white precipitate of quinine with ammonia-water, and the solution assumes a deeper color; but no ferric hydrate is thrown down; when the precipitate is collected upon a filter, washed with a few drops of cold water, and then dissolved in a little chlorine-water, the solution will assume an emerald-green color upon the addition of a few drops of ammonia-water (evidence of the presence of quinine, and distinction from cinchonine and cinchonidine). Solution of quinine ferric citrate gives a brown precipitate of ferric hydrate and quinine with a solution of potassium or sodium hydrate, and with ammonia-water, when heated; a blue one with solution of potassium ferrocyanide, when acidulated with a mineral acid, and a grayish-black one with tannic acid.

Examination:

The absence or admixture of cheaper scaled ferric salts may be ascertained:

1. By the bitter taste, while the other scaled ferric salts, with the exception of strychnine ferric citrate, have a more or less sweetish taste.

2. By the formation, in the cold, of a white precipitate with ammonia-water, which responds to the tests and reactions of quinine, while the ferric citrates and tartrates, and their more soluble combinations with alkaline salts, yield, with the same reagent, no precipitate at all at ordinary temperatures.

3. By giving no odor of ammonia, nor white fumes with a glass rod, moistened with acetic acid, when heated in a test-tube with a solution of potassium or sodium hydrate. Any admixture of ammonio-ferric salt would be recognized by this test.

In order to ascertain the purity of quinine ferric citrate or to determine the proper percentage of quinine contained therein, the following method of examination may be employed. Four grams of the scaled salt are dissolved in 30 cubic centimeters of water, in a capsule, with the aid of a gentle heat. The solution, after being allowed to cool, is transferred to a glass separating funnel, the rinsings of the capsule added thereto, then an aqueous solution of 0.5 gram of tartaric acid added, and the whole well mixed. Solution of sodium hydrate in considerable excess is now added, and the precipitated alkaloid extracted by agitating the mixture with four successive portions of chloroform of 15 cubic centimeters each. After being allowed to subside, the chloroformic layers are separated, subsequently combined, evaporated in a weighed capsule on a water-bath, and the residue finally dried at 100° C. (212° F.), until it ceases to lose weight. The obtained residue should weigh 0.48 gram, corresponding to 12 per cent. of dry quinine.

FERRI ET STRYCHNINÆ CITRAS.

FERRUM ET STRYCHNINUM CITRICUM. STRYCHNINUM FERRO-CITRICUM.

Citrate of Iron and Strychnine. Strychnine Ferric Citrate.

Ger. Strychninhaltiges citronensaures Eisenoxyd; Fr. Citrate de fer et de strychnine; Sp. Citrato de hierro y estricnina.

Thin, transparent, garnet-red scales, deliquescent on exposure to the air. When strongly heated, they are decomposed with the evolution of white fumes, and leave, upon incineration, a residue of ferric oxide, which should not change moistened red litmus-paper (evidence of the absence of alkaline citrates).

Strychnine ferric citrate is readily and completely soluble in water, but only slightly soluble in alcohol. Its aqueous solution possesses a slightly acid reaction, and a bitter, mild, chalybeate taste; when heated, in a test-tube, with a concentrated solution of potassium hydrate, it develops the odor of ammonia, and a brownish-red precipitate of ferric hydrate is produced. If the solution of the salt be boiled with an excess of solution of potassium hydrate, filtered, and the concentrated and cooled filtrate precipitated by solution of calcium chloride, and again filtered, the filtrate thus obtained, when heated to boiling, will yield a white granular precipitate of calcium citrate, which, however, becomes mostly redissolved on cooling. The dilute aqueous solution of the salt is not affected by solution of potassium ferrocyanide until after the addition of a mineral acid, when a deep blue color or precipitate is produced.

Examination:

The identity of strychnine ferric citrate may be determined and its purity approximately ascertained by dissolving 1 gram of the salt in about four times its weight of water, adding thereto 1 gram of a concentrated solution of potassium hydrate, and agitating the mixture with small successive portions of chloroform; the chloroformic layers are separated from the aqueous mixture, and, after evaporation, should leave a residue answering to the reactions and tests of strychnine, and corresponding in amount to one per cent. of the weight of salt employed.

FERRI FERROCYANIDUM.

FERRUM FERROCYANATUM.

Ferrocyanide of Iron. Prussian Blue. Ferric Ferrocyanide.

Ger. Eisencyanür-cyanid (Berliner Blau); Fr. Cyanure de fer (Bleu de Prusse); Sp. Hidrocianato de hierro.

$$Fe_7(CN)_{18} = 3[Fe(CN)_2] + 4[Fe(CN)_3];\ 859.3.$$

A deep-blue, tasteless powder, or hard, brittle, blue masses, showing, on the freshly fractured surfaces, a beautiful bronzed lustre, which disappears when they are powdered. When heated in the air, it burns with the development of colorless vapors, emitting the odor of ammonia and hydrocyanic acid, and leaving a residue of ferric oxide; exposed to a high temperature in a closed vessel, it gives off water, ammonium cyanide, and ammonium carbonate, and carbide of iron is left behind.

Ferric ferrocyanide is insoluble in water, glycerin, and alcohol, and in diluted acids, with the exception of oxalic acid, which dissolves it, with a deep-blue color. Concentrated sulphuric acid converts it into a white pasty mass, which again assumes a blue color upon the addition of water; it is also decomposed by concentrated hydrochloric and nitric acids. Alkaline hydrates and carbonates decompose it, upon heating, with the formation of soluble alkaline ferrocyanide, and leaving rust-brown ferric hydrate behind.

Commercial Prussian blue is not invariably pure ferric ferrocyanide, but generally contains aluminium and potassium salts, and frequently some uncombined ferric hydrate. These impurities may be detected by boiling the triturated Prussian blue with dilute hydrochloric acid, and adding to the filtrate an excess of ammonia-water, when the hydrates of aluminium and iron are precipitated, while pure ferric ferrocyanide, treated in this manner, yields no precipitate. If it is desired to examine the precipitate for aluminium, it is collected upon a filter, washed, and treated with a warm solution of potassium hydrate; the filtered solution will then afford a white flocculent precipitate upon the addition of a solution of ammonium chloride, if aluminium be present.

Examination:

Mineral Admixtures.—A small portion (about 2 grams) of the ferric ferrocyanide is heated, in a porcelain crucible, to redness; when cool, the residue is treated with warm hydrochloric acid, which should afford a complete and clear solution, with slight effervescence; an insoluble residue would indicate fixed mineral admixtures (calcium or barium sulphates or silicates).

Metals.—To the solution obtained in the preceding test, a little potassium chlorate is added, and the solution boiled until the odor of chlorine ceases to be evolved; it is then diluted, filtered, and the filtrate divided into two portions; these are heated, and the one is precipitated with a solution of potassium hydrate, the other with ammonia-water, in excess; after a while, they are filtered, and each of the alkaline filtrates is tested with ammonium sulphide; a black precipitate, in the potassa solution, would indicate *lead;* a blue coloration of the ammoniacal liquid, and a brownish-black precipitate upon the addition of ammonium sulphide, will indicate *copper;* a white turbidity, in either of the liquids, upon the addition of ammonium sulphide, shows *zinc* to be present. For the detection of zinc in the presence of lead or copper, the alkaline solution must be first slightly supersaturated with hydrochloric acid, and the lead or copper subsequently completely precipitated by hydrogen sulphide; the liquid, after filtration, will then afford, upon the addition of ammonia-water, a white precipitate, if zinc be present.

Earthy Carbonates.—The ammoniacal liquid of the preceding test for copper and zinc, from which the latter, if present, have been completely removed, either by saturation with hydrogen sulphide or by the addition of ammonium sulphide, is tested with ammonium carbonate; an ensuing white precipitate would indicate the presence of *barium* or *calcium;* after the removal of the latter by filtration, solution of sodium phosphate is added, when the formation of a white crystalline precipitate will reveal the presence of *magnesium.*

FERRI HYPOPHOSPHIS.

FERRUM HYPOPHOSPHOROSUM.

Hypophosphite of Iron. Ferric Hypophosphite.

Ger. Unterphosphorigsaures Eisenoxyd; Fr. Hypophosphite de fer; Sp. Hipofósfito de hierro.

$Fe_2(H_2PO_2)_6$; 501.8.

A white or grayish-white, odorless powder, permanent in the air; when heated, in a dry test tube, it evolves spontaneously inflammable vapors of hydrogen phosphide, with considerable intumescence, leaving behind ferric pyrophosphate; when heated with a solution of potassium or sodium hydrate, it is decomposed, and assumes a reddish-brown color. Since hypophosphorous acid is very prone to absorb oxygen, the salt is readily decomposed by all oxidizing agents. Ferric hypophosphite is insoluble in cold water, and, when dry, is but sparingly soluble in hypophosphorous acid, but readily dissolves in that liquid when in the moist hydrated condition; it is dissolved by diluted hydrochloric acid, forming a yellow solution, which, when largely diluted, gives a blue precipitate with potassium ferrocyanide, and is also readily soluble in solutions of ferric sulphate and of sodium hypophosphite, and unites with alkaline citrates to form compounds which are readily soluble in water, and of a green color.

Examination:

Ferric phosphate may be recognized by an insoluble residue when a small portion of the salt is dissolved in acetic acid. The acetic solution should afford no precipitate upon the addition of solution of ammonium oxalate; an ensuing white precipitate, soluble in hydrochloric acid, would reveal the presence of *calcium.*

FERRI IODIDUM.

FERRUM IODATUM.

Iodide of Iron. Ferrous Iodide.

Ger. Eisenjodür; Fr. Iodure de fer; Sp. Ioduro de hierro.

FeI_2; 309.1.

Opaque plates or masses, of an iron-gray color, metallic lustre, and crystalline fracture, or, when obtained by the careful evaporation of its concentrated aqueous solution, bright green crystals, having the composition FeI_2+4H_2O, which rapidly suffer oxidation. When heated in a dry test-tube, ferrous iodide fuses, and emits violet iodine vapors, finally leaving behind ferric oxide.

Ferrous iodide is very deliquescent; it is soluble in its own weight of water, and also in alcohol and glycerin, forming yellowish-green solutions, having a styptic taste; its aqueous solution gives a copious blue precipitate with potassium ferricyanide, and, after the addition of a minute quantity of chlorine-water, assumes a fine blue color upon the addition of a little mucilage of starch. Ferrous iodide and its solutions rapidly oxidize, the latter forming a rust-brown sediment, the former becoming less soluble in water, and yielding a brown solution, one drop of which, when diluted with a little water, and subsequently shaken with a few drops of chloroform, imparts to the latter a beautiful violet coloration, which, however, is not the case when the ferrous iodide is fresh, and not yet partly oxidized.

Ferrous iodide is decomposed by, and therefore incompatible with, acids, the alkaline hydrates and carbonates, and those metallic salts which form insoluble iodides.

The oxidation of ferrous iodide is greatly obviated by its admixture with sugar. Upon this fact, the preparation of FERRI IODIDUM SACCHARATUM and of SYRUPUS FERRI IODIDI are based; both share the chemical properties and reactions of the ferrous iodide. The syrup may be preserved without decomposition, when kept in a sunny place, in small, well-corked vials, containing a piece of clean, bright iron wire.

FERRI LACTAS.

FERRUM LACTICUM.

Lactate of Iron. Ferrous Lactate.

Ger. Milchsaures Eisenoxydul; Fr. Lactate de fer; Sp. Lactato de hierro.

$Fe(C_3H_5O_3)_2+3H_2O$; 287.9.

Greenish-white, needle-shaped crystals, crystalline crusts or grains, or a greenish-white powder,* containing three molecules

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* The ferrous lactate of the German manufacturers and shops occurs as a yellowish or grayish-green powder, and is obtained by the following process, which is least subject to the formation of peroxide: An alcoholic solution of sodium lactate is exactly decomposed by a concentrated aqueous solution of ferrous chloride. Allowed to stand for twenty-four hours, in a filled and closely stoppered bottle, in a cool place, the ferrous lactate separates in a thick, crystalline crust, which, after the mother liquor has been removed, is broken by a wooden spatula, and then transferred to a cloth, washed with a little alcohol, and afterward subjected to a moderate pressure, under a small screw-press. The resulting salt cake is broken, dried at a gentle heat, and finally triturated.

(18.8 per cent.) of water of crystallization, which are eliminated, without decomposition of the salt, by heating to 100° C. (212° F.) in a current of hydrogen. When heated, with exposure to the air, the salt acquires at temperatures above 60° C. (140° F.) a gray or brownish color, becomes finally black, and, at 100° C. (212° F.), is chiefly converted into ferric salt; when more strongly heated, the salt froths up, with the evolution of white, acid, inflammable fumes, becomes black, and, when completely incinerated, leaves a residue amounting to 27.8 per cent. of its weight of red ferric oxide, which, when cold, should not act upon moistened red litmus-paper (evidence of the absence of alkaline salts).

Ferrous lactate is slowly soluble in 40 parts of water at 15° C. (59° F.), and more readily in 12 parts of boiling water, but is almost insoluble in alcohol. Its aqueous solution is more or less turbid, and of a yellowish-green color and acid reaction, and has a mild, sweetish, chalybeate taste; by exposure to the air, or more quickly upon boiling, it assumes a brown color, in consequence of its oxidation to ferric salt, and, upon protracted boiling, ferric hydrate is deposited. The concentrated aqueous solution of the salt affords upon the addition of solution of the alkaline hydrates a yellowish precipitate of ferrous hydrate, and yields when saturated with hydrogen sulphide, particularly upon warming, an abundant precipitate of ferrous sulphide. The clear, filtered, aqueous solution should produce upon the addition of a few drops of a solution of potassium ferrocyanide but a slight blue coloration, and should afford with plumbic acetate but a slight opalescence (evidence of the absence of more than traces of ferric salt, and of sulphuric, hydrochloric, tartaric, citric, and malic acids); when acidulated with hydrochloric acid, it should afford upon saturation with hydrogen sulphide but a slight opalescence (absence of foreign metals, lead, copper, etc).

Examination:

In addition to the above-described characters and tests, ferrous lactate should be further examined for the following substances:

Mineral Impurities.—A small portion of the ferrous lactate is completely incinerated in a small porcelain crucible, and the residue subsequently treated with boiling water and filtered; the filtrate must neither act upon test-paper, nor leave any residue upon evaporation on platinum-foil. The ignited residue of ferric oxide is then treated with warm hydrochloric acid, in which it should be completely soluble, and the solution, after warming with a few drops of nitric acid, or the addition of a little chlorine-water, is diluted with water, filtered, heated to boiling, and finally completely precipitated by ammonia-water. The liquid, after filtration, evaporation to dryness, and subsequent ignition, should leave no residue; when tested with ammonium sulphide, a white turbidity would indicate *zinc*, and, after the addition of solution of sodium phosphate, the formation of a white crystalline precipitate would indicate *magnesium salts.*

Gum, starch, dextrin, sugar, and other *carbohydrates* may be detected by their carbonization, becoming brown or blackish, when a little of the ferrous lactate is strewn upon cold concentrated sulphuric acid, and shaken therewith, and, if necessary, allowed to remain in contact for several hours; they may also be detected by boiling a saturated aqueous solution of the salt for a few minutes with a few drops of dilute sulphuric acid, and subsequently neutralizing the solution with potassium or sodium hydrate; the filtered liquid, upon the addition of a few drops of Fehling's solution, and heating to boiling, will afford a precipitate of red cuprous oxide, if the above-mentioned carbohydrates be present.

FERRI OXALAS.

FERRUM OXALICUM.

Oxalate of Iron. Ferrous Oxalate.

Ger. Oxalsaures Eisenoxydul; Fr. Oxalate de fer; Sp. Oxalato de hierro.

$FeC_2O_4 + H_2O$; 161.9.

A lemon-yellow, crystalline powder, permanent in the air; when strongly heated in contact with air, it decomposes with a faint combustion, and leaves a residue of red ferric oxide, amounting to 49.38 per cent. of its weight.

Ferrous oxalate is almost insoluble in water, but readily soluble in hydrochloric acid, affording a solution, which, when largely diluted with water, produces a deep blue coloration upon the addition of a few drops of a solution of potassium ferricyanide. When boiled with a solution of sodium carbonate, filtered, the filtrate supersaturated with acetic acid, and solution of calcium chloride subsequently added, a white precipitate of calcium oxalate will be produced.

Examination:

Ferrous oxalate, when ignited at a red heat, in a small porcelain crucible, affords a residue which is neutral in its action upon litmus; and, if the ignited residue be extracted with boiling water and filtered, the filtrate should afford no residue upon evaporation. When a small portion of the salt is dissolved in hydrochloric acid, the solution diluted with water, filtered, and saturated with hydrogen sulphide, it should afford no dark coloration (absence of foreign metals, *lead, copper*, etc.); the acid solution warmed with a few drops of nitric acid, and subsequently completely precipitated by ammonia-water in excess, and filtered, should afford a filtrate which is not rendered turbid upon the addition of ammonium sulphide (absence of *zinc*), and, when evaporated and strongly heated, should become completely volatilized.

FERRI OXIDUM HYDRATUM.

FERRI PEROXIDUM HYDRATUM. FERRUM OXYDATUM. HYDRICUM FUSCUM.

Hydrated Oxide of Iron. Peroxyhydrate of Iron. Ferric Hydrate.

Ger. Eisenhydroxyd ; Fr. Sesquioxyde de fer hydraté ; Sp. Hidrato de peróxide de hierro.

$Fe_2(HO)_6$; 213.8.

A reddish-brown, tasteless powder, destitute of grittiness, which, when heated in a dry test-tube, emits moisture, but no acid vapors. By exposure for several days to a temperature of 100° C. (212° F.), it forms a scarlet powder, having the composition $Fe_4O_7H_2(2Fe_2O_3 + H_2O)$, and the specific gravity 4.4545, and, upon gentle ignition, is completely converted into red ferric oxide, Fe_2O_3.

Ferric hydrate is slowly but wholly soluble in moderately dilute acids, even in acetic acid, without any considerable effervescence (a small amount of carbonic acid being absorbed by its exposure to the air); when dissolved in cold hydrochloric acid, the solution, after dilution with water, yields a blue precipitate with potassium ferrocyanide, but should not afford a blue coloration with potassium ferricyanide, and, upon saturation with hydrogen sulphide, but a white precipitate of sulphur should be produced. The acid solution, after complete precipitation by ammonia-water in excess, and subsequent filtration, should yield a colorless filtrate, which affords no precipitate upon the subsequent addition of either ammonium sulphide, ammonium oxalate, or sodium phosphate (evidence of the absence of *zinc*, *calcium*, and *magnesium*).

Examination:

Alkaline sulphates or *chlorides* may be detected by agitating the ferric hydrate with a little warm water, acidulating the filtrate with a few drops of nitric acid, and subsequently testing with barium chloride and argentic nitrate; a white precipitate in either case will reveal the presence of such impurities, which may result from imperfect washing, in its preparation from ferric sulphate or chloride.

Ammonia will be detected by its odor, when a small portion of the ferric hydrate is gently heated, in a test-tube, with a concentrated solution of potassium or sodium hydrate; and by the formation of white fumes, when a glass rod, moistened with acetic acid, is held over the mouth of the tube.

Copper may be detected by a blue coloration of ammonia-water or a solution of ammonium carbonate, when agitated with the ferric hydrate, and subsequently filtered; its presence may be confirmed or recognized, when the result of the preceding test is uncertain, by supersaturing the filtrate with acetic acid, and testing it with potassium ferrocyanide; a reddish-brown precipitate would indicate or confirm the presence of copper. Other metallic impurities, if present, will be indicated by the above-described characters and tests, and, when required, their nature may be determined, according to the systematic method of analysis, as described on pages 51–61.

FERRI PHOSPHAS.*

FERRUM PHOSPHORICUM. FERRUM OXYDULATO-OXYDATUM PHOSPHORICUM.

Phosphate of Iron. Ferrous Phosphate.

Ger. Phosphorsaures Eisenoxydul; Fr. Phosphate de fer; Sp. Fosfato de hierro.

$$Fe_3(PO_4)_2 + H_2O;\ 375.7.$$

A fine, amorphous, tasteless powder, of a slate-blue color when dry, but which, upon prolonged boiling with water, assumes a greenish color. When heated in a dry test-tube, it gives off water, and leaves a black residue.

Ferrous phosphate is insoluble in water, but soluble in the mineral acids; with phosphoric acid it forms a clear, colorless solution, whilst its solution in hydrochloric acid, in consequence of the contained ferric salt, a result of superficial oxidation, possesses a yellow color; the latter solution, when largely diluted with water, consequently yields a blue precipitate with both potassium ferricyanide and ferrocyanide, and, upon saturation with hydrogen sulphide, affords a slight white turbidity or opales-

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* The phosphate of iron (Ferri Phosphas) of the U. S. Pharmacopœia is a mixture of ferric phosphate with sodium citrate, prepared by dissolving sodium phosphate in a solution of ferric citrate, evaporating the solution to the consistence of a thick syrup, and spreading it on plates of glass, so that, on drying, the salt may be obtained in scales. It thus forms thin, transparent scales, of a bright green color, permanent in the air, but becoming dark on exposure to the light. It is readily and completely soluble in water, but insoluble in alcohol. Its aqueous solution is neutral in its action upon litmus, yields a blue coloration with solution of potassium ferrocyanide, and, after acidulation with hydrochloric acid, a blue precipitate; when heated with an excess of a concentrated solution of potassium hydrate, it yields a brownish-red precipitate of ferric hydrate, and the filtrate, after supersaturation with acetic acid, yields a light yellow precipitate with solution of argentic nitrate (distinction from ferric pyrophosphate). The salt contains an amount of ferric phosphate corresponding to about 13.5 per cent. of metallic iron.

cence, due to the separation of sulphur, but no dark coloration should be produced.

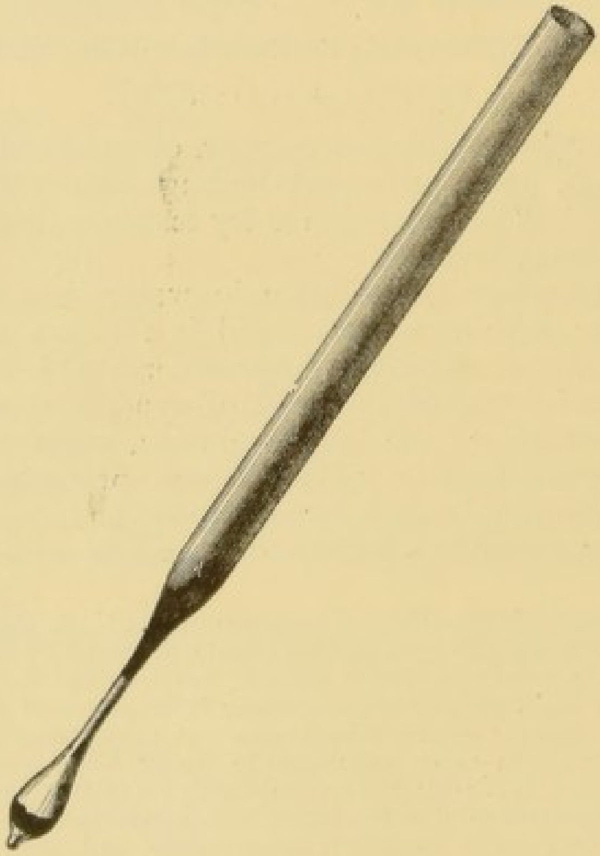
When ferrous phosphate is boiled in a solution of sodium carbonate, and filtered, a filtrate is obtained which, when exactly neutralized with dilute nitric acid, gives a yellow precipitate with argentic nitrate, and a white crystalline precipitate with magnesium mixture, but, after acidulation with hydrochloric acid, should afford upon saturation with hydrogen sulphide, either in the cold or upon warming, no coloration or precipitate (a yellow turbidity would indicate the presence of arsenic).

Examination:

Sodium sulphate, left from insufficient washing, may be detected when a little of the powder is shaken with some hot water, and the filtrate tested with barium chloride.

Metals.—A strong solution of the powder in hydrochloric acid, after dilution with water, is saturated with hydrogen sulphide, and set aside for a few hours, in a closed flask, in a warm place; a slight white turbidity (sulphur) will occur; a dark coloration would indicate *copper*, a yellow one, *arsenic*, which latter, in connection with the above mentioned test, may be confirmed by the odor when a little of the salt is heated upon charcoal, before the

FIG. 117.



blow-pipe, or by the formation of a metallic mirror, in a narrow tube (Fig. 117), upon heating the dried precipitate with about six times its weight of a mixture of equal parts of exsiccated sodium carbonate and potassium cyanide.

FERRI PYROPHOSPHAS.

FERRUM PYROPHOSPHORICUM.

Pyrophosphate of Iron. Ferric Pyrophosphate.

Ger. Pyrophosphorsaures Eisenoxyd; Fr. Pyrophosphate de fer; Sp. Pirofosfato de hierro.

$Fe_4(P_2O_7)_3 + 9H_2O$; 907.6.

A white, tasteless powder, which, when heated in a dry test-tube, loses water and decreases in volume, but remains white. It is insoluble in water, but soluble in hydrochloric acid, and in solutions of sodium pyrophosphate and of alkaline citrates; its solution in dilute hydrochloric acid has a yellowish color, and affords a blue precipitate with potassium ferrocyanide, and, upon saturation with hydrogen sulphide, a white turbidity, due to the separation of sulphur, but no dark coloration is produced. When boiled with a solution of sodium carbonate, ferric pyrophosphate assumes a reddish brown color, and yields a filtrate of the same tint, but which becomes almost decolorized upon slight supersaturation with acetic acid, and gives a dense, white precipitate with argentic nitrate (distinction from ferric orthophosphate, which gives a yellow precipitate, and from ferric metaphosphate, which gives a white gelatinous one).

FERRI PYROPHOSPHAS ET SODII CITRAS.

FERRUM PYROPHOSPHORICUM CUM NATRIO CITRICO.

Pyrophosphate of Iron with Citrate of Sodium. Pyrophosphate of Iron in Scales.

Ger. Pyrophosphorsaures Eisenoxyd mit citronensaurem Natrium; Fr. Pyrophosphate de fer et citrate de soude; Sp. Pirofosfato de hierro y citrato de sodio.

Thin, apple-green, transparent scales, of a mild, acidulous, and slightly saline taste, and permanent in dry air; by exposure to the light the scales lose their transparency and become darker in color.

The salt is freely and completely soluble in twice its weight of water, and is also soluble in glycerin, but insoluble in alcohol.

The dilute aqueous solution is of a bright yellow color, almost tasteless, and neutral in its action upon litmus; it is not precipitated by ammonia-water, but assumes with the latter a brown coloration, and when heated with solution of potassium hydrate, in slight excess, yields a red-brown precipitate of ferric hydrate; if the iron be thus completely precipitated from the solution, filtered, the filtrate supersaturated with acetic acid, and a few drops of solution of argentic nitrate subsequently added, a white precipitate will be produced (distinction from ferric phosphate). The solution affords a blue coloration with solution of potassium ferrocyanide, and, after acidulation with hydrochloric acid, a blue precipitate is produced; when mixed with hydrogen sulphide-water, no immediate change is produced, but the mixture soon assumes a black color.

The dry salt should neither produce effervescence nor a dark coloration when strewn upon cold, concentrated sulphuric acid (absence of carbonates and of foreign organic substances). It contains an amount of ferric pyrophosphate corresponding to about 11.5 per cent. of metallic iron.

FERRI SUBCARBONAS.

FERRUM CARBONICUM. FERRUM SUB-CARBONICUM.

Carbonate of Iron. Basic Ferrous Carbonate.

Ger. Kohlensaures Eisenoxydul; Fr. Sous-carbonate de fer; Sp. Carbonato de hierro.

A fine, amorphous, reddish-brown powder, without odor or taste, which, in consequence of the absorption of oxygen and the elimination of carbonic acid gas, consists for the most part of ferric hydrate (page 356), with small and varying amounts of ferrous carbonate. When gently heated in a dry test-tube, it emits aqueous vapors, which condense in the cooler parts of the tube, and which, when tested with blue litmus-paper, should not alter its color; upon more strongly heating, it is completely converted into red ferric oxide, Fe_2O_3.

Carbonate of iron is insoluble in water, but readily and freely soluble, with slight effervescence, in warm, diluted hydrochloric acid, forming a yellow solution, a few drops of which, when added to water, impart to this the property of yielding a blue precipitate with both potassium ferrocyanide and ferricyanide. The solution therefore affords, with reagents, the reactions of both ferrous and ferric salts.

Examination:

Ferri Subcarbonas is distinguished from Ferri Oxidum Hydratum by its readier solubility in hydrochloric acid, accompanied by active effervescence, and affording a yellow solution, which, when largely diluted with water, yields a blue precipitate with both potassium ferrocyanide and ferricyanide.

Alkaline sulphates may be detected by agitating a small portion of the powder, in a test-tube, with a little warm water, and subsequently filtering; the filtrate should leave no considerable residue upon evaporation on platinum-foil, nor, when acidulated with a few drops of nitric acid, should it yield a white turbidity upon the addition of barium chloride.

Metals.—A small portion of the powder is dissolved in dilute hydrochloric acid, the solution boiled with a few drops of nitric acid, and subsequently precipitated by ammonia-water in slight excess, and filtered; a blue coloration of the filtrate will reveal the presence of *copper*, and a white precipitate upon the addition of a few drops of ammonium sulphide will indicate the presence of *zinc*.

FERRI SULPHAS.

FERRUM SULFURICUM.

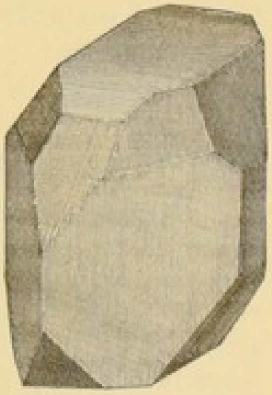
Sulphate of Iron. Ferrous Sulphate.

Ger. Schwefelsaures Eisenoxydul (Eisenvitriol); Fr. Sulfate de fer; Sp. Sulfato de hierro.

$FeSO_4 + 7H_2O$; 277.9.

Transparent, pale bluish-green, monoclinic prisms (Fig. 118), of the specific gravity 1.889, or, when obtained by precipitation, by means of alcohol, a pale bluish-green, crystalline powder (*Ferri Sulphas Præcipitatus*). The crystals are slowly efflorescent in dry air, and by exposure to a moist atmosphere rapidly absorb oxygen, becoming coated with a layer of brownish-yellow, basic ferric sulphate; they contain seven molecules (45.32 per cent.) of water of crystallization, six-sevenths of which they lose at a moderate heat, leaving a greenish or grayish white powder (*Ferri Sulphas Exsiccatus*). At a red heat, the seventh molecule of water, and also the acid is expelled, leaving behind red, anhydrous ferric oxide (*Caput Mortuum*).

Fig. 118.



Ferrous sulphate is soluble in 1.8 parts of water at 15° C. (59° F.), in 0.3 part of boiling water, and is slightly soluble in diluted, but insoluble in absolute, alcohol; its aqueous solution has a greenish-blue color, an unpleasant styptic taste, and a slightly acid reaction; it readily absorbs oxygen, acquiring a yellow color, and becomes turbid by the formation of an insoluble basic ferric sulphate, while a neutral ferric sulphate remains in solution, with the undecomposed ferrous sulphate. The solution of ferrous sulphate, when largely diluted, gives a white precipitate with barium chloride, a blue one with potassium ferricyanide, and, when not yet oxidized, a white one with the ferrocyanide, but, after acidulation with hydrochloric acid, affords no precipitate upon saturation with hydrogen sulphide.

Examination:

Metals.—A small portion of the salt is dissolved in about twice its weight of water, the solution acidulated with a few drops of hydrochloric acid, and subsequently saturated with hydrogen sulphide; no precipitate, or but a white turbidity (sulphur) should be formed; a dark turbidity would indicate *copper*, and perhaps other metals. The liquid is then filtered, evaporated in a porcelain capsule until deprived of odor, subsequently boiled with a few drops of concentrated nitric acid, and finally completely precipitated by ammonia-water, in considerable excess, and filtered. The filtrate is subsequently tested with ammonium sulphide; an ensuing white turbidity would indicate *zinc*, a reddish-white one, *manganese*. Finally, the liquid, after having been filtered, if such reactions have occurred, is tested with ammonium phosphate; a crystalline, white precipitate, occurring after some time, would indicate *magnesium*.

Crude commercial sulphate of iron is generally considerably contaminated with metallic and earthy salts, and not fit for medicinal use; it frequently contains the sulphates of zinc, aluminium, and magnesium, and generally so much sulphate of copper as to deposit a metallic cupreous film upon a bright blade of an iron knife or spatula, when immersed for some hours in the aqueous solution, acidulated with a few drops of sulphuric acid, and may also contain arsenic.

Estimation:

The purity of ferrous sulphate, as based upon the estimation of the equivalent percentage amount of the therein contained metallic iron, may be readily and very accurately determined volumetrically. About one gram of air-dry and uneffloresced crystals of the salt is accurately weighed, and dissolved, in a beaker, in about 200 cubic centimeters of water, the solution subsequently acidulated with dilute sulphuric acid, and a standard solution of potassium permanganate (page 89) allowed to flow into the liquid from a burette until, with constant stirring, the pink tint of the liquid remains for a time unchanged. The factor of the permanganate solution having been previously ascertained (see pages 89–90), and the number of cubic centimeters of the solution required for the complete oxidation of the ferrous to ferric salt, as above described, being known, a simple calculation will determine the amount of iron contained in the ferrous state in the salt, or the percentage amount of pure, crystallized ferrous sulphate.

Another method consists in dissolving 4.167 grams of the salt in water acidulated with diluted sulphuric acid, and allowing a standard solution of potassium bichromate (page 91) to flow into the liquid, until a drop removed by means of a glass rod, and placed on a porcelain plate, no longer gives a blue color with solution of potassium ferricyanide; the number of cubic centimeters of potassium bichromate solution thus required, when multiplied by 2, will represent the percentage amount of unoxidized, crystallized ferrous sulphate.

TABLE *of the percentage strength of solutions of crystallized Ferrous Sulphate* ($FeSO_4+7H_2O$) *of different specific gravities* (*Gerlach*).

Temperature 15° C. (59° F.).

Specific gravity.	Per cent. of $FeSO_4+7H_2O$.	Specific gravity.	Per cent. of $FeSO_4+7H_2O$.	Specific gravity.	Per cent. of $FeSO_4+7H_2O$.
1.005	1	1.077	14	1.155	27
1.011	2	1.082	15	1.161	28
1.016	3	1.088	16	1.168	29
1.021	4	1.094	17	1.174	30
1.027	5	1.100	18	1.180	31
1.032	6	1.106	19	1.187	32
1.037	7	1.112	20	1.193	33
1.043	8	1.118	21	1.200	34
1.048	9	1.125	22	1.206	35
1.054	10	1.131	23	1.213	36
1.059	11	1.137	24	1.219	37
1.065	12	1.143	25	1.226	38
1.071	13	1.149	26	1.232	39

FERRI VALERIANAS.

FERRUM VALERIANICUM.

Valerianate of Iron. Ferric Valerianate.

Ger. Baldriansaures Eisenoxyd; Fr. Valérinate de fer; Sp. Valerianato de hierro.

$Fe_2(C_5H_9O_2)_6,Fe_2(OH)_6$; 931.6.

A dark, brick-red, amorphous powder, permanent in dry air, and possessing the odor of valerianic acid. When gently heated, the salt loses its acid without fusing, but when rapidly heated in a porcelain capsule, it fuses, emits inflammable vapors, and, when incinerated, leaves behind ferric oxide, which should not color moistened turmeric-paper brown, nor dissolve in warm dilute acetic acid.

Ferric valerianate is insoluble in water, and is only miscible therewith after having been previously moistened with a little alcohol; boiling water decomposes it, extracting the valerianic acid, and affording a colorless filtrate, which reddens litmus-paper, but does not become turbid upon the addition of ammonia-water, either before or after saturation with hydrogen sulphide. Acids decompose ferric valerianate, forming soluble ferric salts, and setting free the valerianic acid.

The so-called *soluble valerianate of iron* (Ferrum valerianicum solubile) occurs in thin, reddish scales, and consists of neutral or normal ferric valerianate, $Fe_2(C_5H_9O_2)_6 + 10H_2O$; it is likewise insoluble in water, but is soluble in alcohol (distinction from ferric citrate and tartrate), and exhibits the same behavior by the action of heat or boiling water as the above-described preparation, leaving, however, a much less considerable residue upon ignition.

Examination:

Admixtures of ferric tartrate or citrate, impregnated with oil of valerian or valerianic acid, may readily be recognized by their solubility in water and insolubility in strong alcohol; the latter dissolving the oil of valerian, or valerianic acid, if such be present, which may be readily recognized by the odor, when a portion of the alcohol is evaporated upon the warm hand, while a residue will remain, responding to the tests of ferric citrate or tartrate, as described on pages 343 and 347, if such admixtures be present.

FERRUM.

Iron.

Ger. Eisen; Fr. Fer; Sp. Hierro.

Fe; 55.9.

The source of the medicinal preparations of iron is the refined malleable wrought iron, of which the piano-forte wire is among the best commercial varieties. When iron filings or turnings are employed instead of wire, care has to be taken that they are not derived from crude cast or pig iron, that they are free from rust, and that they are not contaminated with copper or brass filings from the workshops. Cast or pig iron may be recognized by the evolution of gas of a noxious odor, and by a considerable black residue, when the filings or turnings are dissolved, in a test-tube, in a mixture of equal parts of concentrated hydrochloric acid and water. An admixture of copper or brass filings may be recognized, with approximate certainty, by close inspection, with a magnifying-glass, and by chemical tests, as hereafter described.

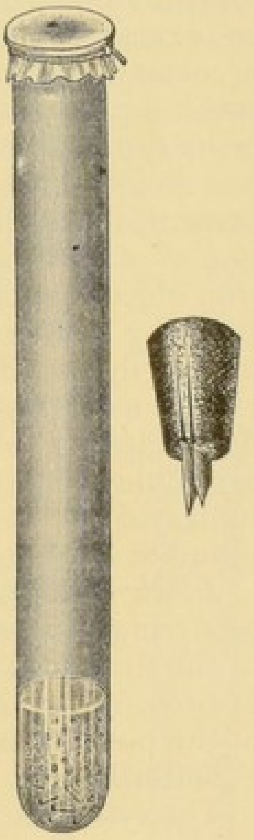
In the preparation of solutions of iron, which are subsequently filtered, filings of cast iron are not exactly objectionable; iron filings or turnings, however, which may contain, or are liable to contain, copper or brass filings, ought not to be employed for medicinal preparations, since copper is dissolved by boiling with an excess of acid, notwithstanding the predominating presence of iron.

FERRUM PULVERATUM.—A fine, gray powder, of a dull, metallic appearance, and having the specific gravity 7.78; when strongly heated, with exposure to the air, it becomes oxidized to black ferroso-ferric oxide, and increasing in weight, if the powder employed was pure and dry. Iron powder dissolves in a mixture of equal parts of hydrochloric acid and water, evolving impure hydrogen gas, of a faint odor, and leaving only a small insoluble black residue; the filtered solution has a light-green color, and affords, when largely diluted with water, a deep-blue turbidity with potassium ferricyanide, and almost white precipitates with the alkaline hydrates and carbonates, which, however, rapidly oxidize, and become green, and ultimately brown.

Examination:

Sulphur, *phosphorus*, and *arsenic*, may be detected, in iron powder, filings, turnings, or wire, by the odor of the evolved gas, when dissolved in dilute hydrochloric or sulphuric acid, and by testing the gas thus evolved, either with a strip of paper moistened with a solution of plumbic acetate and placed over the mouth of the tube, or by loosely inserting a cork provided with two strips of paper, one of which is moistened with a solution of plumbic acetate, and the other with a solution of argentic nitrate (Fig. 119); the blackening of both the lead and silver paper will indicate the presence of sulphur, whilst a blackening of the silver paper alone may arise from the presence of either phosphorus or arsenic.

FIG. 119.



The presence of *sulphur* may be confirmed by dissolving a portion of the iron in dilute nitric acid, and testing the solution with barium nitrate; a white precipitate of barium sulphate will be produced if sulphur were present. The presence of *arsenic*, if indicated by the above test, may also be confirmed by the application of *Marsh's* test, as described on pages 33 to 36.

Phosphorus may also be detected by dissolving a portion of the iron in warm dilute hydrochloric acid, boiling the solution with a few drops of concentrated nitric acid, and filtering, whereby any carbonaceous or siliceous matter will remain principally undissolved, and may be further examined. The solution is then evaporated to remove the excess of acid, diluted with water, again filtered, if necessary, and incompletely precipitated with sodium carbonate, avoiding an excess of the latter. The precipitate of ferric hydrate thus obtained (containing the phosphoric acid) is filtered off, dried, mixed with about four times its weight of exsiccated sodium carbonate, and ignited in a small porcelain crucible. The fused mass is then digested with hot water, the solution filtered, acidulated with hydrochloric acid, and magnesium mixture subsequently added; the formation of a white crystalline precipitate will reveal the presence of phosphorus, which, by the above treatment, is converted into phosphoric acid.

Metallic Impurities.—A portion of the iron is dissolved in dilute hydrochloric acid, the solution boiled with a few drops of concentrated nitric acid, and subsequently completely precipitated by ammonia-water, in excess, and filtered. The filtered solution should afford no turbidity upon the addition of ammonium sulphide; a blue coloration of the ammoniacal liquid will reveal the presence of *copper*, whilst a black precipitate with the last-named reagent may indicate *copper*, *cobalt*, or *nickel*, a flesh-colored precipitate, *manganese*, and a white precipitate, *zinc*.

Copper, *zinc*, and *lead* may also be detected, even when present in very small amount, by dissolving a portion of the iron in an excess of warm concentrated hydrochloric acid, filtering, if necessary, and cautiously pouring upon the acid solution a saturated aqueous solution of hydrogen sulphide; the presence of copper and lead will then be indicated by a brown zone below the line of contact of the two liquids, and as zinc, when present, is usually contained in the form of brass, the confirmation of a contamination with copper would of itself render the iron objectionable. Lead may be specially sought for, when desired, by adding to the solution of the iron in hydrochloric acid a few drops of sulphuric acid, then ammonia-water in slight excess, agitating the mixture, and subsequently adding four or five times its volume of dilute sulphuric acid, and again agitating well; the presence of the smallest amount of lead will thus be indicated by an opalescence, dependent upon the separation of plumbic sulphate.

Black oxide of iron (ferroso-ferric oxide) and *organic matter*, occurring as a contamination of powdered iron, may be detected in the first instance by its much less ready solubility in a mixture of bromine and water, and, in the second instance, by the ignition of the powder in a small glass tube.

Estimation:

The estimation of the purity of metallic iron, when free from oxide, may be readily accomplished volumetrically, by dissolving about 0.2 gram of the substance in a small flask, so arranged as to prevent the oxidation of the iron during solution (Fig. 120), in about 20 cubic centimeters of dilute sulphuric acid, pouring the solution, when cool, together with the rinsings of the flask, into

Fig. 120.

a beaker, diluting with water to about 100 cubic centimeters, and finally allowing a standard decinormal solution of potassium permanganate (page 89) to flow into the liquid from a burette until, with constant stirring, the pink tint of the liquid remains for a time unchanged. The factor of the permanganate solution having been previously ascertained (see pages 89–90), and the number of cubic centimeters of the solution required to produce the above result, or to effect the complete oxidation of the iron, being known, a simple calculation will determine the amount of pure metallic iron contained in the specimen under examination.

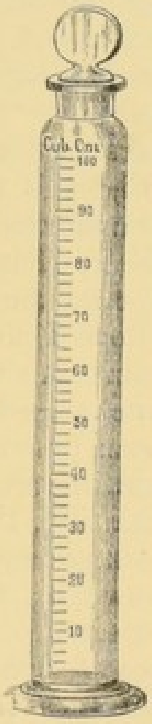
Ferrum Reductum (Ferrum Hydrogenio Reductum).—Iron powder, obtained by the reduction of ferric oxide or hydroxide, or ferrous oxalate, by means of hydrogen, at a strong heat, forms a very fine, gray, loose, lustreless powder, which, when strongly heated, with exposure to the air, becomes oxidized to black ferroso-ferric oxide; when touched with a lighted taper it ignites and burns, affording likewise, as a product of combustion, black ferroso ferric oxide.

Reduced iron is readily and wholly soluble in warm diluted hydrochloric acid, with the evolution of pure hydrogen gas, which is without action upon paper moistened with a solution of plumbic acetate or argentic nitrate, and forming a solution which has the same properties and deportment with reagents as that of powdered iron. If the solution takes place without a copious evolution of gas, and has, when filtered, a yellowish appearance instead of a light-green one, the powder was more or less oxidized, or even so much so as to consist almost wholly of a mixture of ferrous and ferric oxides.

Examination of Ferrum Reductum:

In addition to the above-detailed characters, reduced iron should respond to the following test: When digested for half an hour, at ordinary temperatures, with 25 times its weight of a solution of ferric chloride, of the specific gravity 1.3, in a glass cylinder provided with a glass stopper (Fig. 121), the mixture being repeatedly shaken, the iron should become completely dissolved; any insoluble residue (which may consist of the oxides of iron or other foreign substances) will, according to its amount, determine approximately the value of the specimen under examination.

Fig. 121.



Another test, which may be applied to the determination of the presence of a definite minimum amount of metallic iron in the preparation, consists in digesting for two hours, in a glass vessel, 0.5 part of ferrum reductum with a solution of 1.13 parts of iodine and 1.2 parts of potassium iodide in 25 parts of water; if the solution, at the expiration of two hours, and with the employment of the above proportions, contains no free iodine, but is clear and of a pale greenish color, the presence of at least 50 per cent. of metallic iron in the preparation is assured. The same test may readily be extended in its requirements by the application, in the employment of 0.5 part of ferrum reductum, of 0.226 additional part of iodine, with the proper proportionate amount of potassium iodide, for each 10 per cent. of metallic iron to be indicated.

The United States Pharmacopœia directs that if 1 gram of reduced iron be digested with 3.5 grams of iodine, 2.5 grams of potassium iodide, and 50 cubic centimeters of distilled water, for two hours, the resulting filtrate should have a green color, and should not be rendered blue by gelatinized starch (corresponding to the presence of at least 80 per cent. of metallic iron).

The further testing of ferrrum reductum for *sulphur*, *phosphorus*, *arsenic*, *metallic impurities*, or other admixtures which may be likely to occur, or are otherwise indicated, may be performed according to the methods described under ferrum pulveratum, on pages 365–366.

Estimation of Ferrum Reductum:

I. A convenient and simple method for the estimation of the amount of pure metallic iron in ferrum reductum, and which provides for its admixture with ferroso-ferric oxide, Fe_3O_4, but not for the other oxides or their combinations, is as follows: About 0.2 to 0.3 gram of ferrum reductum, accurately weighed, together with a little pure zinc (about 1 gram), are dissolved in about 20 cubic centimeters of dilute sulphuric acid, in a small flask, so arranged as to prevent the oxidation of the iron during solution (Fig. 120, page 367). The solution, after being allowed to cool, is transferred to a beaker, and, together with the rinsings of the flask, diluted to the measure of 100 cubic centimeters; a standard decinormal solution of potassium permanganate (page 89) is then allowed to flow into the liquid from a burette until, with constant stirring, the pink tint of the liquid remains for a time unchanged. The factor of the permanganate solution having been previously ascertained (pages 89–90), the number of cubic centimeters of the solution employed will indicate, by simple calculation, the total amount of iron present, from which the percentage amount of the latter may be determined. In consideration, however, that the entire amount of iron determined was not originally present as metallic iron, but associated in part with ferroso-ferric oxide, Fe_3O_4, which becomes reduced to ferrous salt through the agency of the nascent hydrogen, the number 72.4

should be subtracted from the total percentage of iron, and the remainder divided by the decimal 0.276, which will yield, as the quotient, the percentage of pure metallic iron contained in the specimen under examination.

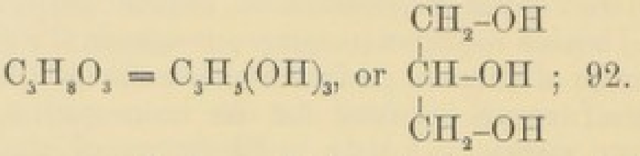
II. Another method, which is based upon the determination of the amount of metallic copper precipitated by a definite amount of reduced iron from a solution of cupric sulphate of known strength, and which requires no correction, as in the above method, for the presence of ferrous or ferric oxides, is as follows: 1 gram of the reduced iron is digested for one hour with a solution of 5 grams of pure cupric sulphate in 25 grams of water, acidulated with 2 drops of dilute sulphuric acid; the solution is then filtered into a previously weighed flask, the filter washed with sufficient distilled water to obtain 50 grams of filtrate, 1 gram of pure powdered iron (the percentage of carbon contained in it should be previously determined) added, and the whole digested until the copper contained in the solution is completely precipitated in a metallic state; 5 grams of pure concentrated sulphuric acid are subsequently added, and the mixture gently heated until the iron is completely dissolved, when the precipitated copper will alone remain, contaminated with a little carbon. The copper is repeatedly washed, by decantation, first with water, afterwards with alcohol, and finally with absolute alcohol and ether; the flask is then quickly dried, by the aid of a gentle heat, weighed, and from the weight of the copper the carbon of the powdered iron (about 0.01 gram) subtracted. Since the difference between the weight of this precipitated copper and the total weight of the metallic copper (1.271 gram) contained in the 5 grams of crystallized sulphate equals the quantity of copper which was precipitated by the metallic iron contained in 1 gram of the reduced iron, the percentage of the unoxidized metal is readily determined from the ascertained weight, and the relation between the atomic weights of copper and iron. The number of centigrams of iron, calculated from the copper which was precipitated in the first part of the process, indicates directly the percentage of metallic iron contained in the reduced iron.

GLYCERINUM.

GLYCERINA.

Glycerin. Triatomic Propenyl Alcohol.

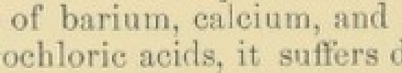
Ger. Glycerin; Fr. Glycérine; Sp. Glicerina.



$$C_3H_8O_3 = C_3H_5(OH)_3, \text{ or } \begin{array}{l} CH_2\text{–}OH \\ \mid \\ CH\text{–}OH \\ \mid \\ CH_2\text{–}OH \end{array} ;\ 92.$$

A colorless and odorless, thick, viscid, neutral liquid, of an intensely sweet taste; when anhydrous, its spec. grav. is 1.267 at 15° C. (59° F.); that of commercial glycerin, containing from 5 to 10 per cent. of water, is from 1.25 to 1.237. When perfectly anhydrous, and exposed to a temperature of 0° C. (32° F.), it is capable, under certain conditions, of assuming the crystalline form; the crystals have a specific gravity of 1.262, belong to the rhombic system, and attract moisture with great avidity, becoming finally liquefied at 10° C. (50° F.), while the melting-point of the perfectly anhydrous crystals is apparently above 23° C. (73.4° F.).

Glycerin is not volatile at common temperatures, but, when exposed in thin layers, is perceptibly volatilized at a temperature of 100° C. (212° F.), and distils unchanged in vacuo, or with aqueous vapor, under pressure; it boils, under ordinary atmospheric pressure, at 290° C. (554° F.), undergoing partial decomposition, and emitting white, irritating, inflammable vapors, which, when ignited, burn with a pale blue flame, leaving no residue.

Glycerin is miscible, in all proportions, with water, solutions of the alkaline hydrates, alcohol, and ether diluted with alcohol, but not with pure ether, chloroform, carbon bisulphide, or benzol; it mixes with concentrated sulphuric acid, with the formation of *sulpho-glyceric acid*,  $C_3H_5\!\left\langle\begin{array}{l}(OH)_2\\ O\text{–}SO_2\text{–}OH\end{array}\right.$, which affords soluble salts with the oxides of barium, calcium, and lead; with concentrated nitric and hydrochloric acids, it suffers decomposition, becoming either oxidized, or forming therewith compound ethers, as in the case of the powerfully explosive, so-called *nitroglycerin*, $C_3H_5(O\text{–}NO_2)_3$. When heated with dehydrating substances (concentrated sulphuric or phosphoric acid, or acid potassium sulphate), glycerin is converted into the strongly irritating substance, *acrolein*, C_3H_4O.

Glycerin possesses extensive powers as a solvent; it dissolves most substances which are soluble in water, although usually in a less degree, but, in some instances, is a better solvent, as, for instance, in the case of alum, borax, and carbolic acid; and dissolves readily many substances which are insoluble or very sparingly soluble in water, such as sulphur and mercuric iodides, bromine, iodine, quinine, morphine, and other alkaloids, as also many metallic oxides, and prevents the precipitation of the latter from their solutions by the alkaline hydrates.

It does not mix with fatty oils, and dissolves essential oils only to a limited extent.

Examination:

A *fatty* or *empyreumatic odor* of glycerin is best recognized by gently warming a little of the sample on a watch-glass, or in a small porcelain capsule, or by the addition of a little dilute sulphuric acid.

Cane-sugar, *glucose*, and *mucilages* are indicated by a more or less brown coloration of the glycerin, when mixed with twice its volume of concentrated sulphuric acid, or when mixed and heated with a strong solution of potassium hydrate; they will also be indicated by a considerable carbonaceous residue, when a little of the glycerin is heated to boiling, in a small platinum capsule, and the vapors ignited.

Glucose may be detected by the occurrence of a brick-red precipitate, when a little of the glycerin, diluted with an equal volume of water, is heated with a few drops of an alkaline solution of cupric tartrate.

Cane-sugar is detected by the same reaction, when the glycerin is boiled for a few minutes with an equal volume of dilute solution of tartaric acid, and the hot mixture tested with Fehling's cupric solution.

Mucilages of gum, *dextrin*, or *glue* are indicated by the formation of a white turbidity, gelatinous or flocculent, when one volume of the glycerin is mixed with four volumes of alcohol.

Metallic salts are detected by agitating one volume of the glycerin with three volumes of a saturated aqueous solution of hydrogen sulphide; any impairment of the colorlessness or transparency of the mixture would indicate metallic impurities; they may be distinguished, as to the group of metals to which they belong, by dividing the liquid into two portions, and adding to the one a little hydrochloric acid, and to the other ammonia-water. *Copper*, *lead*, and *tin* will be indicated by the first test; *iron*, *zinc*, and *aluminium*, by the second. If a precipitate appears in either case, and the nature of the impurity has to be ascertained, the test must be repeated on a larger scale, and the metallic impurity determined by the methods described on pages 51 to 59.

Calcium salts may be detected in the diluted glycerin, by a white turbidity when tested with ammonium oxalate.

Ammonium salts, occasioned by the neutralization of an originally slightly acidulous glycerin with ammonia-water, may be detected by the odor of ammonia when the glycerin is heated, in a test-tube, with an equal volume of a concentrated solution of potassium hydrate, and by the appearance of white fumes, when a glass rod, moistened with acetic acid, is held over the mouth of the tube.

Acids and their Salts.—When diluted with twice its volume of water, the solution must leave litmus-paper unchanged; it is then examined in four separate portions: for *hydrochloric acid* and *chlorides*, by acidulating with nitric acid, and testing with argentic nitrate; for *sulphuric acid* and *sulphates*, by testing the second portion, also acidulated with nitric acid, with barium nitrate; for *oxalic acid*, by testing the third portion, acidulated with acetic acid, with calcium acetate or chloride; and for *nitric acid* and *nitrates*, by adding to the fourth portion a little acetic acid and one drop of neutral indigo solution, and then warming the mixture by dipping the test-tube into hot water; a decoloration of the bluish or bluish-green tint of the liquid will indicate free nitric acid; when the color remains unaltered, a few drops of concentrated sulphuric acid are added to the mixture while still warm; if decoloration takes place now (and the glycerin is free from chlorates), nitrates are indicated.

Another very sensitive test for nitric acid and nitrates, combining the test for *chlorine*, is to mix, in a test-tube, a little mucilage of starch with a few drops of solution of potassium iodide (free from iodate), and a few drops of dilute sulphuric acid, and then to add a small portion of glycerin; when mixed together with a glass rod, the liquid must remain colorless; a blue color would indicate *chlorine;* when the mixture remains colorless, a thin rod of bright zinc is immersed in the centre of the fluid, with care not to agitate the test-tube; if traces of nitric acid or nitrates be present, a bluish coloration, issuing from the zinc, will appear.

Formic acid may be detected by the formation of a black deposit, when a mixture of the glycerin with an equal volume of diluted ammonia-water and a little solution of argentic nitrate is allowed to stand in a corked test-tube, protected from the light, for twenty-four hours.

Butyric acid, and analogous fatty acids, will be indicated by an acid reaction of the glycerin, and may be extracted therefrom by agitation with ether, or may be recognized by the odor of ethyl butyrate (similar to that of artificial essence of pine-apple), when a mixture of two volumes of glycerin with one volume of a mixture of equal parts, by volume, of strong alcohol and concentrated sulphuric acid, is gently warmed by dipping the flask or test-tube into boiling water.

Estimation of Glycerin in Wine, Beer, etc.:

The separation and approximate estimation of glycerin in wine, beer, and other similar liquids, may be accomplished by treating the residue obtained by the evaporation of a measured portion of the liquid, in a small glass flask, with a warm mixture of 1 part of ether and 3 parts of alcohol, which extracts the glycerin, together with some succinic acid and sugar. The liquid is then filtered, if necessary, the filtrate neutralized with milk of lime, the alcohol removed by distillation or evaporation, and the dry residue again extracted with a warm mixture of ether and alcohol, which, after filtration, is allowed to evaporate, upon the water-bath, at the lowest possible temperature. The residue of glycerin thus obtained, after being allowed to stand for two days over sulphuric acid, is finally weighed. The glycerin may be subsequently tested for its identity, if desired, by rendering it slightly alkaline with a dilute solution of sodium hydrate, and moistening therewith a fused bead of borax, contained on the looped end of a platinum-wire: if the borax bead be subsequently held in a non-luminous flame, a deep green tint will be imparted to the latter.

TABLE *of the quantity by weight of Water contained in* 100 *parts by weight of Glycerin of different specific gravities.*

Temperature 17.5° C. (63.5° F.).

Specific gravity.	Per cent. of water.	Specific gravity.	Per cent. of water.	Specific gravity.	Per cent. of water.	Specific gravity.	Per cent. of water.
1.267	0	1.224	13	1.185	26	1.147	39
1.264	1	1.221	14	1.182	27	1.145	40
1.260	2	1.218	15	1.179	28	1.142	41
1.257	3	1.215	16	1.176	29	1.139	42
1.254	4	1.212	17	1.173	30	1.136	43
1.250	5	1.209	18	1.170	31	1.134	44
1.247	6	1.206	19	1.167	32	1.131	45
1.244	7	1.203	20	1.164	33	1.128	46
1.240	8	1.200	21	1.161	34	1.126	47
1.237	9	1.197	22	1.159	35	1.123	48
1.234	10	1.194	23	1.156	36	1.120	49
1.231	11	1.191	24	1.153	37	1.118	50
1.228	12	1.188	25	1.150	38		

HYDRARGYRI CHLORIDUM CORROSIVUM.

HYDRARGYRI PERCHLORIDUM. HYDRARGYRUM BICHLORATUM. HYDRARGYRUM CORROSIVUM SUBLIMATUM.

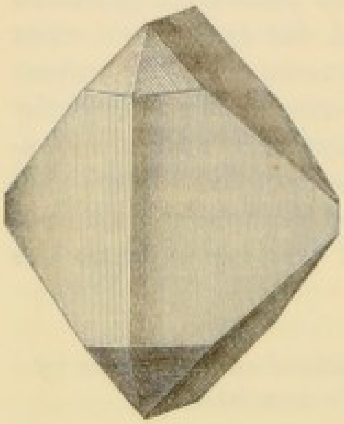
Corrosive Sublimate. Corrosive chloride, Perchloride, or Bichloride of Mercury. Mercuric Chloride.

Ger. Quecksilberchlorid ; Fr. Bichlorure de mercure ;
Sp. Bicloruro de mercurio.

$HgCl_2$; 270.5.

Colorless, translucent, heavy, crystalline masses, when obtained by sublimation, or small, well-developed rhombic prisms (Fig. 122), when obtained by crystallization from its solutions, and having a specific gravity of 5.403; they are permanent in the air, give a dull, white streak when scratched with a knife, fuse at 265° C. (509° F.), and volatilize wholly at 295° C. (563° F.), forming dense, white vapors, which, on cooling, solidify in small, shining needles.

FIG. 122.



Mercuric chloride is soluble in water, requiring, at 10° C. (50° F.), 15.22 parts, at 20° C. (68° F.), 13.53 parts, at 50° C. (122° F.), 8.81 parts, at 80° C. (176° F.), 4.11 parts, and at 100° C. (212° F.), 1.85 parts of water for solution; it is less soluble in glycerin, 100 parts of which dissolve about 7 parts of the salt, but is freely soluble in alcohol and ether, requiring, at 17° C. (62.6° F.), 2.5 parts of alcohol, spec. grav. 0.830, and 4 parts of ether for solution, and is abstracted, for the most part, by the latter, when agitated with its aqueous solution. The aqueous solution reddens blue litmus-paper, and has an acrid, metallic, styptic taste; upon the evaporation of the solution, by the aid of heat, a portion of the salt becomes volatilized with the aqueous vapors.

In the aqueous solution of mercuric chloride, the fixed alkaline and earthy hydrates and alkaline carbonates produce, when added in small quantity, a reddish-brown precipitate; when added in excess, a yellow one; ammonia-water gives a white one; argentic nitrate, a curdy white one; iodides, when added in small quantity, a yellowish, and in larger quantity, a vermilion-red one, soluble in an excess of the precipitant; stannous chloride, when added in small quantity, a white, and when added in excess, a gray precipitate. When an aqueous solution of hydrogen sulphide is gradually added to a solution of mercuric chloride, the precipitation takes place according to the proportions of the reagent and the chloride, in progressive variation of color from white to yellow, orange, reddish-brown, and black; an excess of the reagent produces at once a complete black precipitation. When the aqueous solution of mercuric chloride is rubbed upon bright copper, it coats the latter with a brilliant metallic film. It forms white, insoluble or sparingly soluble compounds with many organic substances, as albumen, fibrin, gluten, etc.; and by exposure to the light, particularly when in contact with organic substances and when possessing an alkaline reaction, it becomes gradually reduced to mercurous chloride (calomel), while its decomposition is prevented or materially retarded by the presence of hydrochloric acid or alkaline chlorides.

Mercuric chloride is soluble, without decomposition, in nitric, hydrochloric, and sulphuric acids; and crystallizes from the solutions on cooling, if they were saturated while hot. With the alkaline chlorides it combines to form double salts, which are mostly well crystallizable, and more readily soluble in water than mercuric chloride.

Examination:

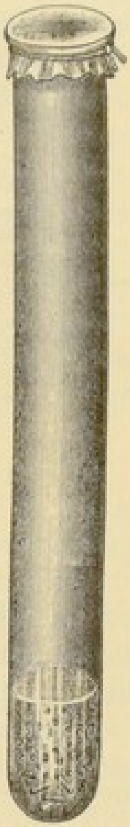
The purity of mercuric chloride will, in most instances, be sufficiently established by its conformity with the above described physical properties, by its complete volatilization upon strongly heating, and its relation to solvents, as also by the several chemical tests.

Arsenic may be readily detected by digesting the powdered mercuric chloride with ammonia-water, or precipitating its aqueous solution by the latter, subsequently filtering, and, after acidulating with dilute sulphuric acid, testing in Marsh's apparatus, page 34; or, after the concentration of the solution by evaporation, the several tests for arsenious acid may be applied, as described under the latter, on pages 127 to 130.

The presence of arsenic may also be quickly determined by dissolving a small portion of the salt in hot water, and adding to the solution, contained in a long test-tube, an excess of a concentrated solution of sodium hydrate, and a few fragments of aluminium wire or pure zinc; a cap of bibulous paper, moistened with a drop of solution of argentic nitrate, is then placed over the orifice of the tube (Fig. 123), and the mixture gently heated; an ensuing dark coloration of the paper or the production of a dark metallic stain will reveal the presence of arsenic.

Mercurous chloride (calomel) and other insoluble impurities or admixtures, will be detected by their remaining undissolved, when the mercuric chloride is digested or gently warmed with about twenty times its weight of water.

Fig. 123.



HYDRARGYRI CHLORIDUM MITE.

HYDRARGYRI SUBCHLORIDUM. HYDRARGYRUM CHLORATUM. MERCURIUS DULCIS.

Calomel. Mild chloride, Sub- or Proto-chloride of Mercury. Mercurous Chloride.

Ger. Quecksilberchlorür; Fr. Protochlorure de mercure; Sp. Protocloruro de mercurio.

HgCl; 235.1.

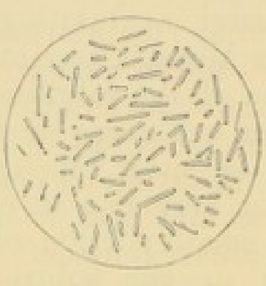
Mercurous chloride varies in the minuteness of its particles, and accordingly in its appearance and in the energy of its physiological action.

When obtained by *sublimation*, it forms ponderous, yellowish-white masses or cakes, of a fibrous, crystalline fracture, yielding a lemon-yellow streak when scratched with a knife, and having a specific gravity of 7.176. When reduced to a fine powder by trituration and levigation, it has a dull-white appearance with a yellowish tint; it becomes slightly yellowish when triturated with strong pressure in a porcelain mortar, and consists, when seen under the microscope, of comparatively large, transparent, crystalline fragments (Fig. 124).

FIG. 124.

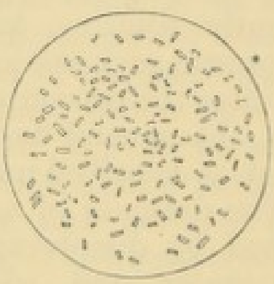
250 diam.

FIG. 125.



250 diam.

FIG. 126.



250 diam.

Prepared by *sublimation* and by *condensation* of the vapor by a current of air or steam, mercurous chloride (Hydrargyri Chloridum Mite vapore paratum) forms a perfectly white and less ponderous powder (specific gravity 6.56), consisting of smaller laminar particles, when seen under the microscope (Fig. 125).

Prepared by *precipitation*, mercurous chloride forms a fine snow-white powder, consisting of minute, amorphous[*] particles (Fig. 126), which are not transparent, and are devoid of odor or taste.

With regard to therapeutical action, mercurous chloride, obtained by sublimation and subsequent trituration and levigation, and consisting of the largest particles, has the mildest effect; next to this comes the calomel obtained by sublimation and condensation by air or steam;[†] that obtained by precipitation, and having the minutest division of its particles, has the more powerful physiological action.

Mercurous chloride, when heated in a dry test-tube, is slowly but completely volatilized with a faint noise and without fusion. It is insoluble in the common solvents, but soluble to some extent in saliva, in the pancreatic juice, in albumen, and animal secre-

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[*] When obtained by precipitating a solution of mercuric chloride with sulphurous-acid gas, the resulting mercurous chloride is of a crystalline structure.

[†] No other kinds of mercurous chloride can as yet be considered officinal, and no others should be dispensed for internal use, unless ordered or prescribed, than "*Calomel via humida paratum*," or "*Calomel precipitatione paratum.*"

tions. When agitated with hot water, with alcohol, or with dilute acetic, hydrochloric, or nitric acids, it is not acted upon by any of them. When boiled for some time with water, it suffers slow decomposition into metallic mercury and mercuric chloride; the decomposition being greater in extent when, instead of pure water, solutions of the alkaline chlorides are employed.

The fixed alkaline hydrates and carbonates, and the hydrates of the alkaline earths, reduce mercurous chloride to black oxide; the same conversion of mercurous chloride to oxide is also occasioned by its exposure to light, and by contact with many organic substances. Concentrated boiling hydrochloric and sulphuric acids decompose the salt; the former producing metallic mercury and mercuric chloride, the latter mercuric sulphate and chloride. Warm concentrated nitric acid also dissolves it gradually, with the evolution of nitric oxide vapors, forming a solution of mercuric chloride and nitrate, which solution blackens bright copper when dropped upon it, and coats it brilliantly when rubbed upon it. Mercurous chloride is also soluble in chlorine-water without acquiring a transient or permanent yellow color (distinction from mercurous bromide).

Examination:

When heated in a narrow test-tube, mercurous chloride must completely sublime, without previous fusion and without emitting ammoniacal odors or yellow nitrous vapors.

Mercuric chloride may be most quickly detected by placing a little of the mercurous chloride, previously moistened with water to the consistence of a thin paste, upon a piece of bright iron, and allowing the mixture to repose thereon for one or two minutes; if mercuric chloride is present, it will become instantly decomposed, and there will appear upon the iron, after the removal of the mixture by rinsing with a little water, a deep, dull-black stain;* it may also be detected by triturating some of the calomel with diluted alcohol, agitating the mixture in a test-tube, and subsequently filtering through a moist double filter; the filtrate must impart no stain to bright copper, nor yield any reaction with hydrogen sulphide or with argentic nitrate.

Ammoniated mercury (white precipitate) may be detected by the development of the odor of ammonia, when the mercurous chloride is heated, in a test-tube, with a concentrated solution of potassium or sodium hydrate; or, when the mercurous chloride of the preceding test, remaining upon the filter, is rinsed with diluted acetic acid through the broken filter into a test-tube, and the mixture agitated for a few minutes and filtered. The filtrate is then tested in separate portions with hydrogen sulphide and

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* Pure mercurous chloride will produce under the same circumstances, by prolonged contact with the iron, a slight grayish film upon the latter, which, however, cannot be mistaken for the characteristic black stain produced by the mercuric salt.

argentic nitrate; a black turbidity in the first instance, and a white one in the second, would indicate ammoniated mercury.

Non-volatile impurities, such as the sulphates or carbonates of the alkaline earths, may readily be detected when a little of the mercurous chloride is completely volatilized by strongly heating in a test-tube; any residue thus obtained may be further examined for its identification, if desired, according to the systematic methods of analysis, as described on pages 51 to 61.

HYDRARGYRI CYANIDUM.

HYDRARGYRUM CYANATUM.

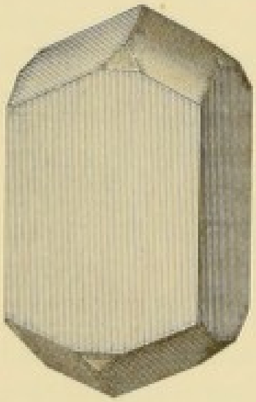
Cyanide of Mercury. Mercuric Cyanide.

Ger. Quecksilbercyanid; Fr. Cyanure de mercure; Sp. Cianuro de mercurio.

$Hg(CN)_2$; 251.7.

Colorless, anhydrous, needle-shaped crystals, or lustrous quadratic prisms (Fig. 127), transparent when freshly prepared, but soon assuming a white and opaque appearance; when perfectly dry, and carefully heated in a dry tube, they become decomposed into metallic mercury and a colorless inflammable gas (cyanogen), which burns, when ignited, with a purple flame; when quickly heated, a black residue of paracyanogen, intermingled with globules of mercury, is left behind, which, however, upon more strongly heating, is completely dissipated; when the salt is humid, traces of hydrocyanic acid, of carbonic acid, and of ammonia, are also formed and evolved.

FIG. 127.



Mercuric cyanide is soluble in 12.8 parts of water and in 14.5 parts of alcohol at 15° C. (59° F.), in 3 parts of boiling water and in 6 parts of boiling alcohol, but almost insoluble in absolute alcohol and ether; its aqueous solution possesses a disagreeable metallic taste, and is decomposed by hydrochloric acid and by hydrogen sulphide, with the liberation of hydrocyanic acid and the formation of mercuric chloride or sulphide, but is not decomposed by dilute sulphuric or nitric acid, and is not precipitated by the alkaline hydrates and carbonates, by argentic nitrate, or by albumen; stannous chloride, containing free hydrochloric acid, precipitates metallic mercury with the evolution of hydrocyanic acid. The solution of mercuric cyanide affords no mercuric stain upon bright metallic copper, unless the latter be previously moistened with hydrochloric acid; it readily dissolves mercuric oxide, and, on evaporating the alkaline solution thus obtained, small needle-shaped crystals of an oxy-cyanide, $Hg_2O(CN)_2$, are formed.

Examination:

Mercuric oxy-cyanide is indicated by an alkaline reaction of the solution upon turmeric-paper.

Mercuric chloride and other *soluble mercuric salts* may be detected in the solution, by the occurrence of a transient turbidity upon the gradual addition of single drops of solution of potassium iodide, or by the production of a precipitate upon the addition of the alkaline hydrates or carbonates.

HYDRARGYRI IODIDUM RUBRUM.

HYDRARGYRUM BIIODATUM.

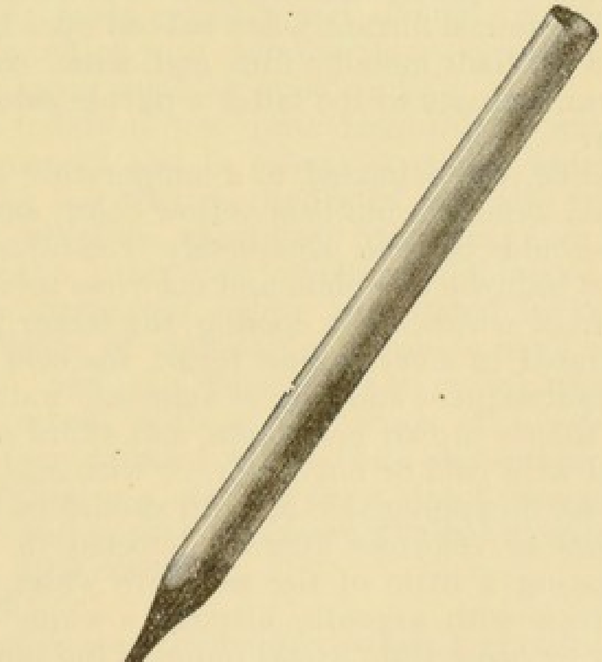
Red Iodide of Mercury. Biniodide of Mercury. Mercuric Iodide.

Ger. Quecksilberjodid; Fr. Bi-iodure de mercure; Sp. Bi-ioduro de mercurio.

HgI_2; 452.9.

A heavy, amorphous, scarlet-red powder, or small, brilliant, octahedral crystals, belonging to the quadratic system, and having a specific gravity of 6.3. When gently heated in a dry tube

FIG. 128.



(Fig. 128) to about 150° C. (302° F.), mercuric iodide first becomes of a pure yellow color, then, when near the melting-point, deep orange, and finally melts at 253–254° C. (487.4–489.2° F.) to a blood-red liquid; at this temperature the volatilization of the iodide begins, when it sublimes undecomposed in the form of yellow rhombic scales, which pass into the red modification of octahedral crystals, slowly on cooling, and at once by concussion.

If the salt be heated with solution of sodium hydrate, and a little sugar of milk added, a precipitate of metallic mercury is produced; and if heated with sulphuric acid and a little manganese dioxide, the vapor of iodine is evolved.

Mercuric iodide is nearly insoluble in cold, and only very sparingly soluble in boiling, water; it is soluble in 130 parts of cold, and 15 parts of boiling, alcohol, less soluble in ether, and very little in glycerin and in oils. Concentrated acids, and the solutions of the alkaline hydrates, decompose it; it is freely soluble in aqueous solutions of potassium and sodium hydrates, of potassium iodide and cyanide, of mercuric chloride, and of sodium chloride and sodium hyposulphite; the latter solution deposits, upon gently heating, if the solvent is not in excess, red mercuric sulphide, while, upon boiling, black mercuric sulphide, mixed with mercurous iodide and metallic mercury, is separated. All its solutions form a black precipitate upon saturation with hydrogen sulphide, either at once, or upon the addition of an acid.

Mercuric iodide is partly decomposed when shaken with chlorine-water; the obtained filtrate, when rubbed upon bright copper, coats it with a brilliant metallic film, and, when shaken with a little chloroform, imparts to the latter a purple color.

Examination:

Mercuric iodide, when heated to a temperature above 150° C. (302° F.), should assume a uniform yellow color, and, at a higher temperature, should become completely volatilized; with hot alcohol it must afford a complete and colorless solution, without acid reaction, from which, upon cooling, the larger portion of the iodide is separated in a crystalline form; the cold filtered solution, upon the subsequent addition of ammonia-water, should not assume more than a brown coloration, and afford no precipitate. When digested with cold or hot water, or with acetic acid of the spec. grav. 1.040, no appreciable amount should be dissolved.

Soluble iodides or *chlorides* may be detected in the mercuric iodide by digesting a little of the salt with water, filtering, and testing the filtrate with argentic nitrate; a white or yellowish-white turbidity or precipitate would indicate the presence of such admixtures.

Mercuric sulphide, red oxide of lead, or other fraudulent admixtures, will remain undissolved upon digesting the powder, either in solution of potassium iodide, or in twenty to twenty-five parts of boiling alcohol. If a residue is left, it is washed with water, and subsequently treated with warm nitric acid, and filtered; the filtrate is slightly diluted, and tested with a few drops of diluted sulphuric acid; an ensuing white precipitate indicates *lead*. If a red residue remains, insoluble in nitric acid, it is tested by heating it upon platinum-foil to redness; if it is wholly volatile, *mercuric sulphide* is recognized, and, if a residue remains, *fixed admixtures* are indicated.

HYDRARGYRI IODIDUM VIRIDE.

HYDRARGYRUM IODATUM.

Green Iodide of Mercury. Protoiodide of Mercury. Mercurous Iodide.

Ger. Quecksilberjodür; Fr. Protoiodure de mercure; Sp. Protoioduro de mercurio.

HgI; 326.3.

A heavy powder, of a dull-green or greenish-yellow color, which suffers gradual decomposition and becomes brownish on exposure to light, heat, and air. When heated in a dry tube (Fig. 128, page 379), it begins, at 70° C. (158° F.), to assume a red color, which increases in intensity until, at 200° C. (392° F.), it acquires a deep garnet-red color; at 220° C. (428° F.) it softens, and melts at 290° C. (554° F.), but begins to sublime, at 190° C. (374° F.), and by slow sublimation forms small, transparent, yellow crystals of the quadratic system, having the specific gravity of 7.6; when quickly and strongly heated, it suffers a partial decomposition into metallic mercury and mercuric iodide, which do not again combine upon cooling.

Mercurous iodide is not quite insoluble in water, but wholly insoluble in alcohol and in ether; it is decomposed by concentrated acids, by the alkaline hydrates, and also by boiling solutions of the alkaline chlorides, bromides, and iodides, being converted by the latter into mercuric iodide and metallic mercury. When mercurous iodide is agitated in a little water to which a few drops of ammonium sulphide have been added, the liquid filtered, and the filtrate, after acidulating with hydrochloric acid, mixed with a few drops of a solution of ferric chloride and then agitated with a little chloroform, the latter will acquire a purplish or violet-red color, due to the presence of free iodine, which will appear still more distinct upon the subsequent addition of a little water.

Examination:

Mercuric iodide may be detected when 1 gram of the powder is agitated and digested with about 10 cubic centimeters of alcohol, subsequently filtered, and the filtrate dropped into water, when not more than a slight transient opalescence should be produced; and when 5 cubic centimeters of the filtrate are evaporated from a white porcelain surface, not more than a faint red stain should remain behind; neither should the filtrate afford more than a very slight coloration or turbidity upon saturation with hydrogen sulphide, otherwise the presence of an undue amount of biniodide or mercuric salt is indicated.

Fixed impurities will remain behind upon the complete volatilization of the mercurous iodide in a dry tube; such would be very likely to originate from either the mercury or the iodine, and, if required, their nature may be determined by the methods described on pages 388–390 and 395–396.

HYDRARGYRI OXIDUM FLAVUM.

HYDRARGYRUM OXYDATUM VIA HUMIDA PARATUM.

Yellow Oxide of Mercury. Precipitated Mercuric Oxide.

Ger. Gelbes Quecksilberoxyd; Fr. Oxyde de mercure jaune; Sp. Protóxido de mercurio.

HgO; 215.7.

A heavy, orange-yellow powder, without crystalline structure when seen under the microscope, permanent in the air, and having a specific gravity of 11.3. It becomes darker on exposure to the light, and assumes a red color on being heated; at a higher temperature it is decomposed with the evolution of oxygen and the separation of mercury, and is finally entirely volatilized. It is more readily acted upon by reagents than the coarser red oxide; the latter remains unchanged when agitated with a warm solution of oxalic acid, while the yellow oxide combines with the oxalic acid, forming white mercuric oxalate; when agitated with a hot alcoholic solution of mercuric chloride, the yellow oxide becomes at once black, in consequence of the formation of mercuric oxychloride ($HgCl_2.2HgO$), while the red oxide remains unchanged for some time.

The chemical reactions of the precipitated yellow mercuric oxide, and its deportment with reagents, correspond with those of the red oxide.

HYDRARGYRI OXIDUM RUBRUM.

HYDRARGYRUM OXYDATUM.

Red Oxide of Mercury. Red Precipitate. Mercuric Oxide.

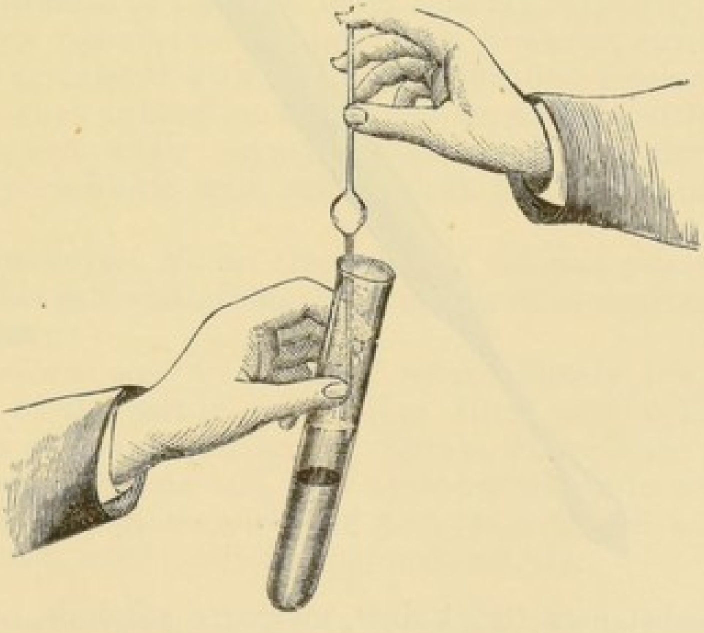
Ger. Rothes Quecksilberoxyd; Fr. Oxyde de mercure rouge; Sp. Deutóxido de mercurio.

HgO; 215.7.

Heavy, coherent masses, consisting of bright, brick-red, crystalline scales, which, when finely pulverized, form a dull orange-red powder, of a specific gravity of 11.136; when heated in a dry tube, red mercuric oxide first changes to a dark cinnabar-red color, and afterwards assumes a black tint, but regains its original color on cooling; at temperatures above 400° C. (752° F.) it is completely resolved into its constituents, and is entirely volatilized below a red heat, while at a much lower temperature it suffers a partial dissociation.

Mercuric oxide is slightly soluble in water, so that, when agitated with boiling water, the filtrate possesses a decided metallic taste, an alkaline reaction upon litmus, and affords with ammonium sulphide a slight brown coloration; it is insoluble in pure glycerin, in alcohol, ether, and chloroform, somewhat soluble in saliva and in albuminous animal secretions, and entirely soluble in strong and in somewhat diluted acids. The fixed alkaline and earthy hydrates and alkaline carbonates produce in solutions of mercuric oxide and its salts, when added in small quantity, a reddish-brown, when added in excess, a yellow precipitate; ammonia-water, a white one; iodides (provided that the solution does not contain a large excess of acid), when added in small quantity, a yellowish, and in a larger quantity, a vermilion-red one, soluble in an excess of the precipitant; stannous chloride, when added in small quantity, gives a white, and, in excess, a gray precipitate. When water saturated with hydrogen sulphide is gradually added to the solution, or when the latter is slowly saturated with the gas, a precipitate is formed which appears, according to the proportion of the reagent, successively white, yellow, orange, reddish-brown, and finally, with an excess of the precipitant, black.

FIG. 129.

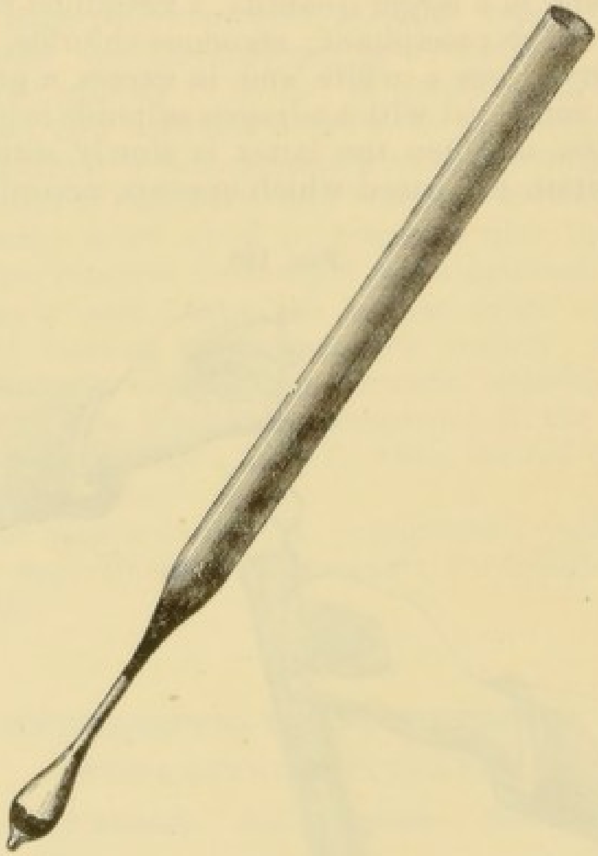


Examination:

Mercuric nitrate is indicated by the disengagement of red nitrous vapors, when the oxide is heated in a dry test-tube. As a confirmatory test, and one permitting the detection of much smaller quantities of nitrate, about 0.5 gram of the oxide is mixed with 10 drops of water, in a test-tube, then three times its volume of concentrated sulphuric acid added, and to the mixture, after being well agitated and subsequently allowed to repose, a saturated solution of ferrous sulphate is carefully added so as to form two layers (Fig. 129); the occurrence of a dark-brown zone at the line of junction of the two liquids will confirm the presence of nitrate.

Admixtures.—A small portion of the oxide is gently heated with about ten times its weight of dilute nitric acid, when complete solution should take place; if the oxide be very old, a slight residue of reduced mercury might remain, which, when separated and heated in a porcelain capsule, should wholly volatilize. If a red or brown residue is left from the solution, an admixture of mineral substances (brick-dust, mercuric sulphide, or red oxide of lead) would be indicated. If the nature of such a residue has to be ascertained, a somewhat larger quantity may be obtained, which, when washed and dried, may be heated in a reducing-tube

Fig. 130.



(Fig. 130); vermilion volatilizes, forming a fine, red sublimate; red oxide of lead fuses, and exhibits, when cooled, a yellow vitrified appearance, and dissolves, when boiled in concentrated nitric acid diluted with an equal bulk of water, leaving behind silicious mineral substances, if such be present. The solution of the oxide in dilute nitric acid may also be tested with argentic nitrate, which should afford no turbidity, thus establishing the absence of *chlorides.*

HYDRARGYRI SUBNITRAS.

HYDRARGYRUM NITRICUM OXYDULATUM.

Subnitrate of Mercury. Mercurous Nitrate.

Ger. Salpetersaures Quecksilberoxydul; Fr. Azotate mercurieux;
Sp. Protonitrato de mercurio.

$HgNO_3 + H_2O$; 279.7.

Colorless, transparent monoclinic tables or prisms,* containing one molecule (6.5 per cent.) of water of crystallization, which is lost on exposure to dry air or by standing over sulphuric acid; they melt at 70° C. (158° F.), and when gradually heated in a dry tube, emit yellow nitrous vapors, become yellow, then red, and are finally resolved into metallic mercury; the crystals become grayish-black when moistened with lime-water.

Mercurous nitrate is soluble in a small amount of warm water, but, upon the addition of more water, it becomes decomposed, with the separation of a yellow basic salt, $HgNO_3 + HgOH$, while an acid nitrate remains in solution; it is, however, entirely soluble in water acidulated with nitric acid, forming a colorless solution, which, when rubbed on bright copper, coats it with a white, metallic film, and, when largely diluted, yields a white precipitate with hydrochloric acid, and a black one with ammonia or lime-water.

Liquor Hydrargyri Nitrici Oxydulati of German pharmacy is a solution of this salt, containing 10 per cent. of mercurous nitrate.

Examination:

Mercuric nitrate may be detected by completely precipitating the solution of the salt in cold dilute nitric acid with diluted hydrochloric acid, and testing the filtrate, in separate portions, with hydrogen sulphide and with stannous chloride, and warming; a black precipitate with the first reagent, and a gray one with the second, would indicate mercuric nitrate.

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* According to the proportion between the mercury and the nitric acid employed in the preparation, there is formed a normal or a basic mercurous nitrate, which correspond in their chemical and therapeutical properties, except that, when rubbed with a little sodium chloride, the normal salt remains white, while the basic salt gives a grayish-green mixture.

HYDRARGYRI SUBSULPHAS FLAVUS.

HYDRARGYRUM SULFURICUM FLAVUM. TURPETHUM MINERALE.

Yellow Subsulphate of Mercury. Basic Mercuric Sulphate. Turpeth Mineral.

Ger. Basisch Schwefelsaures Quecksilberoxyd; Fr. Sous-sulfate de mercure; Sp. Sulfato básico de mercurio.

$HgSO_4 + 2HgO$; 727.1.

A heavy, lemon-yellow powder, of a crystalline structure when seen under the microscope, having a specific gravity of 8.3, and possessing an acrid taste. When heated in a dry tube, it assumes a reddish-brown hue, but regains its original color on cooling; at a higher temperature it volatilizes without fusion, yielding a white sublimate (mercuric sulphate) intermingled with gray metallic mercury; it is decomposed and entirely volatilized at a red heat, evolving vapors of mercury and of sulphurous acid.

Basic mercuric sulphate is almost insoluble in cold, and sparingly soluble in hot, water, but soluble in diluted hydrochloric and nitric acids, forming colorless solutions which, when diluted, give a white precipitate with soluble barium salts, and which otherwise, in their deportment with reagents, resemble the solutions of mercuric chloride and oxide (pages 374 and 383).

HYDRARGYRI SULPHIDUM RUBRUM.

HYDRARGYRUM SULFURATUM RUBRUM. CINNABARIS.

Red Sulphide of Mercury. Cinnabar. Vermilion. Mercuric Sulphide.

Ger. Schwefelquecksilber, Zinnober; Fr. Sulfure de mercure rouge; Sp. Deutosulfuro de mercurio.

HgS; 231.7.

Heavy masses, or cakes, of a specific gravity of 8.124, and of a dull blackish-red color, and a brilliant crystalline texture, yielding a red streak when scratched with a knife, and a magnificent scarlet powder, which becomes black when moistened with an ammoniacal solution of argentic nitrate. When heated to 250° C. (482° F.), mercuric sulphide becomes brown, at a higher temperature, black, and, on cooling, reassumes its red color; at a strong heat, with exposure to the air, it is wholly dissipated, burning with a bluish flame, and emitting the odor of sulphurous acid; when gently heated in a small glass tube, it softens, and sublimes without previous fusion, but undergoes partial dissociation into a black mixture of mercuric sulphide, mercury, and sulphur, with the evolution of a little sulphurous acid; when heated in closed vessels, with exclusion of the air, it sublimes below a red heat, without decomposition, in the form of beautiful red, crystalline crusts.

Mercuric sulphide is insoluble in the common solvents, nor is it acted upon by officinal hydrochloric or nitric acid, or by alkaline hydrates, at common temperatures; boiling concentrated sulphuric acid decomposes it, with the formation of mercuric sulphate, attended by the separation of sulphur and the evolution of sulphur dioxide; it is also soluble in concentrated hydriodic acid in the cold, and in the dilute acid when warmed, with the evolution of hydrogen sulphide; nitro-hydrochloric acid (aqua regia) dissolves it readily, even in the cold, with the formation of mercuric chloride and sulphuric acid, and the separation of sulphur, and yielding a colorless solution which, when diluted with water, gives a white precipitate with barium chloride, coats metallic copper with a film of mercury, and corresponds in its deportment with reagents to solutions of mercuric salts (pages 374 and 383).

Examination:

Oxides of Lead and Iron.—Such admixtures will be indicated by the incomplete volatilization of the mercuric sulphide when strongly heated in a small glass tube; their presence may be confirmed by agitating a small portion of the salt, in a test-tube, with about five times its weight of concentrated nitric acid; the scarlet color must remain unaltered, as change to a darker tint would indicate red oxide of lead; the mixture is then gently heated by immersing the test-tube in hot water, and is subsequently diluted with twice its volume of water, and filtered; the filtrate should be colorless; a yellowish appearance would indicate red *basic plumbic chromate*, or mercuric chromate (chromic cinnabar); it is then tested in separate portions with hydrogen sulphide, with sulphuric acid, and with potassium iodide, for lead; another portion is tested with potassium ferrocyanide for ferric oxide; if this be present, the yellowish color of the nitric acid, agitated with the cinnabar, may be due only to iron.

Chromates may be detected or confirmed by the occurrence of red irritating fumes of chloro-chromic anhydride (CrO_2Cl_2), when a small portion of the mercuric sulphide is carefully mixed and heated in a test-tube with a few small fragments of dry sodium chloride and a few drops of concentrated sulphuric acid.

Mercuric Iodide, Realgar, and Antimonic Cinnabar.—A portion of the mercuric sulphide is agitated with about five times its weight of a warm concentrated solution of potassium hydrate, the liquid subsequently diluted with an equal volume of water, and filtered; the filtrate should be colorless, should cause neither a coloration nor a turbidity when dropped into chlorine-water, and should not afford a colored precipitate when dropped into a dilute solution of plumbic acetate. A yellow or reddish coloration of the chlorine-water would indicate mercuric iodide, and a black precipitate with plumbic acetate, red arsenic sulphide (Realgar), or antimonic oxy-sulphide (Antimonic Cinnabar). If either of the latter two be indicated, the alkaline filtrate will give, upon supersaturation with hydrochloric acid, a yellow precipitate when the first compound is present, and an orange-red one with the second.

HYDRARGYRUM.

Mercury. Quicksilver.

Ger. Quecksilber; Fr. Mercure; Sp. Mercurio.

Hg; 199.7.

A silver-white and brilliantly lustrous metal, having a specific gravity of 13.595 at 0° C. (32° F.) compared with water at 4° C. (39.2° F.), or 13.573 at 15° C. (59° F.). It is liquid at common temperatures, and easily divisible into spherical globules, but solidifies when cooled to —39.38° C. (—38.88° F.), forming at and below that temperature a ductile, malleable mass, capable of being cut with a knife, and crystallizing in octahedrons of the regular system, which have a specific gravity of 14.39; it boils at 357.25° C. (675.05° F.), forming a transparent, colorless vapor, but is volatile to a perceptible extent at ordinary temperatures, both in a vacuum and in air. When pure, it is unalterable by the action of the air at common temperatures, and remains bright and brilliant.

Mercury is insoluble in the common solvents, in concentrated hydrochloric acid, and, at common temperatures, also in sulphuric acid; but it is dissolved by the latter when boiled with it, and is readily dissolved without residue by nitric acid, forming a solution, which contains mercuric nitrate when heat is applied and an excess of concentrated acid, and mercurous nitrate when the metal is in excess or is acted upon by cold and diluted nitric acid.

Examination:

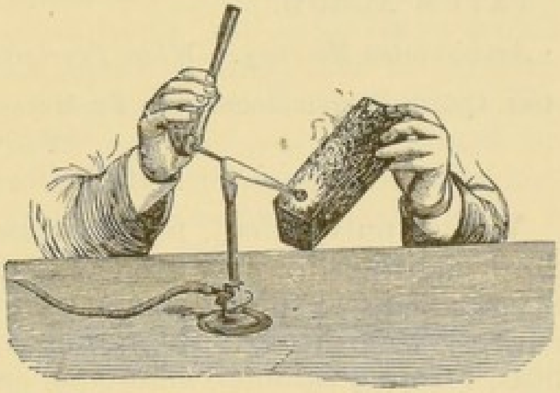
Mercury amalgamates with many metals, and, to a certain extent, without change of its appearance and properties; the most common of such metallic impurities are lead and tin, and occasionally zinc and bismuth; their presence in the commercial metal is indicated by a dull, tarnished appearance, and a black, powdery coating of the surfaces of the metal, and of the inside of the vessels containing it, and by lead-gray streaks upon white paper when a few globules of the metal are allowed to roll over it.

Such contamination may be ascertained by agitating for a few minutes a little of the mercury, in a strong bottle, with a moderately dilute solution of ferric chloride (free from ferrous salt); after subsiding, the aqueous liquid is poured into a test-tube, diluted with an equal volume of water, and tested with a few drops of a solution of potassium ferricyanide; a blue turbidity will indicate the above-mentioned metallic impurities.

When their nature has to be determined, the following method is practicable and simple. About 20 grams of the metal, including as much of the powdery coating on the surfaces of the metal and the bottle as can be collected, is heated and volatilized in a small porcelain crucible, in a place where the vapors are readily removed by draught; if a non-volatile residue remains, it is heated to redness. A small part of the residue is then heated in a test-tube with a few drops of concentrated hydrochloric acid; the solution is decanted from the insoluble residue, and, after the addition of a little nitric acid or chlorine-water, one drop of solution of auric chloride is added; an ensuing purple or violet-red turbidity would indicate *tin*.

The rest of the residue in the crucible is treated with warm concentrated nitric acid; if only partial solution takes place, and at the same time a white precipitate is formed, this may be oxide of tin or antimony; in order to distinguish them, the precipitate is separated from the acid solution, washed with a little water, and subsequently heated upon charcoal before the blow-pipe; *stannous oxide* remains unchanged, while *antimonic oxide* volatilizes in white fumes, forming a white concentric incrustation on the coal (Fig. 131).

FIG. 131.



The nitric acid solution is diluted with an equal bulk of water, and part of it is tested with solution of sodium sulphate; a white precipitate would indicate *lead;* another part is poured into a large beaker full of water; a white opalescence or turbidity of the water indicates *bismuth*.

If lead be present, the rest of the nitric acid solution is saturated and completely precipitated with hydrogen sulphide, and allowed to stand in a corked test-tube for some hours; it is then filtered and supersaturated with ammonia-water; a white precipitate would indicate *zinc*.

If the precipitate is not quite white, and the lead has been completely removed, it might be due to traces of *iron*, of which metal, however, mercury can only contain traces, since it does not amalgamate with it.

An efficient and satisfactory method for the purification of mercury, when contaminated with foreign metals, consists in shaking it vigorously with an equal volume of a solution composed of 5 grams of potassium bichromate and 5 grams of pure concentrated sulphuric acid in 1 liter of water. The metal is reduced to small globules, while a very small part of it is converted into red chromate. The agitation is continued until the red powder has disappeared and the aqueous solution has acquired a pure green color, due to the chromium sulphate formed. By means of a powerful current of water, which is passed into the flask, the gray powder upon the surface of the mercury, which is composed of the oxides of the metallic impurities, is washed away. The process of oxidation is repeated once or twice, according to the degree of impurity, until gray powdery particles are no longer formed, when the mercury is finally thoroughly washed with distilled water until it remains perfectly clear.

HYDRARGYRUM AMMONIATUM.

HYDRARGYRUM AMIDATO-BICHLORATUM. HYDRARGYRUM AMMONIATUM BICHLORATUM. HYDRARGYRUM PRÆCIPITATUM ALBUM.

Ammoniated Mercury. White Precipitate. Mercurammonium Chloride.

Ger. Quecksilberamidochlorid; Fr. Mercure précipité blanc; Sp. Precipitado blanco.

NH_2HgCl; 251.1.

White, pulverulent, friable masses, or a perfectly white, inodorous powder, having a specific gravity of 6.7, and developing a styptic taste when placed upon the tongue; it is decomposed and entirely volatilized, without fusion, at temperatures below a red-heat, forming calomel, ammonia, and nitrogen:

$$6NH_2HgCl = 6HgCl + 4NH_3 + N_2.$$

It becomes black in contact with hydrogen sulphide, gray when boiled with solution of stannous chloride, and pale yellow, with the evolution of ammonia, when heated with a solution of potassium or sodium hydrate. When intimately mixed and triturated, in its dry condition, with iodine, it becomes gradually decomposed with slight deflagration, and with the formation of mercuric chloride and iodide, ammonium chloride, ammonia, and nitrogen gases; the reaction is facilitated by the presence of a little water, but, if alcohol be poured upon the mixture, a violent explosion ensues.

Ammoniated mercury is insoluble in the common solvents, and is gradually decomposed by prolonged washing with cold water, more quickly by boiling water, into ammonium chloride, and a heavy, yellow, insoluble powder of hydrated dimercurammonium chloride [$Hg_2(NH)_2ClO$]; it is readily and wholly soluble without effervescence in warm hydrochloric, nitric, and acetic acids, forming colorless solutions, which, after dilution with water, yield a white precipitate with a cold solution of potassium hydrate and with argentic nitrate, a black one with an excess of hydrogen sulphide, and a red one with potassium iodide, and which produce a black stain upon bright, metallic copper, coating it, when rubbed thereon, with a brilliant metallic film.

Examination:

Mercuric chloride is detected by agitating a small portion of the powder with about ten times its weight of diluted alcohol, filtering, and testing the filtrate with hydrogen sulphide and with potassium iodide; a black precipitate with the first-named reagent, and a red one with the latter, soluble in an excess of the precipitant, will indicate mercuric chloride.

Mercurous chloride may be detected by a black coloration of the powder, when it is triturated with lime-water, or by dissolving a small portion of the powder in warm diluted nitric acid; if an insoluble residue remains, it is washed by decantation, and, when the water ceases to act on blue litmus-paper, the residue is agitated with lime-water; if mercurous chloride, it will become black.

Plumbic Carbonate and *Chloride*, and *Calcium Carbonate.*—Carbonates are indicated by effervescence of the powder with acids, and plumbic chloride by its solubility in hot water (from which it separates in a crystalline form upon cooling), and by its very sparing solubilty in diluted hydrochloric and nitric acids. The presence of lead and calcium salts may be further confirmed by dissolving a portion of the powder in warm acetic acid, filtering, and testing a little of the filtrate with sulphuric acid, when a white precipitate will indicate *lead*, and, if the solution is not too dilute, the possible presence also of calcium; if a precipitate is produced, the remaining portion of the acetic acid solution is completely saturated with hydrogen sulphide, subsequently filtered, and the filtrate tested with ammonium oxalate, when a white precipitate will reveal the presence of *calcium.*

Zinc and *magnesium oxides* may be detected in the solution of the powder in hydrochloric acid, after dilution with water, by complete precipitation with hydrogen sulphide, and by subsequent neutralization of the filtrate with ammonia-water, and the addition of ammonium sulphide; a white precipitate will indicate *zinc;* after the complete precipitation of the latter, and subsequent filtration, the solution is boiled for a few minutes, and, after being allowed to cool, is tested by the addition of a solution of sodium phosphate and a little ammonia-water, when the formation of a white crystalline precipitate will reveal the presence of *magnesium.*

These and all other non-volatile admixtures are also indicated by remaining behind when a few grains of the ammoniated mercury are heated and volatilized, in a narrow, dry test-tube.

Mercurdiammonium chloride, $(NH_3)_2HgCl_2$, or fusible white precipitate, will be indicated in this test by a partial or complete fusion of the powder, previous to its volatilization, provided that the ammoniated mercury be free from any fixed fusible admixture.

Starch.—An admixture of starch is detected by the microscope, by the powder becoming charred when strongly heated on platinum-foil, and also by a blue coloration, when a small portion of the powder is triturated, and subsequently heated to boiling, with a little water, and then tested with one drop of iodinized potassium iodide.

HYOSCYAMINÆ SULPHAS.

HYOSCYAMINUM SULFURICUM.

Sulphate of Hyoscyamine. Hyoscyamine Sulphate.

Ger. Schwefelsaures Hyoscyamin; Fr. Sulfate de hyoscyamine;
Sp. Sulfato de hiosciamina.

$(C_{17}H_{23}NO_3)_2.H_2SO_4$; 676.

Small, golden-yellow, or yellowish-white scales or crystals, or a yellowish-white, amorphous powder, deliquescent on exposure to the air. When heated on platinum-foil, the salt is decomposed with the separation of carbon, and is finally completely dissipated. Hyoscyamine sulphate is very freely soluble in water and in alcohol. Its aqueous solution is neutral in its action upon litmus, possesses a bitter and acrid taste, and yields with solution of barium chloride a white precipitate, insoluble in hydrochloric acid; it is also precipitated by most alkaloidal reagents, potassio-mercuric iodide, iodinized potassium iodide, picric acid, etc., but not by solution of platinic chloride; with auric chloride, however, it yields a precipitate, which, when recrystallized from boiling water acidulated with hydrochloric acid, is deposited, on cooling, in brilliant, lustrous, golden-yellow scales, without rendering the liquid turbid (distinction from atropine).

IODOFORMUM.

IODOFORMIUM.

Iodoform. Teriodide of Formyl. Methenyl Iodide.

Ger. Jodoform; Fr. Iodoforme; Sp. Iodoformo.

CHI_3; 392.8.

Small, lemon-yellow, friable, six-sided scales (Fig. 132), of a pearly lustre, a peculiar, penetrating, and persistent odor, and a

FIG. 132.

sweetish taste, and with a somewhat unctuous feel to the touch. Iodoform has a spec. grav. of 2.0, is volatile at common temperatures, and when heated in a dry tube, by immersing it in boiling water, sublimes rapidly at about 95° C. (203° F.), solidifying in small scales, and may be distilled with aqueous vapor without decomposition; it fuses at 120° C. (248° F.), and is decomposed above this temperature, or when quickly heated, forming violet vapors, and being resolved into iodine and hydriodic acid, with a residue of carbon, which burns away at a stronger heat.

Iodoform is almost insoluble in water, glycerin, diluted acids, and aqueous solutions of the alkaline and earthy hydrates, but is soluble in 80 parts of cold, and 12 parts of boiling, alcohol, in 5.2 parts of ether, and readily in chloroform, carbon bisulphide, benzol, benzin, and in the fixed and volatile oils. Concentrated mineral acids, when cold, have no action on iodoform; when heated, it remains unchanged with hydrochloric acid, gives a reddish-brown solution with nitric acid, remaining limpid and brown on dilution with water; it is freely dissolved, with a violet color, by hot sulphuric acid; upon dilution, however, the color disappears, and the iodoform is separated again in small yellow scales. It is not acted upon by the aqueous solutions of the alkaline hydrates, but their alcoholic solutions dissolve and decompose it, forming alkaline iodide and formiate.

Examination:

Chlorides, *Iodides*, and *Sulphates.*—A small portion of the iodoform is agitated with a little water for a few minutes, filtered, and the filtrate, after acidulation with a few drops of nitric acid, tested in separate portions with argentic nitrate and barium chloride; a white, curdy precipitate with the first-named reagent will indicate a contamination with chlorides or iodides, while a heavy white precipitate with the latter will reveal the presence of sulphates.

IODUM.

IODINUM. IODINIUM.

Iodine.

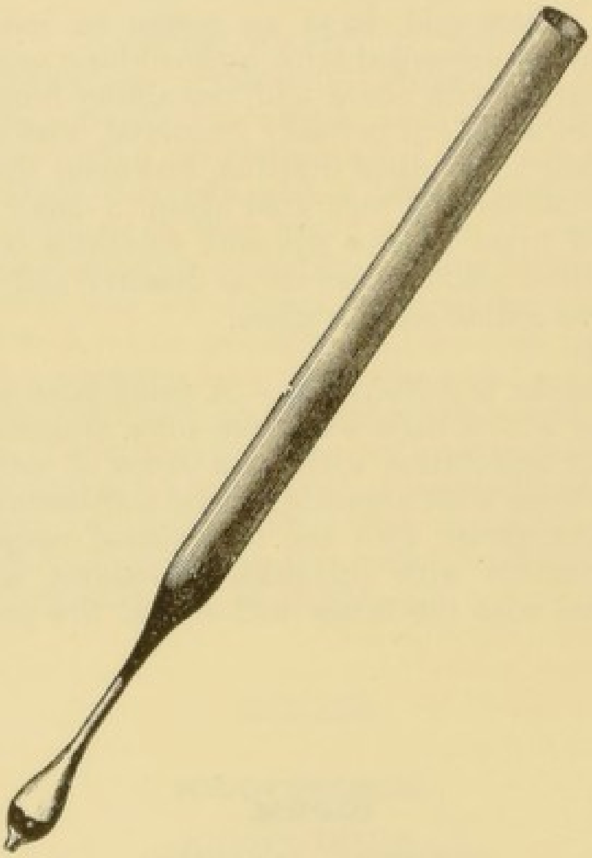
Ger. Jod; Fr. Iode; Sp. Iodo.

I; 126.6.

Heavy, brilliant, crystalline plates or scales, of an opaque bluish-black appearance and imperfect metallic lustre, which may be obtained from their solution in hydriodic acid in well developed octahedral combinations of prisms or pyramids of the rhombic system (Fig. 133). Iodine possesses a peculiar odor, less penetrating than, although similar to, that of chlorine and bromine. Its specific gravity is 4.948 at 17° C. (62.6° F.); it melts at 114° C. (237.2° F.), and boils at a temperature above 200° C. (392° F.), giving rise to a vapor which, seen by transmitted white light, possesses, when chemically pure, a splendid deep blue color, but when mixed with air, a reddish-violet color; it is, however, slowly volatile at common temperatures. When heated in a dry tube (Fig. 134), the vapors condense in the cooler parts of the tube to small, brilliant crystals.

FIG. 133.

FIG. 134.



Iodine is but sparingly soluble in water, requiring 4500 parts of it at 15° C. (59° F.), and imparting to it a faint brownish-yellow tinge. It is more soluble in glycerin, 100 parts of which dissolve a little more than 1.5 parts of iodine. It is also soluble to some extent in the aqueous solutions of certain salts, as for instance of ammonium chloride and nitrate. Aqueous solutions of hydriodic acid and of the alkaline iodides and bromides, dissolve iodine freely, as do also alcohol and ether, with a reddish-brown color, benzol and chloroform with a violet-red, and carbon bisulphide with a rich purple. An aqueous solution of sodium hyposulphite dissolves iodine at first without color, and afterward with a brownish-red tint.

Chloroform and carbon bisulphide, when shaken with an aqueous solution of iodine, deprive it of most of the iodine, and assume, when the fluids have separated, a more or less red color, while the aqueous solution appears almost colorless.

Iodine forms with starch a deep-blue compound, which offers a very delicate test for iodine in all solutions and in bodies which contain it in the free state; the reaction is, however, impaired by the presence of certain nitrogenized organic substances, such as albumen, etc., as also by quinine and tannic acid.

Examination:

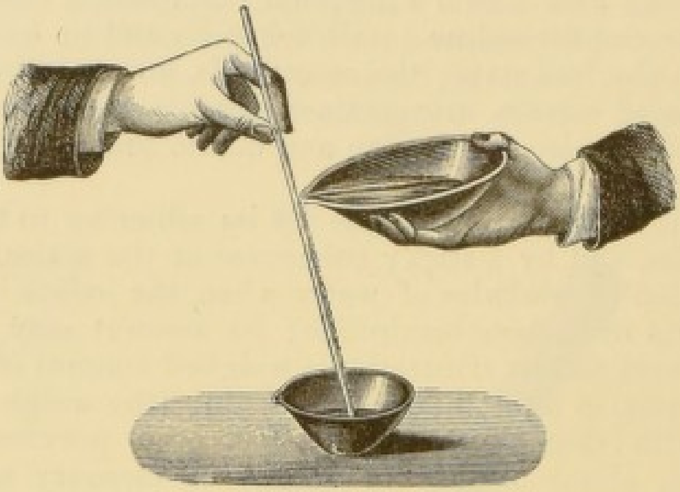
Moisture is indicated in iodine by its adhering to the surface of the bottles, and by a sticky coherence of the scales, as also by the separation of globules of water when the iodine is dissolved in chloroform or carbon bisulphide; its amount may be quantitatively determined by triturating a weighed amount of the iodine (about 2 grams) in a small porcelain capsule (the weight of which, together with that of the pestle, has been previously determined) with about double its weight of mercury and a little alcohol, sufficient to moisten the mixture, until complete combination is effected and free iodine can no longer be detected, either by the eye or by its odor; the mixture of mercurous iodide and mercury is then heated to 100° C. (212° F.) until its weight remains constant, when the weight of the applied iodine and mercury, minus the weight of the dried mixture, will represent the amount of water contained in the iodine employed.

Iodine cyanide, ICN, will be indicated by its exceedingly irritating odor, and may be detected by agitating the iodine with a little water for a few minutes, filtering, and adding to the filtrate sufficient of a solution of potassium hydrate to produce a colorless or nearly colorless solution; a few drops of a solution of ferrous sulphate and ferric chloride are then added, and subsequently hydrochloric acid in slight excess, when the formation of a blue precipitate, either at once or upon standing, will confirm the presence of iodine cyanide.

Chlorine and *Bromine*.—A small portion of the iodine is dissolved in sulphurous acid, the colorless solution strongly supersaturated with ammonia-water, and subsequently completely precipitated by argentic nitrate, and filtered; the filtrate, upon supersaturation with nitric acid, should not become cloudy nor yield a precipitate; a white precipitate will indicate the presence of chlorine or bromine, as also of cyanogen, in case the latter should have been confirmed by the preceding test.

Fixed and *insoluble admixtures* (graphite, coal, carburet of iron, metallic oxides or sulphides) are detected by remaining behind upon the volatilization of a little of the iodine in a test-tube, or upon solution of it in alcohol or in an aqueous solution of potassium hydrate or sodium hyposulphite. If the nature of such admixtures has to be determined, the residue is collected and washed upon a filter, and afterward treated with warm hydrochloric acid diluted with an equal bulk of water, which dissolves metallic oxides, and to some extent the sulphides, with the evolution of hydrogen sulphide. The obtained solution may further be examined for metals, as described in the systematic course of analysis (pages 51 to 61). The insoluble residue left from the solution in hydrochloric acid is levigated (Fig. 135), whereby graphite and carburet of iron may be separated and distinguished from heavier mineral substances.

FIG. 135.



Estimation:

About 0.5 gram of the iodine, accurately weighed, is dissolved, in a small flask, in about 10 cubic centimeters of an aqueous ten per cent. solution of potassium iodide. When complete solution has taken place, a standard solution of sodium hyposulphite (page 94) is allowed to flow into the liquid from a burette, until a slight excess has been employed and complete decolorization of the liquid is effected; a little mucilage of starch being then added, the solution is subsequently titrated with a standard solution of iodine (page 93), until a permanent blue coloration is produced. The number of cubic centimeters of the sodium hyposulphite solution employed, minus that of the standard iodine solution, when multiplied by its previously accurately determined factor (page 95), will represent the amount of pure iodine in the quantity applied for the test, from which the percentage of impurities may readily be calculated. By the employment of 0.633

gram of iodine, dissolved in a solution of 1 gram of potassium iodide in 25 cubic centimeters of water, and a precisely decinormal solution of sodium hyposulphite, the number of cubic centimeters required of the latter, when multiplied by 2, will represent, without further calculation, the exact percentage amount of pure iodine in the specimen under examination.

LIQUOR AMMONII ACETATIS.

LIQUOR AMMONII ACETICI

Solution of Ammonium Acetate. Spirit of Mindererus.

Ger. Essigsaure Ammoniumlösung; Fr. Acétate d'ammoniaque liquide; Sp. Solucion de acetato de amoniaco.

A clear, colorless liquid, without empyreumatic odor, and of a mild, saline taste; it contains about 7.6 per cent. of neutral ammonium acetate, and has a spec. grav. of 1.022 (1.032–1.034, Pharm. German., corresponding to 15 per cent. of ammonium acetate); it is wholly volatile upon evaporation, and emits the odor of ammonia when heated with potassium hydrate, and that of acetic acid when heated with sulphuric acid; it assumes a red color upon the addition of a trace of ferric chloride, and, upon heating, the entire amount of iron is precipitated as a basic salt.

Examination:

Metallic impurities may be detected in the solution, after acidulation with hydrochloric acid, by a dark coloration or precipitate upon saturation with hydrogen sulphide, and, after filtration, if necessary, and subsequent neutralization with ammonia-water, by a turbidity or precipitate on the addition of ammonium sulphide.

Sulphates and *chlorides* may be detected by a white turbidity, when the liquid is acidulated with nitric acid and tested, in separate portions, with barium nitrate for the former salts, and with argentic nitrate for the latter.

LIQUOR ANTIMONII CHLORIDI.

LIQUOR STIBII CHLORATI. BUTYRUM ANTIMONII CHLORIDI.

Solution of Trichloride of Antimony or of Antimonious Chloride.

Ger. Antimonchlorürlösung; Fr. Chlorure d'antimoine liquide; Sp. Solucion de cloruro de antimonio.

A dense, transparent, colorless or pale-yellow liquid, having a specific gravity of about 1.470. Dropped into water, it gives a white, bulky precipitate (antimonious chloride with antimonious oxide—*Algaroth's Powder*), which is re-dissolved upon the addition of potassium hydrate or tartaric acid. The solution with potassium hydrate remains unchanged, or gives only a slight turbidity, with hydrogen sulphide, and yields a black precipitate with argentic nitrate; while the solution with tartaric acid gives a copious orange-red precipitate with hydrogen sulphide, and a white one with argentic nitrate.

Examination:

A small portion of the solution, when exposed to a moderate heat in a porcelain capsule, should be completely volatilized.

Antimonic chloride is detected in the solution, diluted with an aqueous ten per cent. solution of tartaric acid, in order to avoid precipitation, by the occurrence of a brown coloration on the addition of a few drops of a solution of potassium iodide.

Iron and *copper* may be detected in the solution, after complete precipitation with hot water and subsequent filtration, by the addition of a few drops of solution of potassium ferrocyanide; a blue coloration or precipitate will reveal the presence of *iron*, a reddish-brown one, that of *copper*.

Lead will be indicated by the separation of a white precipitate when the solution of antimonious chloride is mixed with twice its volume of alcohol, and may be further confirmed by the following test: A small portion of the solution is diluted with water, and subsequently solution of potassium hydrate added until the transparency of the liquid is again restored; it is then saturated with hydrogen sulphide, when a black coloration will reveal the presence of *lead*, a white turbidity, that of *zinc*.

Arsenic.—A portion of the solution is completely precipitated by hot water, filtered, and the filtrate saturated with hydrogen sulphide. The ensuing precipitate, which may consist of arsenic trisulphide, accompanied by a small amount of antimony, is collected upon a filter, washed with water, and digested with a concentrated solution of ammonium carbonate. The latter solution is then filtered, and, upon evaporation to dryness, will leave the arsenic, if present, in the form of yellow arsenic trisulphide; the latter may be further examined, if required, by fusing it with a mixture of sodium nitrate and carbonate in a small porcelain crucible, dissolving the fused mass in a little water, and testing it in Marsh's apparatus (Fig. 20, p. 34), or it may be mixed with a little exsiccated sodium carbonate and potassium cyanide, and heated in a small reduction-tube (Fig. 64, p. 128), when a mirror of metallic arsenic will be produced.

Sulphuric and *Nitric Acids.*—A portion of the solution is completely precipitated with water, filtered, and the filtrate tested, with barium chloride for sulphuric acid, and, in another portion, by the addition of a drop of indigo solution and heating, for nitric acid; the presence of the latter will be indicated by ensuing decoloration of the liquid.

LIQUOR CALCIS.

AQUA CALCIS. AQUA CALCARIÆ.

Lime-Water. Solution of Calcium Hydrate.

Ger. Kalkwasser; Fr. Eau de chaux; Sp. Agua de cal.

A clear, colorless, and odorless liquid, consisting of a saturated solution of calcium hydrate, and having, at 15° C. (59° F.), a specific gravity of 1.0015. It possesses a saline and feebly caustic taste and an alkaline reaction, and contains in solution about 0.128 per cent. of calcium oxide, or 0.17 per cent. of calcium hydrate. Lime-water readily absorbs carbonic acid from the air, forming on its surface a pellicle consisting of minute plates of calcium carbonate; its alkaline reaction disappears when an excess of carbonic acid gas has been passed through it, and the excess has been expelled afterward by boiling.

Lime-water affords no precipitate with sulphuric acid (distinction from solution of barium or strontium hydrate), but it forms white precipitates with carbonic, boracic, phosphoric, arsenious and arsenic, oxalic, and tartaric acids and their salts, and precipitates the solutions of those salts whose metallic oxides or hydrates are insoluble in water.

The quality of lime-water is best ascertained by its property, when warmed in a test-tube, of separating nearly half the quantity of calcium hydrate in minute hexagonal prisms; upon cooling, the crystals redissolve, and the water becomes perfectly clear again. The presence or absence of alkalies (potassium or sodium hydrate) or alkaline carbonates may be determined by saturating the lime-water with carbonic acid gas, and subsequently heating to boiling; the filtered liquid must be neutral to test-paper; an alkaline reaction would indicate the above-mentioned impurities.

LIQUOR FERRI ACETATIS.

LIQUOR FERRI ACETICI.*

Solution of Acetate of Iron. Solution of Ferric Acetate.

Ger. Essigsaure Eisenoxydlösung; Fr. Liqueur d'acétate de fer; Sp. Acetato de hierro liquido.

A transparent, dark reddish-brown liquid, containing 33 per cent. of anhydrous ferric acetate, $Fe_2(C_2H_3O_2)_6$, corresponding to

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* *Liquor Ferri Acetici*, of the Pharmacopoea Germanica, is prepared by the precipitation of 10 parts of solution of ferric chloride, of 1.280 to 1.282 spec. grav., diluted with 50 parts of water, with a mixture of 10 parts of ammonia-water, spec. grav. 960, and 200 parts of water; the precipitate is collected and washed

7.93 per cent. of metallic iron, and having a spec. grav. of 1.160 at 15° C. = 59° F. (1.081 to 1.083, Pharm. Germ., corresponding to from 4.5 to 5 per cent. of metallic iron, or from 18.7 to 20.8 per cent. of anhydrous ferric acetate); it has a faint odor of acetic acid, which becomes more evident upon warming; this may also be recognized by the formation of white vapors, when a glass rod, moistened with ammonia-water, is held over the liquid. Solution of ferric acetate yields with ammonia-water a reddish-brown precipitate, and with potassium ferrocyanide, a deep-blue one; and, when largely diluted with water, should afford with a few drops of a freshly prepared solution of potassium ferricyanide a pure greenish-brown coloration, without a blue tint (evidence of the absence of ferrous salts). If the solution be heated to boiling, it becomes turbid, in consequence of the separation of insoluble basic ferric acetate.

Examination:

A small portion of the liquid is diluted with twice its volume of water, and the iron completely precipitated by the addition of a considerable excess of ammonia-water and heating to boiling; the filtrate must be wholly volatile when a few drops of it are evaporated in a porcelain capsule or on platinum-foil; a viscid residue, which becomes charred at a stronger heat, with the evolution of vapors having the odor of caramel, would indicate *sugar* or *fruit-acids*, which, when present in considerable quantities, prevent the complete precipitation of the ferric solution by ammonia-water. A bluish tint of the filtrate would indicate *copper*, which, with other metallic impurities, may be further determined by saturating it with hydrogen sulphide, both before and after acidulation with hydrochloric acid.

Hydrochloric and *Sulphuric Acids.*—A portion of the solution, diluted with an equal volume of water, is heated until the iron has become completely precipitated, and filtered; the filtrate, after acidulation with nitric acid, is then tested, in separate portions, with argentic nitrate for hydrochloric acid, and with barium nitrate or chloride for sulphuric acid. The verification of the proper amount of iron in the solution may be accomplished by reference to its specific gravity, and by evaporating 10 grams of the solution, to which a few drops of nitric acid have been added, to dryness, in a small platinum capsule, and subsequently igniting at a red heat; the residue of ferric oxide thus obtained should weigh 1.13 grams.

upon a flannel or felt filter, and afterward subjected to strong pressure. The soft, humid mass of ferric hydrate is then transferred to a flask, 8 parts of dilute acetic acid, spec grav. 1.041, added, and the mixture allowed to stand in a cool place, with frequent agitation, until the precipitate has become entirely dissolved, or but a slight insoluble residue remains; so much water is then added that the solution shall have the spec. grav. 1.081 to 1.083.

LIQUOR FERRI CHLORIDI.

LIQUOR FERRI SESQUICHLORATI.*

Solution of Chloride or Perchloride of Iron. Solution of Ferric Chloride.

Ger. Eisenchloridlösung; Fr. Chlorure de fer liquide; Sp. Solucion de percloruro de hierro.

A dark reddish-brown liquid, having a faint odor of hydrochloric acid, an acid, strongly styptic taste, and an acid reaction. Its specific gravity is 1.405 at 15° C. (59° F.), and it contains 37.8 per cent. of anhydrous ferric chloride. It is miscible in all proportions with alcohol, water, and glycerin, and the solution after admixture with alcohol is not rendered turbid on the subsequent addition of ether. The diluted aqueous solution affords a brownish-red precipitate on the addition of ammonia-water, a blue one with potassium ferrocyanide, and a white one, insoluble in nitric acid, with solution of argentic nitrate.

Examination:

Ferric oxy-chloride may be detected by the occurrence of a turbidity, when 3 parts of the solution are diluted with water to the measure of 100 parts, and subsequently heated to boiling.

Ferrous chloride may be recognized in the diluted solution by an ensuing blue coloration or precipitate on the addition of a freshly prepared solution of potassium ferricyanide.

A portion of the solution, diluted with an equal volume of water, is completely precipitated by an excess of ammonia-water, filtered, and the filtrate divided into four portions, which may be employed for the following tests:

Fixed alkalies or *alkaline salts* may be detected by a non-volatile residue upon evaporating a portion of the filtrate to dryness, and subsequent ignition at a gentle heat.

Metallic Impurities.—Copper will be indicated by a blue color of the ammoniacal liquid; and *zinc* may be detected by a white turbidity or precipitate on the addition of a few drops of ammonium sulphide, or, after acidulation with hydrochloric acid, by a white precipitate on the addition of solution of potassium ferrocyanide.

Sulphuric acid will be indicated in the filtrate, after supersaturation with nitric acid, by a white precipitate on the addition of solution of barium chloride.

Nitric acid may be detected in another portion of the filtrate, concentrated by evaporation, if necessary, by the addition of a slight excess of concentrated sulphuric acid, a drop of indigo solution, and gently heating; ensuing decoloration of the liquid will

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* Liquor Ferri sesquichlorati, of the Pharmacopoea Germanica, has the spec. grav. 1.280 to 1.282, and contains 29 per cent. of anhydrous ferric chloride, corresponding to 10 per cent. of metallic iron.

reveal the presence of nitric acid. Or, to a portion of the liquid, mixed with an excess of concentrated sulphuric acid, a crystal of ferrous sulphate is added, or a concentrated solution of the latter salt is carefully poured upon the liquid, so as to form two layers (Fig. 129, p. 383), when a dark coloration of the crystal, or a brown or violet-colored zone at the line of contact of the two liquids, will likewise indicate the presence of nitric acid.

Estimation:

The determination of the strength of liquor ferri chloridi may be readily accomplished, in addition to the verification of the proper specific gravity, by diluting 10 grams of the solution with an equal volume of water, heating to the boiling-point, and completely precipitating the iron by the addition of ammonia-water in excess. The precipitate of ferric hydrate, when collected on a filter, thoroughly washed, dried, and ignited, should leave a residue of ferric oxide weighing 1.86 grams.

LIQUOR FERRI CITRATIS.

LIQUOR FERRI CITRICI.

Solution of Citrate of Iron. Solution of Ferric Citrate.

A dark brown, transparent liquid, without odor, and having a slightly ferruginous taste, and an acid reaction. It has a spec. grav. of 1.260, and contains about 35.5 per cent. of anhydrous ferric citrate, $Fe_2(C_6H_5O_7)_2$, corresponding to 8.1 per cent. of metallic iron. When the solution is concentrated by evaporation, at a gentle heat, and spread upon plates of glass, it forms, upon drying, transparent, garnet-red scales, which are easily detached from the glass. If 100 parts of the solution be thus treated, from 43 to 44 parts of the scaled salt should be obtained, which, when completely incinerated at a strong heat, in a small porcelain crucible, should leave a residue of ferric oxide, amounting to about 11 parts.

Solution of ferric citrate is not precipitated, but is rendered somewhat darker, on the addition of ammonia-water; and yields, with solution of potassium ferrocyanide, a bluish-green color or precipitate, which is rendered dark blue on the subsequent addition of hydrochloric acid. If the solution be boiled with an excess of solution of potassium hydrate, a reddish-brown precipitate of ferric hydrate is produced; the filtrate therefrom, after concentration and being allowed to cool, is precipitated by solution of calcium chloride, and the filtrate from the latter precipitate, when heated to boiling, yields a white, granular precipitate of calcium citrate.

LIQUOR FERRI ET QUININÆ CITRATIS.

LIQUOR FERRI CITRICI CUM CHININO CITRICO.

Solution of Citrate of Iron and Quinine. Solution of Ferric and Quinine Citrates.

A dark greenish-yellow to yellowish brown liquid, transparent when diluted or in thin layers, without odor, and having a bitter and mildly ferruginous taste, and a slightly acid reaction. It contains 6 per cent. of quinine, which has been dried at 100° C. (212° F.).

If the solution be supersaturated with a slight excess of ammonia-water, a white, curdy precipitate is produced, which corresponds to the reactions and tests of quinine, and the liquid assumes a somewhat darker color. If the mixture be then filtered, and a portion of the filtrate slightly supersaturated with hydrochloric acid, a deep blue precipitate is produced. Another portion of the filtrate, when heated with an excess of solution of potassium hydrate, yields a reddish-brown precipitate of ferric hydrate; the filtrate therefrom, after concentration and being allowed to cool, is precipitated by solution of calcium chloride, and the filtrate from the latter precipitate, when heated to boiling, yields a white granular precipitate of calcium citrate.

On heating the solution with a strong solution of potassium hydrate, vapors of ammonia are evolved.

Estimation of the Quinine in Solution of Citrate of Iron and Quinine:

Eight grams of the solution, contained in a closely fitting, glass-stoppered bottle or flask, are diluted with water to the measure of 30 cubic centimeters, an aqueous solution of 0.5 gram of tartaric acid added, and subsequently solution of sodium or potassium hydrate, in slight excess. The mixture is then agitated with four successive portions of chloroform, of about 15 cubic centimeters each, the chloroformic layers being removed by means of a glass separating funnel, afterward mixed, and allowed to evaporate spontaneously in a weighed glass or porcelain capsule, and finally dried at 100° C. (212° F.), until of constant weight. The residue of quinine thus obtained should weigh 0.48 gram, corresponding to 6 per cent. of the weight of solution employed.

LIQUOR FERRI NITRATIS.

LIQUOR FERRI NITRICI. LIQUOR FERRI PERNITRATIS.

Solution of Nitrate or Pernitrate of Iron. Solution of Ferric Nitrate.

Ger. Eisenoxydnitratlösung; Fr. Solution d'azotate de fer;
Sp. Solucion de pernitrato de hierro.

A transparent amber-colored or reddish-yellow liquid, having an acid, strongly styptic taste, and an acid reaction. Its specific gravity is 1.050 at 15° C. (59° F.), and it contains about 6 per cent. of anhydrous ferric nitrate. Diluted with water, it gives a deep-blue precipitate with potassium ferrocyanide, but none with potassium ferricyanide, and yields a reddish-brown precipitate with ammonia-water; when a few drops of a concentrated solution of ferrous sulphate are added to a little of the solution of ferric nitrate, and the mixture is carefully transferred upon concentrated sulphuric acid (Fig. 129, p. 383), a dark zone, indicating nitric acid, will ensue upon the line of contact between the two liquids.

Examination:

To a portion of the solution ammonia-water in slight excess is added, the liquid filtered from the precipitate of ferric hydrate, and the filtrate employed for the following tests:

Metallic Impurities.—Copper will be indicated by a blue color of the ammoniacal liquid; and *zinc* may be detected by a white turbidity or precipitate on the addition of a few drops of ammonium sulphide, or, after acidulating with hydrochloric acid, by a white precipitate when tested with potassium ferrocyanide.

Hydrochloric and *sulphuric acids* may be detected in another portion of the filtrate, supersaturated with nitric acid, when tested respectively with argentic nitrate and barium nitrate or chloride.

Estimation:

In addition to the verification of the proper specific gravity, the strength of liquor ferri nitratis may readily be determined by completely precipitating 100 grams of the solution with ammonia-water. The precipitate of ferric hydrate, when collected on a filter, thoroughly washed, dried, and ignited, should leave a residue of ferric oxide weighing 2 grams.

LIQUOR FERRI SULPHATIS.

LIQUOR FERRI SULFURICI OXYDATI.

Solution of Persulphate of Iron. Solution of Ferric Sulphate.

Ger. Eisenoxydsulfatlösung; Fr. Liqueur de persulfate de fer; Sp. Solucion de persulfato de hierro.

The U. S. Pharmacopœia has two solutions of ferric sulphate, *Liquor Ferri Subsulphatis*, having a spec. grav. of 1.555, and *Liquor Ferri Tersulphatis*, having a spec. grav. of 1.320. The former is a solution of basic ferric sulphate [$Fe_4O(SO_4)_5$], containing 43.7 per cent. of the salt; the latter, a solution of normal ferric sulphate, $Fe_2(SO_4)_3$, containing 28.7 per cent. of the salt.* The *Liquor Ferri Persulphatis* of the British Pharmacopœia has the spec. grav. of 1.441, and that of the Pharmacopoea Germanica a spec. grav. of 1.428 to 1.430.

They all are transparent, red or reddish-brown liquids, without odor, of an astringent, metallic taste, and miscible in all proportions, with water, alcohol, and glycerin, without decomposition. A few drops of either of them, added to water, form a mixture in which potassium ferricyanide produces no reaction, but ferrocyanide gives a dark-blue precipitate, ammonia-water a bulky, reddish-brown one, and barium chloride a white one, the latter insoluble in hydrochloric acid.

Examination:

Copper and Zinc.—A small portion of either of the above solutions of ferric sulphate is mixed with about an equal volume of water, heated to boiling, and the iron completely precipitated by the addition of ammonia-water in excess, and filtered. The filtrate will appear bluish, if *copper* be present, and should be entirely volatilized when heated upon platinum-foil; a fixed residue would indicate *alkaline*, *earthy*, or *metallic impurities*. Part of the filtrate is then saturated with hydrogen sulphide, an ensuing white precipitate would indicate *zinc*, and a dark one, insoluble upon supersaturation with hydrochloric acid, *copper*.

Nitric acid and *nitrates* may be detected in a portion of the filtrate of the preceding test, by supersaturating it with concentrated sulphuric acid, and by subsequently adding one drop of a solution of potassium permanganate, or indigo solution, and gently warming; ensuing decoloration will indicate *nitric acid* or *nitrates*.

Estimation:

In addition to the verification of the proper specific gravity, the strength of solutions of ferric sulphate may be readily determined

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* The two preparations may readily be distinguished by slowly mixing, in a beaker, 2 volumes of the solution with 1 volume of concentrated sulphuric acid; the liquor ferri subsulphatis separates a solid white mass on standing, while the liquor ferri tersulphatis retains its fluidity.

by completely precipitating 10 grams of the solution with an excess of ammonia-water, collecting the precipitate of ferric hydrate on a filter, washing it thoroughly with water, and, after drying, igniting in a porcelain crucible at a red heat. Ten grams of liquor ferri subsulphatis should thus afford a residue of ferric oxide weighing 1.938 grams; and the same amount of liquor ferri tersulphatis, a residue of ferric oxide weighing 1.147 grams.

LIQUOR HYDRARGYRI NITRATIS.

LIQUOR HYDRARGYRI NITRICI OXYDATI.

Solution of Nitrate or Pernitrate of Mercury. Solution of Mercuric Nitrate.

Ger. Salpetersaure Quecksilberoxydlösung; Fr. Nitrate de mercure liquide;
Sp. Solucion de pernitrato de mercurio.

A dense, transparent, nearly colorless, acid liquid, having a faint odor of nitric acid, and, even when diluted, a very acid, caustic and metallic taste. It has a specific gravity of 2.100 at 15° C. (59° F.), when prepared according to the U. S. Pharmacopœia, and of 2.246, when prepared according to the British Pharmacopœia, containing, in the first instance, about 50 per cent. of mercuric nitrate in solution.

When a few drops of the liquid are evaporated at a gentle heat, upon platinum-foil, they leave a white residue, which, upon increased heat, becomes successively yellow, red, and brown, and is finally wholly dissipated. The solution remains limpid on the addition of water or of diluted hydrochloric acid (evidence of the absence of mercurous nitrate); it gives a dull yellow precipitate with an excess of the fixed alkaline and earthy hydrates, a white one with ammonia-water, a bright red one with potassium iodide, soluble in an excess of the reagent, and a black one with an excess of hydrogen sulphide; it deposits a brilliant metallic coating on bright copper, and shares, in its deportment with reagents, the general characteristics of mercuric salts, as described under mercuric chloride and oxide (pages 374 and 383). It causes a crystal of ferrous sulphate, dropped into it, as well as the liquid around the salt, to assume a deep-brown color.

When diluted with about ten times its volume of water, it should not give a turbidity when tested, in separate portions, with a few drops of solutions of argentic and of barium nitrates (absence of *chlorides* and *sulphates*).

LIQUOR PLUMBI SUBACETATIS.

LIQUOR PLUMBI SUBACETICI. ACETUM PLUMBICUM.

Solution of Subacetate of Lead. Solution of Triplumbic Acetate.

Ger. Bleiessig; Fr. Sous-acétate de plomb liquide;
Sp. Subacetato de plomo líquido.

A dense, clear, colorless liquid, of 1.228 spec. grav. (1.235–1.240 Pharmacopoea Germanica), having an alkaline reaction and a sweet, astringent taste, and becoming turbid by absorption of atmospheric carbonic acid, and by dilution with water containing carbonates, sulphates, or carbonic acid. It is precipitated, whether diluted with water or not, by the alkaline and alkaline-earthy hydrates and carbonates, by sulphuric, hydrochloric, oxalic, tannic, and other acids and their salts, and by almost all neutral salts; it forms white, opaque, insoluble compounds with vegetable gums, mucilages, and extracts, and with vegetable and albuminous substances.

Liquor plumbi subacetatis gives a yellow precipitate with potassium iodide, and a black one with hydrogen sulphide; it forms an opaque, white jelly when mixed with mucilage of gum; it may be recognized as containing an acetate, by evolving the odor of acetic acid, when heated with a few drops of sulphuric acid, and by affording a deep-red color, accompanied by the separation of plumbic chloride, on the addition of a few drops of a dilute solution of ferric chloride.

Traces of copper are indicated by a faint greenish color of the liquid, and may be further recognized by a bluish coloration of the filtrate, when a little of the liquor plumbi subacetatis is mixed with an excess of ammonia-water.

Estimation:

13.7 grams of the solution should require for complete precipitation 25 cubic centimeters of normal solution of oxalic acid (page 82), corresponding to 25 per cent. of basic plumbic acetate. By the employment of other quantities of the solution than that above mentioned, the calculation may also readily be made, with the consideration that 1 cubic centimeter of normal oxalic acid solution corresponds to 0.13675 gram of basic plumbic acetate, $Pb_2O(C_2H_3O_2)_2$.

LIQUOR POTASSÆ.

LIQUOR POTASSII HYDRICI. LIQUOR KALII CAUSTICI.

Solution of Potassa. Solution of Potassium Hydrate.

Ger. Kalilauge ; Fr. Liqueur de potasse ; Sp. Solucion de potasa.

A transparent, colorless, limpid liquid, without odor, of an extremely acrid and caustic taste and strongly alkaline reaction, and having a soapy feel when rubbed between the fingers. It has a destructive action on many vegetable and animal substances, is a powerful solvent for many organic and mineral compounds, and readily absorbs carbonic acid gas by exposure to the air; when dropped into a concentrated solution of tartaric acid, a white crystalline precipitate is produced, which is re-dissolved by an excess of the alkali. The specific gravity of the solution is 1.036 at 15° C. (59° F.), and it contains about 5 per cent. of potassium hydrate.*

Examination:

Carbonate is indicated by effervescence or by the formation of gas-bubbles, when the liquor potassæ is added to an excess of hydrochloric or nitric acid; it may also be detected by the formation of a white precipitate when a little of the liquor potassæ is mixed with an equal volume of water, and is then added to lime-water.

Sodium hydrate may be detected by the following method, which is based upon the solubility of sodium bitartrate, and the insolubility of potassium bitartrate, in alcohol. A weighed portion of the liquor potassæ is exactly neutralized with tartaric acid, and to the solution as much tartaric acid subsequently added as was previously required for neutralization. Alcohol is then added until a precipitate ceases to be produced, and the liquid filtered. The filtrate, which will contain the sodium in the form of bitartrate, will deposit the latter upon evaporation, and, upon ignition, will leave a black, strongly alkaline residue of carbon and sodium carbonate. If this residue be dissolved in water, the solution filtered, neutralized with dilute nitric acid, and concentrated by evaporation, rhombohedral crystals of sodium nitrate may be obtained, which impart an intense yellow color to the non-luminous flame.

Potassium chloride, *sulphide*, and *hyposulphite* may be detected by dropping a little of the liquor potassæ into diluted solution of argentic nitrate; a grayish-brown precipitate will be produced, which, however, should be completely soluble upon the addition of nitric acid in excess; if the precipitate does not wholly dis-

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* Liquor Kalii caustici, of the Pharmacopoea Germanica, has a spec. grav. of from 1.142 to 1.146, and contains about 15 per cent. of potassium hydrate.

solve, and leaves behind a white residue, *chloride* is indicated; when the residue is black, *sulphide* or *hyposulphite*.

Sulphate, *Silicate*, and *Alumina*.—A little of the liquor potassæ is slightly supersaturated with diluted nitric acid; part of the solution is tested with barium nitrate for *sulphate;* another part may also be tested with argentic nitrate for *chloride;* the rest of the solution is evaporated, in a porcelain capsule, to dryness; the remaining salt must yield a limpid solution with water; a white insoluble residue would indicate silicate; the solution, when necessary, is filtered, and then tested by the addition of a little ammonium chloride and ammonia-water for *alumina*, which, when present, will afford a white flocculent precipitate.

Calcium salts may be detected, in the diluted liquor potassæ, previously neutralized with nitric acid, by a white precipitate with ammonium oxalate, or with sodium carbonate.

Metallic impurities are indicated by a dark coloration or turbidity when the liquor potassæ is saturated with hydrogen sulphide, either before or after supersaturation with hydrochloric acid.

Estimation:

The amount of pure potassium hydrate contained in liquor potassæ may readily be determined volumetrically. About 20 grams of the liquid are accurately weighed in a beaker or small flask, a few drops of litmus solution added, and subsequently a standard solution of oxalic or sulphuric acid (page 82) allowed to flow into the liquid from a burette until, with constant stirring, the blue tint of the liquid is just changed to a cherry-red. From the number of cubic centimeters of the acid solution thus required for exact neutralization, the amount of pure potassium hydrate may be calculated: one cubic centimeter of normal acid corresponding to 0.056 gram of potassium hydrate, KHO. By the employment of 28 grams of the officinal liquor potassæ, not less than 25 cubic centimeters of the normal acid solution should be required for exact neutralization, indicating a strength of at least 5 per cent. of potassium hydrate.

If the liquor potassæ contain carbonate, the amount of carbon dioxide contained in a weighed portion of the solution must be determined, as described on pages 85–86. For 1 part of carbon dioxide, CO_2, 2.545 parts of potassium hydrate, KHO, are deducted from the amount volumetrically indicated, and the balance then calculated as pure potassium hydrate.

TABLE *of the quantity by weight of Potassium Oxide and Hydrate contained in* 100 *parts by weight of solution* (*Liquor Potassæ*) *of different specific gravities* (*Gerlach*).

Temperature 15° C. (59° F.).

Per ct. of K_2O or KHO.	Specific gravity for K_2O.	Specific gravity for KHO.	Per ct. of K_2O or KHO.	Specific gravity for K_2O.	Specific gravity for KHO.	Per ct. of K_2O or KHO.	Specific gravity for K_2O.	Specific gravity for KHO.
1	1.010	1.009	21	1.230	1.188	41	1.522	1.425
2	1.020	1.017	22	1.242	1.198	42	1.539	1.438
3	1.030	1.025	23	1.256	1.209	43	1.554	1.450
4	1·339	1.033	24	1.270	1.220	44	1.570	1.462
5	1.048	1.041	25	1.285	1.230	45	1.584	1.474
6	1.058	1.049	26	1.300	1.241	46	1.600	1.488
7	1.068	1.058	27	1.312	1.252	47	1.615	1.499
8	1.078	1.065	28	1.326	1.264	48	1.630	1.511
9	1.089	1.074	29	1.340	1.276	49	1.645	1.527
10	1.099	1.083	30	1.355	1.288	50	1.660	1.539
11	1.110	1.092	31	1.370	1.300	51	1.676	1.552
12	1.121	1.101	32	1.385	1.311	52	1.690	1.565
13	1.132	1.111	33	1.402	1.324	53	1.705	1.578
14	1.143	1.119	34	1.418	1.336	54	1.720	1.590
15	1.154	1.128	35	1.431	1.349	55	1.733	1.604
16	1.166	1.137	36	1.445	1.361	56	1.746	1.618
17	1.178	1.146	37	1.460	1.374	57	1.762	1.630
18	1.190	1.155	38	1.475	1.387	58	1.780	1.641
19	1·202	1.166	39	1.490	1.400	59	1.795	1.655
20	1.215	1.177	40	1.504	1.411	60	1.810	1.667

With the decrease and increase of temperature, the specific gravity of the solution suffers a corresponding increase or decrease, amounting for each degree of the centigrade thermometer in either direction—

For solution of a specific gravity of 1.810 to that of 1.504 to about 0.00055
“ “ “ 1.490 “ 1.355 “ 0.0005
“ “ “ 1.340 “ 1.230 “ 0.0004
“ “ “ 1.215 “ 1.010 “ 0.00033

LIQUOR POTASSII ARSENITIS.

LIQUOR POTASSII ARSENICOSI. LIQUOR KALII ARSENICOSI.

Solution of Potassium Arsenite. Fowler's Solution.

Ger. Fowler'sche Tropfen; Fr. Solution arsenicale de Fowler;
Sp. Solucion de arsenito de potasa.

The officinal solution of potassium arsenite contains 1.656 per cent. of primary potassium arsenite, KH_2AsO_3, corresponding to 1 per cent. of arsenic trioxide, As_2O_3;* it has a slight alkaline

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* Liquor Kalii arsenicosi of the Pharmacopoea Germanica is an aqueous solution of potassium metaarsenite, $KAsO_2$; and probably, also, of potassium ortho-arsenites, corresponding in amount to 1 per cent. of arsenic trioxide, As_2O_3.

reaction, and gives, with nitrate of silver, a bright-yellow precipitate, soluble in ammonia-water; this solution, when gently warmed for some time, by immersing the test-tube in hot water, suffers a reduction of the silver salt, and deposits the metal, as a brilliant coating, upon the walls of the test-tube. Hydrogen sulphide produces no immediate precipitate in the solution of potassium arsenite, but, upon the addition of hydrochloric acid, there at once appears a lemon-yellow precipitate, soluble in ammonia-water or in a concentrated solution of ammonium carbonate.

Estimation:

A quantitative estimation of the amount of arsenic trioxide (arsenious acid), corresponding to the amount of potassium arsenite contained in liquor potassii arsenitis, may be made by diluting 10 grams of the solution with an equal volume of water, acidulating with hydrochloric acid, and subsequently completely precipitating with hydrogen sulphide. The precipitate is collected and washed upon a tared filter, and, after drying at 100° C. (212° F.), is weighed. The weight of the arsenious sulphide, divided by 1.242, gives the quantity of arsenious acid contained in 10 grams of the solution, which should be 0.1 gram.

The quantitative estimation may also be made volumetrically, by the following method: 10 grams of the solution of potassium arsenite are accurately weighed in a beaker, and the solution diluted with about twice its volume of water. 2 grams of crystallized sodium carbonate are then dissolved in the liquid, a little mucilage of starch added, and subsequently a decinormal solution of iodine (page 93) allowed to flow into the liquid, from a burette, until a permanent blue coloration of the liquid is just produced. 20.2 cubic centimeters of the iodine solution should be required to produce this reaction, as corresponding to 0.1 gram of arsenic trioxide, or, the amount of the latter may readily be calculated, with the consideration that 1 cubic centimeter of decinormal iodine solution corresponds to 0.00495 gram of arsenic trioxide, As_2O_3.

The United States Pharmacopœia directs that if 24.7 grams of the solution are boiled with 0.5 gram of sodium bicarbonate, the liquid, when cold, diluted with 100 cubic centimeters of water, and some mucilage of starch added, should require from 48.5 to 50 cubic centimeters of the volumetric solution of iodine, before the blue color ceases to disappear on stirring (corresponding to 1 per cent. of arsenious acid of the required purity, or, at least, 0.97 per cent. of pure arsenious acid).

LIQUOR SODÆ.

LIQUOR SODII HYDRICI. LIQUOR NATRII CAUSTICI.

Solution of Soda. Solution of Sodium Hydrate.

Ger. Natronlauge ; Fr. Soude caustique liquide ; Sp. Solucion de sosa.

A transparent, colorless, limpid liquid, without odor, of an extremely acrid and caustic taste and strongly alkaline reaction, and having a soapy feel when rubbed between the fingers. It has a destructive action on many vegetable and mineral substances, is a powerful solvent for many organic and mineral compounds, and readily absorbs carbonic acid by exposure to the air; when dropped into a concentrated solution of tartaric acid, no precipitate is produced (distinction from solution of potassium hydrate); when a drop of the solution, contained on the looped end of a platinum-wire, is held in the non-luminous flame, it imparts to the latter an intense yellow color. The specific gravity of the solution is about 1.059 at 15° C. (59° F.), and it contains about 5 per cent. of sodium hydrate.*

Examination:

Sodium carbonate is indicated by effervescence, or by the formation of gas-bubbles, when the liquid is added to an excess of concentrated hydrochloric or nitric acid; it may also be detected by the formation of a white precipitate upon mixing a little of the liquid with twice its volume of lime-water.

Sodium sulphate and *chloride* are indicated by white precipitates, when the diluted liquid is slightly supersaturated with nitric acid, and tested with barium nitrate for sulphate, and with argentic nitrate for chloride.

Calcium salts may be detected by a white precipitate, when the diluted liquid, previously neutralized with nitric acid, is tested with solution of ammonium oxalate or sodium carbonate.

Potassium hydrate may be recognized by a white, granular precipitate, on dropping the liquid into a strong solution of tartaric acid, allowing the latter to remain in excess.

Metallic impurities are indicated by a dark coloration or turbidity when the liquor sodæ is saturated with hydrogen sulphide, either before or after supersaturation with hydrochloric acid.

Estimation:

The amount of pure sodium hydrate contained in liquor sodæ may readily be determined volumetrically. About 20 grams of the liquid are accurately weighed in a beaker or small flask, a few drops of litmus solution added, and subsequently a standard solution of oxalic or sulphuric acid (page 82) allowed to flow into

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* Liquor Natrii caustici of the Pharmacopoea Germanica has a spec. grav. of from 1.159 to 1.163, and contains about 15 per cent. of sodium hydrate.

the liquid from a burette, until, with constant stirring, the blue tint of the liquid is just changed to a cherry-red. From the number of cubic centimeters of the acid solution thus required for exact neutralization, the amount of pure sodium hydrate may be calculated: one cubic centimeter of normal acid corresponding to 0.040 gram of sodium hydrate, NaHO. By the employment of 20 grams of the officinal liquor sodæ, not less than 25 cubic centimeters of the normal acid solution should be required for exact neutralization, indicating a strength of at least 5 per cent. of sodium hydrate.

If the liquor sodæ contains carbonate, the amount of carbon dioxide contained in a weighed portion of the solution must be determined, as described on pages 85–86. For 1 part of carbon dioxide, CO_2, 1.818 parts of sodium hydrate, NaHO, are deducted from the amount volumetrically indicated, and the balance then calculated as pure sodium hydrate.

TABLE *of the quantity by weight of Sodium Oxide and Hydrate contained in* 100 *parts by weight of solution* (*Liquor Sodæ*) *of different specific gravities* (*Gerlach*).

Temperature 15° C. (59° F.).

Per ct. of Na_2O or NaHO.	Specific gravity for Na_2O.	Specific gravity for NaHO.	Per ct. of Na_2O or NaHO.	Specific gravity for Na_2O.	Specific gravity for NaHO.	Per ct. of Na_2O or NaHO.	Specific gravity for Na_2O.	Specific gravity for NaHO.
1	1.015	1.012	21	1.300	1.236	41	1.570	1.447
2	1.029	1.023	22	1.315	1.247	42	1.583	1.456
3	1.043	1.035	23	1.329	1.258	43	1.597	1.468
4	1.058	1.046	24	1.341	1.269	44	1.610	1.478
5	1.074	1.059	25	1.355	1.279	45	1.623	1.488
6	1.089	1.070	26	1.369	1.290	46	1.637	1.499
7	1.104	1.081	27	1.381	1.300	47	1.650	1.508
8	1.119	1.092	28	1.395	1.310	48	1.663	1.519
9	1.132	1.103	29	1.410	1.321	49	1.678	1.529
10	1.145	1.115	30	1.422	1.332	50	1.690	1.540
11	1.160	1.126	31	1.438	1.343	51	1.705	1.550
12	1.175	1.137	32	1.450	1.351	52	1.719	1.560
13	1.190	1.148	33	1.462	1.363	53	1.730	1.570
14	1.203	1.159	34	1.475	1.374	54	1.745	1.580
15	1.219	1.170	35	1.480	1.384	55	1.760	1.591
16	1.233	1.181	36	1.500	1.395	56	1.770	1.601
17	1.245	1.191	37	1.515	1.405	57	1.785	1.611
18	1.258	1.202	38	1.530	1.415	58	1.800	1.622
19	1.270	1.213	39	1.543	1.420	59	1.815	1.633
20	1.285	1.225	40	1.558	1.437	60	1.830	1.643

With the decrease and increase of temperature, the specific gravity of the solution suffers a corresponding increase or decrease, amounting, for each degree of the centigrade thermometer in either direction—

For solution of a specific gravity of 1.830 to that of 1.355 to about 0.00045
" " " " 1.341 " 1.219 " 0.0004
" " " " 1.203 " 1.015 " 0.00033

LIQUOR SODÆ CHLORATÆ.

LIQUOR SODÆ CHLORINATÆ. LIQUOR NATRII HYPOCHLOROSI.

Solution of Chlorinated Soda. Solution of Sodium Hypochlorite.

Ger. Unterchlorigsaure Natriumlösung; Fr. Eau de Labarraque;
Sp. Licor de Labarraque.

A transparent liquid of a pale greenish-yellow color, having a faint odor, resembling that of chlorine, and a disagreeable alkaline taste and alkaline reaction. Its specific gravity is 1.044 at 15° C. (59° F.), and it contains about 2 per cent. of available chlorine.

Solution of chlorinated soda becomes decomposed upon heating, with the formation of sodium chlorate and chloride, and, upon exposure to sunlight, liberates oxygen, with the simultaneous formation of sodium chlorate, chlorite, and chloride. It possesses oxidizing properties, and is rendered much more energetic in its action by the addition of acids, in consequence of the developed chlorine; it rapidly decolorizes solution of indigo and other vegetable colors, and produces in the solutions of many metallic salts, such as lead, manganese, cobalt, and nickel, brown or black precipitates of the respective peroxides or perhydrates; when added to a solution of ferrous sulphate, a copious, light-brown precipitate is produced, and with solution of mercuric chloride it affords a brown precipitate of mercuric oxychloride, Hg_2Cl_2O.

Examination:

Calcium salts will be indicated by a white precipitate on the addition of solution of sodium carbonate.

Sodium carbonate, when present in any considerable excess, will be indicated by the formation of a precipitate, when the solution of chlorinated soda is mixed with twice its volume of alcohol.

Estimation:

The value of solution of chlorinated soda depends upon the amount of available chlorine which it contains, which may readily be determined by the following method. 8.88 grams of the solution are mixed, in a beaker, with a solution of 2.6 grams of potassium iodide in 200 cubic centimeters of water; 18 grams of hydrochloric acid are subsequently added to the solution, together with a few drops of mucilage of starch, and, after being well mixed, a standard solution of sodium hyposulphite (page 94) is allowed to flow into the liquid from a burette until, with constant stirring, complete decoloration of the liquid is effected. If the solution be of the proper strength, not less than 50 cubic centimeters of the solution of sodium hyposulphite should be required to produce this reaction, indicating at least 2 per cent. of available chlorine.

By the employment of other amounts of the solution of chlori nated soda, or, when the proportions above indicated are observed, the exact amount of available chlorine contained in the solution may also be calculated, by the consideration that 1 cubic centimeter of standard sodium hyposulphite solution corresponds to 0.0035 gram of free chlorine.

LITHII BENZOAS.

LITHIUM BENZOICUM.

Benzoate of Lithium. Lithium Benzoate.

Ger. Benzoësaures Lithium; Fr. Benzoate de lithium; Sp. Benzoato de litina.

$LiC_7H_5O_2$; 128.

A white powder, or small shining scales, permanent in the air, of a faint benzoin-like odor, a cooling and sweetish taste, and a faintly acid reaction. On being heated, the salt first fuses, then, at a higher temperature, it chars, emitting inflammable vapors of a benzoin-like odor, and finally leaves a black residue of an alkaline reaction. A little of the salt, when heated on the looped end of a platinum wire, in the non-luminous flame, imparts to the latter an intense carmine-red color.

Lithium benzoate is soluble in 4 parts of water and 12 parts of alcohol at 15° C. (59° F.), in 2.5 parts of boiling water and in 10 parts of boiling alcohol, but is insoluble in ether. Its aqueous solution yields on the addition of a dilute solution of ferric chloride a flesh-colored precipitate of basic ferric benzoate, and with hydrochloric acid a precipitate of benzoic acid, which redissolves on the subsequent addition of alcohol.

Examination:

Sulphates and *chlorides* may be detected in the diluted aqueous solution of the salt, strongly acidulated with nitric acid, and filtered, if necessary, by testing it in separate portions, with barium nitrate for the former, and with argentic nitrate for the latter.

Potassium and *Sodium Salts.*—A small portion of the salt is ignited, in a porcelain crucible, at a red heat, the ignited residue dissolved in diluted hydrochloric acid, and the solution filtered and evaporated to dryness. 1 part of this residue should be completely soluble in 3 parts of absolute alcohol, forming a solution which, when ignited, burns with a crimson flame, and which is not precipitated by the subsequent addition of an equal volume of stronger ether; if the ignited residue be incompletely soluble in alcohol, the presence of salts of the alkalies will be indicated.

Calcium salts may be detected in the aqueous solution of the above-described ignited residue, by the formation of a white precipitate when tested with solution of ammonium oxalate.

Metallic impurities may be detected in the aqueous solution of the salt, acidulated with hydrochloric acid, and filtered, if necessary, by a dark coloration or a turbidity when saturated with hydrogen sulphide, or, after neutralization with ammonia-water, by the addition of ammonium sulphide.

LITHII BROMIDUM.

LITHIUM BROMATUM.

Bromide of Lithium. Lithium Bromide.

Ger. Bromlithium; Fr. Bromure de lithium; Sp. Bromuro de litio.

$LiBr$; 86.8.

A white, granular salt, very deliquescent on exposure to the air, neutral in its action upon litmus, and possessing a sharp and slightly bitter taste. On exposure to a low, red heat the salt fuses, and, at a higher temperature, it is slowly volatilized. A fragment of the salt, contained on the looped end of a platinum-wire, when brought into the non-luminous flame, imparts to the latter a carmine red color.

Lithium bromide is very freely soluble in both water and alcohol; its aqueous solution yields on the addition of a solution of argentic nitrate a yellowish-white precipitate, which is soluble in a large excess of ammonia-water. If a little carbon bisulphide be poured upon a solution of the salt, a few drops of chlorine-water subsequently added, drop by drop, and the whole well agitated, the carbon bisulphide will acquire a yellowish or brownish-red color, but should show no violet tint.

Examination:

Alkaline bromides, iodides, and *chlorides* may be tested for by dissolving 0.1 gram of the dry lithium bromide in 10 cubic centimeters of water, adding thereto a solution of 0.2 gram of argentic nitrate in about 10 cubic centimeters of water, agitating the mixture, and filtering. The filtrate should not become turbid on the subsequent addition of solution of argentic nitrate, and the above-obtained precipitate should be completely soluble in a large excess of ammonia water; a turbidity in the first instance would indicate chloride, and incomplete solubility in the second instance, the presence of iodide. As a special test for potassium bromide, 0.1 gram of the dry lithium bromide and 0.19 gram of argentic nitrate are dissolved, separately, in small portions of water, the solutions mixed, agitated, and filtered; the filtrate should remain clear upon the addition of a few drops of hydrochloric acid; if a precipitate is thereby produced, the presence of potassium bromide or other potassium or sodium compounds will be indicated.

Potassium and *Sodium Salts.*—These impurities, in addition to the above tests, will be indicated by dissolving one part of the lithium bromide in three parts of absolute alcohol; a clear solution should be formed, which should not be rendered turbid nor yield any precipitate on the subsequent addition of an equal volume of stronger ether, otherwise an admixture with salts of other alkalies will be indicated.

Calcium salts may be detected in the aqueous solution of lithium bromide by a white precipitate when tested with solution of ammonium oxalate.

Metallic impurities may be recognized in the aqueous solution of the salt, acidulated with hydrochloric acid, by a dark coloration or a turbidity when saturated with hydrogen sulphide, or, after neutralization with ammonia-water, by the addition of ammonium sulphide.

LITHII CARBONAS.

LITHIUM CARBONICUM.

Carbonate of Lithium. Lithium Carbonate.

Ger. Kohlensaures Lithium; Fr. Carbonate de lithium; Sp. Carbonato de litina.

Li_2CO_3; 74.

A white, amorphous, or indistinctly crystalline powder, permanent in the air, odorless, of an alkaline taste and reaction, and having a specific gravity of 2.11. When a small portion of the salt is heated on the looped end of a platinum-wire, in the non-luminous flame, it fuses to a clear, colorless bead, and imparts to the flame a bright carmine-red color.

Lithium carbonate is soluble in 130 parts of water at 15° C. (59° F.), and in about the same quantity of boiling water; it is more freely soluble in solutions of ammonium salts, and is readily dissolved by dilute acids, with copious evolution of carbon dioxide, but is insoluble in alcohol. If the solution of the salt in diluted hydrochloric acid be evaporated to dryness, the residue should be completely soluble in three parts of absolute alcohol, affording a solution which, when ignited, burns with a crimson flame, and which is not precipitated by the addition of an equal volume of stronger ether (distinction from potassium and sodium chlorides); if the acid solution of the salt be neutralized by sodium hydrate, and a few drops of solution of sodium phosphate are subsequently added, and gently heated, a white, crystalline precipitate of lithium phosphate, readily soluble in hydrochloric acid, will appear.

Examination:

Potassium and *Sodium Carbonates.*—The presence of these salts may readily be ascertained by a greater solubility in water than that above indicated, as also by the above-described method, depending upon the solubility of lithium chloride in a mixture of alcohol and ether.

Their presence may also be determined by the amount of acid required to exactly neutralize a definite amount of the salt: 0.74 part of lithium carbonate, when mixed with a warm solution of 1.26 parts of oxalic acid in 13 parts of water, should afford a clear and neutral solution; or, 1 gram of lithium carbonate, if perfectly pure, should be exactly neutralized by 27.02 cubic centimeters of normal sulphuric acid. Potassium salts may be specially tested for, if desired, by dissolving a portion of the salt, in a test-tube, in an excess of solution of tartaric acid, and drawing a glass rod over the interior surface of the tube; the gradual formation of a white, crystalline precipitate will reveal the presence of potassium salts. Sodium salts may also be further recognized by their property of imparting an intense yellow color to the non-luminous flame, when a portion of the carbonate, moistened with hydrochloric acid, is heated on the looped end of a platinum-wire.

Ammonium salts may be recognized by the odor of ammonia, when a portion of the carbonate is heated, in a test-tube, with a concentrated solution of potassium or sodium hydrate.

Calcium and *magnesium salts*, if present in the form of carbonates, will remain undissolved when the lithium carbonate is agitated with 150 times its weight of water; they will also be indicated in the neutral solution of the salt (1 : 150) in diluted hydrochloric acid by a white precipitate on the addition of an excess of sodium carbonate. The presence of calcium salts may be further detected in the aqueous solution of the lithium carbonate, previously neutralized with hydrochloric acid, by a white turbidity with ammonium oxalate; after filtration, if necessary, and the addition of ammonium chloride, ammonia-water, and solution of sodium phosphate, an ensuing white crystalline precipitate will reveal the presence of magnesium.

Sulphates and *chlorides* may be detected in the solution of the carbonate in diluted nitric acid, when tested, in separate portions, with barium and argentic nitrates respectively.

Metallic impurities may be recognized in the solution of the salt in diluted hydrochloric acid by a dark coloration or a turbidity upon saturation with hydrogen sulphide, or, after neutralization with ammonia-water, by the subsequent addition of ammonium sulphide.

LITHII CITRAS.

LITHIUM CITRICUM.

Citrate of Lithium. Lithium Citrate.

Ger. Citronensaures Lithium; Fr. Citrate de lithium; Sp. Citrato de litina.

$Li_3C_6H_5O_7$; 210.

A white, amorphous, deliquescent powder, possessing a slightly cooling and faintly alkaline taste, and neutral in its action upon litmus. When exposed to a red heat, the salt chars, evolves inflammable vapors, and leaves a black residue of an alkaline reaction, which, when dissolved in a little alcohol, with one or two drops of hydrochloric acid, and ignited, imparts a crimson color to the flame.

Lithium citrate is soluble in 5.5 parts of water at 15° C. (59° F.), and in 2.5 parts of boiling water, but is almost insoluble in alcohol and ether. When the aqueous solution of the salt is completely precipitated with calcium chloride, the filtrate, when heated, will become turbid, and when filtered after cooling, and the filtrate reheated to boiling, it becomes turbid again (evidence of the presence of a citrate).

Examination:

The purity of lithium citrate may be approximately determined by adding to 1 gram of the salt, previously dried at 120° C. (248° F.), and contained in a porcelain crucible, about 3 grams of concentrated sulphuric acid, and gently heating. After complete carbonization, the residue is strongly ignited at a red heat, and, after cooling, is weighed. The weight of the lithium sulphate thus obtained should not exceed 0.79 gram, and, when multiplied by 1.273, will indicate the corresponding amount of pure lithium citrate.

Potassium salts are detected in the concentrated solution of the citrate, by a white, crystalline precipitate, upon the addition of a few drops of concentrated solution of sodium bitartrate.

Sodium salts are detected in the solution by a white precipitate when tested with potassium antimoniate, or by a persistent yellow color imparted to the non-luminous flame, when heated on the looped end of a platinum-wire.

The presence of potassium and sodium salts may also be ascertained by dissolving, in one or two drops of diluted hydrochloric acid, the residue of lithium carbonate obtained by incineration of the citrate; this solution is evaporated to dryness, and is subsequently dissolved in a few drops of a mixture of equal parts of alcohol and ether; a complete solution should result, as an insoluble residue would indicate potassium or sodium chlorides.

Metallic impurities may be detected in the solution, acidulated with hydrochloric acid, by a dark coloration or a turbidity upon saturation with hydrogen sulphide, or, after neutralization with ammonia-water, by the subsequent addition of ammonium sulphide.

LITHII SALICYLAS.

LITHIUM SALICYLICUM.

Salicylate of Lithium. Lithium Salicylate.

Ger. Salicylsaures Lithium ; Fr. Salicylate de lithium ; Sp. Salicílato de litina.

$2LiC_7H_5O_3.H_2O$; 306.

A white powder, deliquescent on exposure to the air, and containing, for two molecules of the salt, one molecule (5.88 per cent.) of water. When strongly heated, the salt chars, emits inflammable vapors, and leaves finally a blackened residue of an alkaline reaction. A small portion of the salt, when heated on the looped end of a platinum-wire in the non-luminous flame, imparts to the latter a bright carmine-red color.

Lithium salicylate is very freely soluble in both water and alcohol. Its aqueous solution possesses a sweetish taste, and a faintly acid reaction, and yields, upon supersaturation with hydrochloric acid, a bulky white precipitate of salicylic acid, which is soluble in boiling water, and from which it recrystallizes on cooling; the precipitate is also readily soluble in alcohol and ether, and the solutions assume, on the addition of a drop of solution of ferric chloride, an intense violet color.

Examination:

Organic impurities may, in most cases, be detected by agitating 1 part of the salt with about 15 parts of concentrated sulphuric acid, when no color should be imparted to the acid within 15 minutes; an ensuing dark coloration would indicate the presence of foreign organic substances.

Carbonate will be indicated by effervescence, when a small portion of the salt is added to diluted hydrochloric or acetic acid.

Potassium and *sodium salts* may be recognized by igniting a portion of the lithium salicylate at a red heat, dissolving the residue in diluted hydrochloric acid, and evaporating the clear, filtered solution to dryness. The residue of lithium chloride thus obtained should be completely soluble in 3 parts of stronger alcohol, affording a solution, which, when ignited, burns with a crimson flame, and the transparency of which is not disturbed by the subsequent addition of an equal volume of stronger ether; if an insoluble residue remains, the presence of potassium or sodium salts or other impurities will be indicated.

Metallic impurities may be detected in the aqueous solution of the salt, acidulated with hydrochloric acid, by a dark coloration or a turbidity upon saturation with hydrogen sulphide, or, after neutralization with ammonia-water, by the subsequent addition of ammonium sulphide.

MAGNESIA.

MAGNESIA USTA. MAGNESII OXIDUM. MAGNESIUM OXYDATUM.

Magnesia. Calcined Magnesia. Magnesium Oxide.

Ger. Gebrannte Magnesia; Fr. Magnésie calcinée; Sp. Magnesia calcinada.

MgO; 40.

A white, inodorous, bulky, more or less light powder,* of an earthy, but not saline taste, and a slightly alkaline reaction upon moistened red litmus-paper; when exposed to a moderate heat, it suffers no change, but at very high temperatures it is rendered more dense, loses its property of combining with water, and is much more slowly soluble in acids.

Magnesia is almost insoluble in water, requiring 55,368 parts of the latter for solution, but is much more soluble in solutions of various salts, particularly the ammonium salts; it is insoluble in alcohol. If one part of magnesia be stirred, in a beaker, with 15 parts of water, and the mixture allowed to stand for about half an hour, it readily unites with the water with the formation of a gelatinous hydrate, which is of sufficient firmness to prevent it from falling out when the glass is inverted, and gradually absorbs carbonic acid by exposure to the air. When magnesia is dissolved in diluted sulphuric acid, it affords a solution which, after the addition of ammonium chloride and supersaturation with ammonia-water, yields a white, crystalline precipitate on the addition of solution of sodium phosphate.

Examination:

When triturated with hot water, and the mixture poured into an excess of dilute sulphuric acid, magnesia must dissolve without effervescence (evidence of the absence of *carbonate*), and must form a clear solution (evidence of the absence of *calcium*, *barium*, and *strontium oxides*); this solution may be divided into two portions, one of which is saturated with hydrogen sulphide, and after filtration, if necessary, and neutralization with ammonia-water, tested with ammonium sulphide; a dark coloration or a turbidity in either instance will indicate the presence of *metallic*

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* In the U. S. Pharmacopœia magnesia is officinal in two forms, as Magnesia, or *light* magnesia, and Magnesia Ponderosa, or *heavy* magnesia, which differ in their densities, but correspond in all their other properties and reactions.

impurities; the remaining portion of the solution, after the addition of a little ammonium chloride and ammonia-water, is tested with ammonium oxalate, when a white precipitate will reveal the presence of *calcium*. Another portion of the magnesia may be dissolved in dilute nitric acid, and the solution tested, in separate portions with argentic nitrate for *chlorides*, and with barium nitrate or chloride for *sulphates*.

Magnesia is liable to contain the impurities of the magnesium carbonate from which it has been obtained, and may be further examined for them, if they have not been ascertained by the preceding tests for identity and purity, by the methods described on page 423.

MAGNESII CARBONAS.

MAGNESIUM CARBONICUM. MAGNESIA ALBA.

Carbonate of Magnesium. Magnesium Carbonate.

Ger. Basisch kohlensaures Magnesium; Fr. Carbonate de magnésie;
Sp. Carbonato de magnesia.

$(MgCO_3)_4.Mg(OH)_2 + 6H_2O$;* 522.

White, bulky, pulverulent masses, commonly in square cakes, or a light, white powder, smooth to the touch, and nearly insoluble in water, but soluble with effervescence in dilute acids, yielding limpid, colorless solutions; these, after the addition of a little solution of ammonium chloride, are not precipitated upon slight supersaturation with ammonia-water, but, upon the subsequent addition of sodium phosphate, afford a white crystalline precipitate of ammonio-magnesium phosphate. It is also soluble in solutions of the alkaline carbonates, potassium chloride, sulphate, and nitrate, borax, and particularly in solutions of ammonium salts, with the formation of soluble double salts.

Magnesium carbonate is decomposed at a red heat, and also by all acids, and by the fixed alkaline hydrates. 100 parts of it, when ignited at a red heat until the weight remains constant, should leave a residue of magnesium oxide amounting to at least 40 parts.

Examination:

A small portion (about 1 gram) of the powdered magnesium carbonate is mixed and agitated with about 20 times its weight of warm water, and filtered; the filtrate is tested with turmeric paper, and, if this becomes brown, *alkaline carbonates* are indicated; when

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* The composition of magnesium carbonate differs somewhat according to the method of preparation. Although the commercial article usually corresponds to the above formula, the amount of water varies between 4 and 6 molecules.

a few drops of the filtrate are evaporated upon platinum-foil, only a very slight residue should remain. The magnesium carbonate left on the filter is rinsed into a flask, by means of a wash-bottle, the mixture warmed, and sulphuric acid added, drop by drop, until solution is effected; a remaining slight turbidity would indicate traces of *silicic acid.* The solution is filtered, if necessary, and saturated with hydrogen sulphide, when a dark coloration or precipitate will indicate *lead* or *copper;* after filtration, if necessary, the liquid is rendered alkaline by the addition of ammonia-water; an ensuing black precipitate would indicate salts of *iron;* a light reddish one, salts of *manganese;* a white one, salts of *aluminium* or *zinc* (the incidental presence of phosphates would also give a white precipitate). In order to distinguish the latter, the precipitate is washed, subsequently dissolved in a little dilute hydrochloric acid, and, after gently heating to expel the hydrogen sulphide, the solution is supersaturated with ammonia-water; the *aluminium* is thereby precipitated, while *zinc* remains in solution, and may be recognized by re-precipitation with hydrogen sulphide or ammonium sulphide.

The ammoniacal filtrate is then tested with a few drops of ammonium oxalate; a white precipitate, insoluble upon the addition of ammonium chloride, would indicate salts of *calcium.* The latter may be further specially tested for, if required, by igniting a portion of the magnesium carbonate, extracting with water and filtering, and, after the addition of a little ammonium chloride and ammonia-water, testing the filtrate with ammonium oxalate.

Chlorides and *sulphates* may be detected, in the diluted solution of the magnesium carbonate in diluted nitric acid, by testing the same in separate portions, with barium nitrate for sulphates, and with argentic nitrate for chloride.

MAGNESII SULPHAS.

MAGNESIUM SULFURICUM.

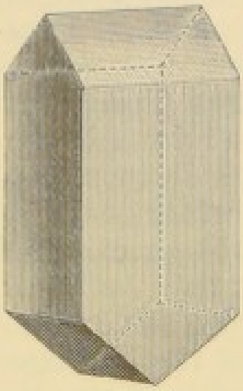
Epsom Salt. Sulphate of Magnesium. Magnesium Sulphate.

Ger. Schwefelsaures Magnesium, Bittersalz; Fr. Sulfate de magnésie; Sp. Sulfato de magnesia.

$MgSO_4 + 7H_2O$; 246.

Colorless, transparent, four-sided rhombic prisms (Fig. 136), but usually met with in commerce as small, acicular needles; they contain seven molecules (51.22 per cent.) of water of crystallization, six of which are eliminated at 120° C. (248° F.), while the last molecule is not expelled at temperatures below 220° C. (428° F.); the crystals do not effloresce at common temperatures and in ordinary atmospheric humidity, but they do so slowly in warm, dry air. When heated, they lose their water of crystallization without previously undergoing aqueous fusion, and at a red heat undergo igneous fusion, with partial decomposition.

FIG. 136.



Magnesium sulphate is soluble in 0.8 part of water at 15° C. (59° F.), and in 0.15 part of boiling water, but is insoluble in alcohol; its aqueous solution has a nauseous, bitter taste, and is neutral in its action upon litmus; it is decomposed, and gives white precipitates, with the fixed alkaline hydrates and carbonates, and also with the earthy hydrates and their soluble salts; ammonia-water and ammonium carbonate, however, do not at once cause a precipitate in dilute solutions of magnesium sulphate, or, if so, but a very slight one, since ammonium salts when present, or when formed by the neutralization of acidulous solutions, act as a solvent for magnesium hydrate or carbonate, and thereby retard or prevent their precipitation; but, on the subsequent addition of phosphoric acid or solutions of tri-basic phosphates, a complete precipitation takes place, which precipitate, however, is soluble in dilute acids.

The crystals of magnesium sulphate are isomorphous with those of zinc sulphate, and cannot be distinguished from them by the eye; it is easy, however, to discriminate between them, not only by the difference in taste, but also by the action of a few drops of ammonium sulphide or solution of potassium ferrocyanide on their aqueous solutions; that of magnesium sulphate remains unaffected by these reagents, whereas solution of zinc sulphate yields, in either instance, a white precipitate.

Examination:

Metallic impurities may be detected in the solution of the salt, acidulated with hydrochloric acid, by the occurrence of a turbidity or precipitate upon saturation with hydrogen sulphide (an ensuing white turbidity may be due simply to sulphur, a lemon-yellow one will indicate *arsenic*), and, after filtration, if necessary, and neutralization with ammonia-water, by the subsequent addition of ammonium sulphide; a white precipitate with the latter reagent would indicate *zinc;* when a dark precipitate is formed, both with the hydrogen sulphide and ammonium sulphide, *copper* and *iron* are indicated, and may be confirmed in the slightly acidulated solution of the salt, the former by a reddish-brown precipitate, the latter by a blue one, with potassium ferrocyanide.

Alkaline sulphates may be detected by triturating 2 parts of the magnesium sulphate with an equal weight of dry calcium hydrate (from which any free alkali must have been previously removed by washing with water, and again drying), and adding this mixture to a mixture of 10 parts of alcohol and 10 parts of water. The mixture is then allowed to stand for about two hours, with frequent agitation, when 40 parts of absolute alcohol are added, and, after active agitation, the mixture poured upon a filter which has been previously moistened with alcohol. If an alkaline sulphate be present in the magnesium sulphate, it will be contained in the alcoholic filtrate in the form of hydrate, and may then readily be detected by its action upon turmeric paper; if litmus paper be employed, the alcoholic liquid should be mixed with a little water, and the alcohol dissipated by the aid of heat before the application of the test.

Ammonium salts may be detected by the odor of ammonia, when a little of the salt is heated, in a test-tube, with a strong solution of potassium hydrate, or by the development of white fumes when a glass rod, moistened with acetic acid, is held over the orifice of the tube.

Aluminium and *Calcium Salts.*—The former may be detected in the solution of magnesium sulphate, to which a sufficient amount of ammonium chloride has been added, by the formation of a colorless, flocculent precipitate on the addition of ammonia-water; and the latter by a white precipitate on the addition of ammonium oxalate.

Chlorides may be detected in the diluted solution of the salt, acidulated with nitric acid, by a white turbidity on the addition of solution of argentic nitrate.

Estimation:

One hundred parts of magnesium sulphate, dissolved in boiling water, and completely precipitated by a boiling solution of sodium carbonate, yield a precipitate which, when washed, dried, and ignited at a red heat, weighs 16.26 parts.

The quantitative estimation of magnesium in magnesium sulphate is, however, usually effected by its precipitation as ammonio-magnesium phosphate, and the conversion of the latter, by ignition, into magnesium pyrophosphate; from the weight of the latter, the amount of magnesium oxide, or the corresponding amount of crystallized magnesium sulphate may readily be calculated. To the aqueous solution of a weighed amount of the salt, ammonium chloride and ammonia-water are added, and subsequently solution of sodium phosphate until no further precipitate is produced; the mixture is allowed to stand for ten or twelve hours, when the precipitate is collected upon a filter, washed with a mixture of about one part of ammonia-water and three parts of water, and, when dry, completely incinerated in a porcelain crucible. Of the residue of magnesium pyrophosphate, $Mg_2P_2O_7$, thus obtained, 100 parts correspond to 36.03 parts of magnesium oxide, MgO, or 221.62 parts of crystallized magnesium sulphate, $MgSO_4 + 7H_2O$.

MAGNESII SULPHIS.

MAGNESIUM SULFUROSUM.

Sulphite of Magnesium. Magnesium Sulphite.

Ger. Schwefligsaures Magnesium; Fr. Sulfite de magnésie;
Sp. Súlfito de magnesia.

$MgSO_3 + 6H_2O$; 212.

A white, crystalline powder, containing 6 molecules (50.94 per cent.) of water of crystallization; it is odorless, but possesses a slightly bitter, somewhat sulphurous, taste, and a neutral or slightly alkaline reaction; on exposure to the air, it gradually absorbs oxygen, and becomes converted into magnesium sulphate. When heated to 200° C. (392° F.), the salt loses its water of crystallization, and becomes decomposed, being converted into magnesium oxide and anhydrous magnesium sulphate.

Magnesium sulphite is soluble in 20 parts of water at 15° C. (59° F.), and in 19 parts of boiling water; it is insoluble in alcohol. The aqueous solution, when mixed with solution of ammonium chloride and ammonia-water, yields, upon the subsequent addition of solution of sodium phosphate, a white crystalline precipitate, which is insoluble in water or dilute ammonia-water, but readily soluble in acids.

Magnesium sulphite is also completely soluble in 4 times its weight of dilute hydrochloric acid, with the development of the odor of burning sulphur, but without producing any turbidity (distinction from magnesium hyposulphite). A 1 per cent. aqueous solution of the salt, strongly acidulated with hydrochloric acid, should not afford more than a slight cloudiness on the addition of solution of barium chloride (absence of and distinction from magnesium sulphate).

MANGANI OXIDUM NIGRUM.

MANGANUM HYPEROXYDATUM. MANGANESIUM OXYDATUM NATIVUM.

Black Oxide of Manganese. Pyrolusite. Manganese Dioxide.

Ger. Mangansuperoxyd, Braunstein; Fr. Oxyde de manganèse;
Sp. Peróxido de manganeso.

MnO_2; 86.

Heavy, compact masses, of a dull-black or brownish-black, earthy appearance, or masses of acicular or rhombic crystals of a black, metallic lustre, and, if pure pyrolusite, of a spec. grav. of 4.9. In commerce, it occurs usually ground, as a coarse, dull, black powder, consisting of manganese dioxide, sesqui-oxide, and monoxide, and is contaminated with the gangue (quartz, felspar, barytes, limestone, etc.), which frequently amounts to 40 or 50 per cent.

Manganese dioxide is infusible, permanent in the air, and insoluble in water or alcohol. When exposed to a strong red heat, it loses one-third of its oxygen, and is converted into reddish-brown mangano-manganic oxide, Mn_3O_4: $3MnO_2 = Mn_3O_4 + O_2$.

It is not attacked by cold concentrated sulphuric acid, but, upon heating with the latter, it is converted into manganous sulphate, with the evolution of oxygen: $MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$.

If, however, oxalic acid, or other readily oxidizable organic substances are present, manganese dioxide is also dissolved by dilute sulphuric acid, with the evolution of carbon dioxide:

$$MnO_2 + H_2SO_4 + C_2H_2O_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

When heated with hydrochloric acid, it is converted into manganous chloride, with the development of chlorine:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The resulting brownish solution, when filtered and neutralized with ammonia-water, yields, with hydrogen sulphide or ammonium sulphide, a flesh-colored precipitate of manganous sulphide; the color of this precipitate is, however, frequently rendered darker, or even brownish-black, by the presence of oxides of iron and other metals.

When a small portion of manganese dioxide is mixed with about an equal weight of potassium hydrate and a little potassium nitrate or chlorate, and the mixture heated to redness upon platinum-foil, it yields a dark green mass, which dissolves in water with a green color, changing to purple when the solution is boiled or on the addition of dilute sulphuric acid.

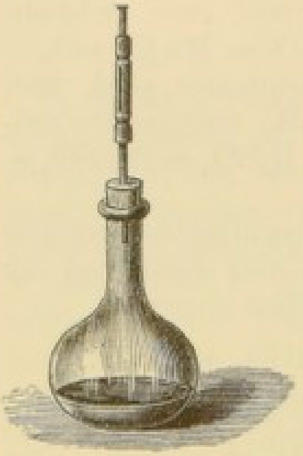
Examination:

As manganese dioxide is frequently employed in connection with potassium chlorate for the generation of oxygen gas, its perfect freedom from organic contaminations should be conclusively established, as the latter may give rise to violent and dangerous explosions. The presence of organic impurities in general may be determined by strongly heating a little of the powdered manganese dioxide in a glass tube, when no combustion should take place, nor should carbonic acid gas be evolved.

Black antimonious sulphide, which, by accident or through carelessness, may become mixed with or substituted for manganese dioxide, may be readily detected by the development of the odor of hydrogen sulphide in contact with dilute hydrochloric acid, and, after boiling with the latter, and filtering, by the production of an orange-colored precipitate upon saturation with hydrogen sulphide.

Since, however, the value of commercial black oxide of manganese or pyrolusite, for most of its applications in the arts and trades, depends less upon the nature of its impurities than upon the percentage of real manganese dioxide, an examination of the mineral is invariably required before its application, and is mainly directed to the determination of the amount of dioxide.

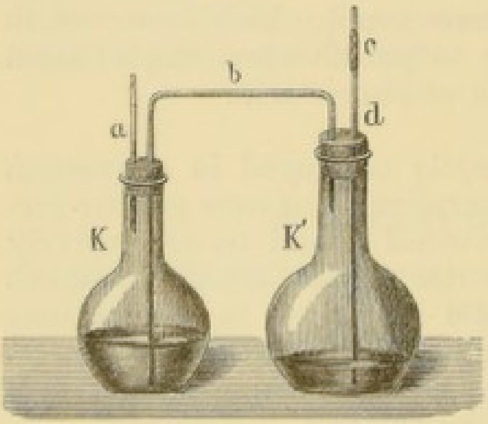
FIG. 137.



Among the several methods of conducting the assay, the two following are simple and accurate, the one being an approximate, the other a quantitative one:

I. Five grams of the finely powdered black oxide of manganese are added, in a small flask (Fig. 137), to a solution of 21 grams of crystallized or granular ferrous sulphate in 15 grams of water and 45 grams of hydrochloric acid, and, when mixed by gentle agitation, the whole is heated for a few minutes to boiling; after being allowed to cool, the liquid is filtered, and the filtrate subsequently tested with potassium ferricyanide; if it gives no blue precipitate, the test bears evidence that the pyrolusite contains at least 66 per cent. of real manganese dioxide; if a blue precipitate is produced, the peroxide is wanting in that strength in proportion to the amount of the precipitate.

FIG. 138.



II. Three grams of the black oxide of manganese, in fine powder, and previously dried at about 120° C. (248° F.), are carefully introduced into the flask K′ (Fig. 138) of the little apparatus described on page 86, into which previously has been poured sufficient of a mixture of 1 part of concentrated sulphuric acid and 2 parts of water to fill the flask to about one-third of its capacity. The apparatus is then brought upon the balance, and, together with from 8 to 9 grams of pure crystallized oxalic acid, is accurately weighed. The oxalic acid is then added to the mixture, being careful to avoid any loss, the cork carrying the tubes is adjusted, and the ensuing reaction effected by gentle agitation; the flask K is charged with a little concentrated sulphuric acid, through which the evolved carbonic acid gas has to pass, and which absorbs and retains the moisture; gentle heat is applied to the flask K′, as long as a brisk evolution of gas takes place; the process is completed when this action and the passage of gas-bubbles through the sulphuric acid both cease, and the black color of the mixture has changed to a more or less brown one; the residual gas is then driven off, by momentary ebullition, and the apparatus again weighed. Every two molecules of carbonic acid evolved correspond to one molecule of manganese dioxide decomposed; the molecular weight of the latter (87) being so nearly equal to twice that of carbonic acid (44), that the loss of weight suffered by the apparatus may be taken to represent the quantity of real manganese dioxide in the 3 grams of the sample employed; and it has only to be divided by 3 and multiplied by 100 in order to express the percentage.

MANGANI SULPHAS.

MANGANUM SULFURICUM.

Sulphate of Manganese. Manganous Sulphate.

Ger. Schwefelsaures Mangan; Fr. Sulfate de manganèse;
Sp. Sulfato de manganeso.

$MnSO_4 + 4H_2O$; 222.

Colorless or pale rose-colored prismatic crystals, occurring in three different forms, with different quantities of water of crystallization: (1) Monoclinic prisms (isomorphous with ferrous sulphate), containing seven molecules of water of crystallization, and obtained when crystallized at a temperature below 6° C. (42.8° F.); (2) Triclinic prisms (isomorphous with cupric sulphate), containing five molecules of water of crystallization, obtained when crystallized at a temperature between 7° and 20° C. (44.6° and 68° F.); and (3) Quadratic crystals or large monoclinic prisms, containing four molecules of water of crystallization, and obtained when crystallized between 20° and 30° C. (68° and 86° F.).

The latter salt is the one commonly met with. The crystals are permanent in the air, though slightly efflorescent in air that is dry and warm; they are soluble in 0.8 part of water at 15° C. (59° F.), and in 1 part of boiling water, but insoluble in alcohol; the aqueous solution is neutral and colorless, or has, when concentrated, a faint rose-color; its taste is astringent, and it affords, with the alkaline hydrates and carbonates, white precipitates, of which those with the hydrates gradually become yellow, and finally dark-brown, by oxidation; ammonium sulphide produces a flesh-colored precipitate soluble in dilute mineral acids, and also in acetic acid (distinction from zinc); tannic acid or tincture of nutgall does not act upon the solution; potassium ferrocyanide produces a reddish-white precipitate, and potassium ferricyanide a brown one; with barium nitrate or chloride it yields a white precipitate, insoluble in hydrochloric acid.

When a fragment of a crystal of manganous sulphate is heated with one or two drops of solution of potassium hydrate and a little potassium chlorate or nitrate, upon platinum-foil, it yields a bluish-green fuse.

Examination:

Ferrous and *cupric sulphates* are detected, in the diluted solution, acidulated with hydrochloric acid, the former by a blue precipitate with potassium ferrocyanide, the latter by a reddish-brown one with the same reagent, or a black one with hydrogen sulphide.

Magnesium and *alkaline sulphates* may be detected by completely precipitating the dilute solution of the salt with ammonium sulphide, and by testing part of the filtrate with sodium phosphate; a white, crystalline precipitate will indicate *magnesium sulphate:* if no reaction has taken place, another portion of the filtrate is evaporated in a porcelain capsule, and the residue heated to redness upon platinum-foil; a fixed remainder would indicate *potassium* or *sodium* salts.

MORPHINA.

MORPHIUM. MORPHINUM.

Morphine. Morphia.

Ger. Morphin; Fr. Morphine; Sp. Morfina.

$C_{17}H_{19}NO_3.H_2O$; 303.

Small, brilliant, prismatic crystals, transparent and colorless, or a white, crystalline powder, containing one molecule (5.94 per cent.) of water of crystallization. When heated to 120° C. (248° F.), the crystals lose their water of crystallization and become opaque, and, when cautiously further heated, they melt without decomposition, assuming a crystalline form on cooling; at temperatures above 200° C. (392° F.), they become decomposed and blackened, and, when strongly heated on platinum-foil, they burn away, leaving a carbonaceous residue, which is wholly dissipated at a red heat.

Morphine is but sparingly soluble in cold water, requiring at 15° C. (59° F.) 1000 parts of the latter for solution, but is soluble in 500 parts of boiling water, in 100 parts of alcohol at 15° C. (59° F.), and in 36 parts of boiling alcohol; it is very sparingly soluble in ether and chloroform, and insoluble in benzol, petroleum benzin, and carbon bisulphide (distinction from narcotine and codeine), but is quite readily soluble in hot amylic alcohol; it dissolves freely in dilute acids, in the fixed alkaline hydrates, and in lime-water, but is almost insoluble in ammonia-water; its alkaline solutions gradually absorb oxygen and become decomposed, acquiring thereby a brown color. The aqueous solution of morphine, and the alcoholic solution to a still greater extent, possess a bitter taste and an alkaline reaction.

A solution of morphine in acidulated water, if not too dilute, affords upon the addition of a solution of potassium or sodium hydrate, ammonia-water, sodium carbonate or bicarbonate, a white crystalline precipitate of morphine, which, however, is readily soluble in an excess of potassium or sodium hydrate, but very sparingly soluble in ammonia-water; it is not precipitated by tannic acid, but affords a white precipitate with potassio-mercuric iodide, and a brown one with iodinized potassium iodide.

In addition to the above described characters, morphine may be recognized and distinguished from all other alkaloids by the following specific reactions and tests:

Strong sulphuric acid dissolves morphine without coloration, but if the solution be quite strongly heated, and, after being allowed to cool, a drop of diluted nitric acid added, the liquid assumes a deep blood-red color; if the solution in sulphuric acid, after heating and being again allowed to cool, be diluted with water, and a fragment of potassium bichromate added, an intense mahogany-brown color is produced. With concentrated nitric acid, morphine produces a blood-red color, which gradually changes to yellow; this coloration, however, is not changed to violet by the addition of stannous chloride or ammonium sulphide (distinction from brucine). If morphine or its salts be intimately mixed with about four times its weight of cane-sugar, and the mixture added to concentrated sulphuric acid, a dark red coloration is produced; if the amount of alkaloid be very small, the mixture will assume a wine-red or rose-red color. If to a trace of morphine or its salts a freshly prepared solution of molybdic acid or ammonium molybdate in concentrated sulphuric acid be added, a fine violet color is soon produced, which afterwards changes to blue, then to a dirty-green, and finally disappears; by the addition of water the coloration is immediately destroyed. A particularly characteristic reaction of morphine or its salts, when free from other reducing substances, consists in adding a few drops of its solution to a solution of iodic acid, whereby iodine is liberated, imparting a yellowish or brownish color to the solution; if then a few drops of chloroform or carbon bisulphide be added, and agitated with the liquid, the iodine will be absorbed, with a fine violet or purple color; and by the employment of a few drops of mucilage of starch instead of chloroform or carbon bisulphide, a fine deep blue color will be produced. If morphine or a perfectly neutral solution of one of its salts be brought in contact with a few drops of a diluted neutral solution of ferric chloride, a blue color is produced;

this reaction is very characteristic, as being produced by no other alkaloid, but the color is destroyed or will not be produced in the presence of free acids or alcohol. If to a diluted solution of potassium ferricyanide a drop of a solution of ferric chloride be added, and subsequently a drop of a solution of morphine or its salts, a deep blue coloration or precipitate will be produced.

Examination:

Narcotine is indicated by a white, crystalline residue, left upon evaporating, on a watch-glass, a little pure ether which has been agitated with a small portion of the morphine.

Inorganic impurities or admixtures may be detected by a fixed residue, upon complete incineration of a little of the morphine on platinum-foil, as well as by their insolubility, when a small portion of morphine is dissolved in about fifty times its weight of boiling alcohol.

For the separation of morphine from other alkaloids or complex organic principles with which it may be associated, see page 111.

MORPHINÆ ACETAS.

MORPHIUM SEU MORPHINUM ACETICUM.

Acetate of Morphine or Morphia. Morphine Acetate.

Ger. Essigsaures Morphin; Fr. Acetate de morphine; Sp. Acetato de morfina.

$C_{17}H_{19}NO_3.C_2H_4O_2+3H_2O$; 399.

A white or yellowish-white, indistinctly crystalline or amorphous powder, having a faintly acetous odor, and containing 3 molecules (13.5 per cent.) of water. It gradually loses water and acetic acid on exposure to the air, and, when heated at 100° C. (212° F.), rapidly loses the entire amount of water, and acquires a brown color; when heated upon platinum-foil, it fuses, and is wholly dissipated at a red heat. It remains colorless when moistened with concentrated sulphuric acid, with the evolution of vapors of acetic acid, and dissolves in concentrated nitric acid, with a scarlet-red color.

Morphine acetate, when freshly prepared, is soluble in 12 parts of water, and in 68 parts of alcohol at 15° C. (59° F.); when kept for some time, however, it requires, in consequence of the loss of acetic acid, a larger amount of water for complete solution, unless a few drops of acetic acid be added. It is also soluble in 1.5 parts of boiling water, in 60 parts of chloroform, and freely soluble in diluted acids, but is insoluble in ether and petroleum benzin; it is decomposed by the action of boiling alcohol, and, upon the subsequent addition of water, a precipitate of morphine is produced.

Its saturated aqueous solution has a bitter taste, and is neutral, or possesses but a slightly acid reaction; it is rendered turbid by tannic acid, but becomes transparent again upon the addition of an excess of the reagent (evidence of the absence of narcotine); it is not permanently precipitated by potassium hydrate, when added in slight excess (distinction from most alkaloids), and assumes a greenish-blue color with a dilute neutral solution of ferric chloride. In its general behavior toward reagents, morphine acetate corresponds to the tests for morphine, as described under the latter, on page 431.

Examination:

Morphine acetate should be completely soluble in 40 parts of water, leaving at most but a slight residue, which should respond to the tests for pure morphine; and when strongly heated on platinum-foil should be completely dissipated.

Sulphates and *chlorides* may be detected in the aqueous solution of the salt, acidulated with diluted nitric acid, when tested with barium nitrate or chloride for the former, and with argentic nitrate for the latter.

MORPHINÆ HYDROCHLORAS.

MORPHIUM SEU MORPHINUM HYDROCHLORICUM. MORPHIÆ MURIAS.

Hydrochlorate of Morphine or Morphia. Morphine Hydrochlorate.

Ger. Chlorwasserstoffsaures Morphin; Fr. Chlorhydrate de morphine; Sp. Hidroclorato de morfina.

$C_{17}H_{19}NO_3.HCl+3H_2O$; 375.4.

White, flexible, acicular crystals, of a silky lustre, or larger transparent prisms, containing 3 molecules (14.4 per cent.) of water of crystallization, and permanent in the air. When heated to 130° C. (266° F.), the salt loses its water of crystallization, and when heated upon platinum-foil, it first fuses, and afterwards, at a higher temperature, burns away without residue.

Morphine hydrochlorate is soluble in 24 parts of water and in 63 parts of alcohol at 15° C. (59° F.); in about 0.5 part of boiling water and 31 parts of boiling alcohol; and is also soluble in 20 parts of glycerin, but insoluble in ether. Its aqueous solution is neutral, has a bitter taste, and assumes a yellowish-red color upon the addition of strong nitric acid, and a bluish one with a dilute neutral solution of ferric chloride; it affords no permanent turbidity with solution of potassium hydrate, when added in slight excess, but is precipitated by ammonia-water; with tannic acid it affords a slight turbidity, which disappears on the addition of an excess of the reagent; and with argentic nitrate it gives a white, curdy precipitate, insoluble in nitric acid, but soluble in ammonia-water, which solution, when heated in a test-tube, separates metallic silver.

When a little dry morphine hydrochlorate is added to a mixture of two parts of concentrated sulphuric acid and one part of water, in a small test-tube, no change of color of the liquid takes place, either at common temperatures, or when gently warmed by immersing the test-tube in hot water (evidence of the absence of salicin and other bitter substances); when this liquid is divided into two portions, and one drop of strong nitric acid is added to the one part, a red coloration occurs, and on adding a trace of potassium bichromate to the other part, only a slight yellowish-green coloration takes place.

Morphine hydrochlorate dissolves in chlorine-water, with a yellowish color, which becomes brown upon the addition of ammonia-water (distinction from quinine, which yields an emerald-green color). In its general behavior toward re-agents, morphine hydrochlorate corresponds to the tests for morphine, as described under the latter, on page 431.

MORPHINÆ SULPHAS.

MORPHIUM SEU MORPHINUM SULFURICUM.

Sulphate of Morphine or Morphia. Morphine Sulphate.

Ger. Schwefelsaures Morphin ; Fr. Sulfate de morphine ;
Sp. Sulfato de morfina.

$(C_{17}H_{19}NO_3)_2.H_2SO_4+5H_2O$; 758.

White, fasciculate, feathery crystals, of a silky lustre, containing 5 molecules (11.87 per cent.) of water of crystallization, and permanent in the air. When heated to 130° C. (266° F.), the salt loses its water of crystallization, and, when strongly heated on platinum-foil, burns entirely away without residue.

Morphine sulphate is soluble in 24 parts of water and in 702 parts of alcohol at 15° C. (59° F.), and in about 0.5 part of boiling water and 31 parts of boiling alcohol (distinction from quinine sulphate); it is almost insoluble in ether and in chloroform. Its aqueous solution is neutral and very bitter; it gives no permanent precipitate with potassium hydrate when added in slight excess, but yields with ammonia-water and the alkaline carbonates and bicarbonates a white crystalline precipitate of morphine. It affords a blue color with a dilute, neutral solution of ferric chloride, and a white precipitate, insoluble in acids, with barium chloride.

Morphine sulphate dissolves in strong sulphuric acid without coloration, even when gently warmed by dipping the test-tube in warm water (evidence of the absence of salicin and other bitter glucosides); it dissolves in concentrated nitric acid with a yellowish-red coloration (distinction from quinine). When dissolved in a little chlorine-water, morphine sulphate yields a greenish-yellow solution, which becomes dark-brown upon the addition of ammonia-water (further distinction from quinine, which yields an emerald-green color). In its general behavior toward reagents, morphine sulphate corresponds to the tests for morphine, as described under the latter on page 431.

Examination:

Sodium sulphate, which has been found to occur as an adulterant of morphine sulphate, may be detected, as well as other inorganic salts, by a non-volatile residue, when a little of the morphine sulphate is strongly heated on platinum-foil.

Ammonium salts may be recognized by the odor of ammonia, when a little of the salt is heated, in a test-tube, with a strong solution of potassium hydrate; and by the formation of white fumes, when a glass rod, moistened with acetic acid, is held over the orifice of the tube.

Morphiometric Assay of Opium:

Since the therapeutical and commercial value of opium mainly depends upon the quantity of morphine which it contains, an examination of opium is invariably required before its introduction into the market or its application for the manufacture of the opium alkaloids, or for medication. Among the various methods for the estimation of the morphine strength of opium, the following are simple in execution, require comparatively little time, and render approximately correct results.

I. *Flückiger's Process.* — Eight grams of powdered air-dry opium are digested for twelve hours, with frequent agitation, with 80 grams of cold water, and subsequently filtered. 42.5 grams of the filtrate (representing the soluble matter of one-half of the opium employed) are then brought into a tared flask, and to the solution 12 grams of alcohol, of about 0.820 spec. grav., and 10 grams of ether are added, whereby no turbidity should ensue; a portion of the ether forming a colorless layer on the surface of the mixture. 1.5 grams of ammonia-water, spec. grav. 0.960, are then added, and, after thorough agitation, the mixture allowed to repose for 24 hours, when the morphine will be deposited in white crystals. The crystals of the alkaloid are afterwards collected on a folded double filter having a diameter of about 10 centimeters (four inches), the flask rinsed with 10 grams of a mixture of equal parts of alcohol and ether, and finally with 10 grams of pure ether, and these liquids gradually poured on the crystals of morphine in order to wash them. The crystals are subsequently cautiously pressed between the folds of the two filters, which will almost completely absorb the mother liquor which the crystals of morphine may still retain. The alkaloid may now readily be removed from the filter, and having been brought into the tared flask, which may still contain a few crystals of morphine attached to its sides, the whole is dried at 100° C. (212° F.), and its weight determined. From the weight of the alkaloid, which, at 100° C. (212° F.), corresponds to the formula $C_{17}H_{19}NO_3+H_2O$, the percentage of morphine may be calculated. As by the above method a small amount of morphine remains dissolved in the liquid from which it has separated, the error which would thereby be occasioned may be eliminated by adding 0.088 gram to the amount of alkaloid obtained. As a test for the purity of the crystals obtained, they should, although slowly, be completely soluble in 100 times their weight of officinal lime-water. An air-dried opium, of good quality, when submitted to the above method of examination, should yield from 0.40 to 0.48 gram of alkaloid, corresponding to from 10 to 12 per cent. of pure morphine.

II. *Squibb's Modification of Flückiger's Process.*—Ten grams (154.32 grains) of commercial opium, in its moist or powdered condition, and representing the average quality of the specimen, are brought into a flask or wide-mouthed bottle of 120 cubic centimeters (4 fluidounces) capacity, which has been previously weighed and fitted with a good cork; 100 cubic centimeters (3.3 fluidounces) of water are then added, and the mixture well shaken. It is then allowed to macerate over night, or for about twelve hours, with occasional shaking, and then, after shaking well, the magma is transferred to a filter of about 10 centimeters (4 inches) diameter, which has been placed in a funnel and well wetted.

The solution is now filtered into a tared or marked vessel, and the residue on the filter percolated with water dropped on to the edges of the filter and the residue until the filtrate measures about 120 cubic centimeters (4 fluidounces), and this strong solution set aside. The residue is then returned to the flask or bottle by means of a very small spatula, without breaking or disturbing the filter in the funnel, 30 cubic centimeters (1 fluidounce) of water added, the mixture well shaken, and the magma returned to the filter. After being allowed to drain, the bottle is rinsed twice, each time with 10 cubic centimeters (0.33 fluidounce) of water, and the rinsings poured upon the residue. When this has passed through, the filter and residue are washed with 20 cubic centimeters (0.66 fluidounce) of water, applied drop by drop around the edges of the filter and upon the contents. This (120+70) 190 cubic centimeters (6.33 fluidounces) of total solution will practically exhaust almost any sample of 10 grams of opium; but occasionally a particularly rich opium, or one in coarse powder, or an originally moist opium which has by slow drying become hard and flinty, will require further exhaustion.

In all such cases, or cases of doubt, the residue should be again removed from the filter and shaken with 30 cubic centimeters (1 fluidounce) of water, and returned and again washed as before. The filter and residue are now dried at 100° C. (212° F.) until they cease to lose weight; and if any residue remains in the bottle, the bottle is also to be dried in an inverted position, and weighed. The weaker solution is then evaporated in a tared capsule of about 200 cubic centimeters (6.6 fluidounces) capacity, without a stirrer, on a water-bath, until reduced to about 20 grams (309 grains), the 120 cubic centimeters of stronger solution subsequently added, and the whole again evaporated to about 20 grams (309 grains). The capsule and contents are cooled, and, when cool, 5 cubic centimeters (0.17 fluidounce) of alcohol, spec. grav. 0.820, added, and the mixture stirred until a uniform solution is obtained and no adhering extract remains undissolved on the capsule. If this solution should contain an appreciable precipitate, it must be filtered, the filter carefully washed, and the filtrate evaporated to 25 or 30 grams. The concentrated solution from the capsule is poured into a tared flask of about 100 cubic centimeters (3.33 fluidounces) capacity, the capsule rinsed with about 5 cubic centimeters of water, used in successive portions, and the rinsings added to the contents of the flask. If the solution has not required filtering, then 5 cubic centimeters (0.17 fluidounce) more of alcohol are added; if it has been filtered and evaporated, 10 cubic centimeters (0.33 fluidounce) of alcohol are added and shaken well. Then 30 cubic centimeters (1 fluidounce) of ether are added, and again shaken well. Four cubic centimeters (0.133 fluidounce) of ammonia-water, spec. grav. 0.960, are now added, the flask shaken vigorously until the crystals begin to separate, then set aside in a cool place for 12 hours, that the crystallization may be completed.

The ethereal stratum is poured off from the flask, as closely as possible, on to a tared filter of about 10 centimeters (4 inches) diameter, which has been well wetted with ether, 20 cubic centimeters (0.66 fluidounce) of ether added to the contents of the flask, which is rinsed around without shaking, and the ethereal stratum again poured off as closely as possible on to the filter, keeping the funnel covered. When the ethereal solution has nearly all passed through, the edges and sides of the filter are washed with 5 cubic centimeters (0.17 fluidounce) of ether, and the filter allowed to drain with the cover off. The remaining contents of the flask are then placed on the filter, and the funnel covered. When the liquid has nearly all passed through, the flask is rinsed twice with two portions of water of 5 cubic centimeters (0.17 fluidounce) each, pouring the rinsings with all the crystals that can be loosened on to the filter, the flask dried in an inverted or horizontal position, and, when thoroughly dried, weighed. The filter and crystals are then washed with 10 cubic centimeters (0.33 fluidounce) of water, applied drop by drop to the edges of the filter, and, when drained, the filter and contents removed from the funnel, the edges of the filter closed together, and the filter compressed gently between many folds of bibulous paper. It is then dried at 100° C. (212° F.) and weighed, the crystals of morphine removed from the filter, and the latter brushed off and reweighed, to get the tare to be subtracted. The remainder, added to the weight of the crystals in the flask, will give the total yield of morphine, in clean, distinct, small, light-brown crystals. As a test of purity for the obtained morphine, 0.1 gram of the finely powdered crystals should be completely soluble in 10 cubic centimeters of officinal lime-water.

III. *United States Pharmacopœia Process.*—Seven grams of opium (in any condition to be valued) are triturated, in a mortar, with 3 grams of freshly slaked lime and 20 cubic centimeters of distilled water, until a uniform mixture results, after which 50 cubic centimeters of distilled water are added, and the mixture stirred occasionally during half an hour. It is then filtered through a plaited filter, having a diameter of 75 to 90 millimeters (3 to 3.5 inches), into a wide-mouthed bottle or stoppered flask (having a capacity of about 120 cubic centimeters and marked at 50 cubic centimeters) until the filtrate reaches this mark. To the filtered liquid (representing 5 grams of opium) 5 cubic centimeters of alcohol and 25 cubic centimeters of stronger alcohol are added, and, after shaking the mixture, 3 grams of ammonium chloride are added, the mixture again shaken well and frequently during half an hour, and then set aside for twelve hours. After counterpoising two small filters, one is placed within the other in a small funnel, and the ethereal layer decanted as completely as practicable upon the filter. Ten cubic centimeters of stronger ether are then added to the contents of the bottle and the mixture rotated, the ethereal layer again decanted upon the filter, and the latter afterward washed with 5 cubic centimeters of stronger ether, added slowly and in small portions. The filter is now allowed to dry in the air, and the liquid in the bottle poured upon it, in portions, in such a way as to transfer the greater portion of the crystals to the filter. The bottle is then washed, and the remaining crystals transferred to the filter, with several small portions of distilled water, using not much more than 10 cubic centimeters in all, and distributing the portions evenly upon the filter. After allowing the filter to drain, it is dried, first by pressing it between sheets of bibulous paper, and afterward at a temperature between 55 and 60° C. (131 to 140° F.). The crystals in the inner filter are now weighed, using the outer filter as a counterpoise. The weight of the crystals in grams, multiplied by 20, represents the percentage of morphine in the opium employed.

The U. S. Pharmacopœia directs that opium, in its normal, moist condition, should yield not less than 9 per cent. of morphine; and powdered opium not less than 12 nor more than 16 per cent. of morphine, when assayed by the above process.

Morphiometric Assay of Tincture of Opium:

When *tincture of opium* has to be examined for the quantity of morphine it contains, this may be ascertained by either of the following methods:

I. To forty grams of the tincture (corresponding to 4 grams of powdered opium when prepared according to the United States and German Pharmacopœias), contained in a tared flask, 1.5 cubic centimeters of ammonia-water, spec. grav. 0.960, and 13 cubic centimeters of ether are added; after being well mixed by agitation the mixture is allowed to repose for at least thirty-six hours, when the crystals of morphine may be collected and further treated as described under *Flückiger's* morphiometric process on page 435.

To the amount of alkaloid obtained from the stated amount of tincture, about 0.1 gram should be added, as representing approximately the amount of morphine remaining dissolved in the liquid from which it has been precipitated. The total weight of alkaloid should be not less than 0.48, nor more than 0.64 gram, indicating the employment of an opium containing not less than 12, nor more than 16 per cent. of morphine.

II. One hundred and twenty cubic centimeters (4 fluidounces) of the tincture, or other liquid preparations, are evaporated at a low temperature to 10 grams (155 grains), and the process then conducted exactly as described under *Squibb's* modified method of assay, on page 436, using, however, 5 cubic centimeters of alcohol, instead of 10, and 2.5 to 3 cubic centimeters of ammonia-water, instead of 4 cubic centimeters.

NICOTINA.

NICOTINUM.

Nicotine. Nicotia.

Ger. Nicotin; Fr. Nicotine; Sp. Nicotina.

$C_{10}H_{14}N_2$; 162.

A colorless or nearly colorless, oily, and volatile liquid, having the specific gravity 1.027 at 15° C. (59° F.), a pungent odor, resembling that of tobacco, and an acrid, burning taste. By exposure to the air, it becomes gradually brown and thick; it begins to volatilize at 146° C. (294.8° F.), and boils in an atmosphere of hydrogen at from 240 to 242° C. (464 to 467.6° F.); when heated on platinum-foil it volatilizes completely, forming irritating vapors, which readily take fire, and burn with a bright, sooty flame. When dropped into concentrated sulphuric acid, it dissolves, with a red color, and, when one drop of solution of potassium bichromate is added, the solution becomes brown, and subsequently green; when mixed with hydrochloric acid and cautiously warmed, a reddish-brown mixture is formed, which, by further evaporation and cooling, yields, upon the subsequent addition of nitric acid, a violet coloration, gradually changing to orange.

Nicotine produces white fumes with hydrochloric and acetic acids, precisely like ammonia-water; it sinks when dropped into water (distinction from coniine, which floats), but is miscible with water in all proportions, and becomes again separated on the addition of solid potassium or sodium hydrate; it also dissolves in alcohol, ether, amylic alcohol, carbon bisulphide, chloroform, petroleum benzin, and in most of the fixed and volatile oils; its solutions have an alkaline reaction, and an acrid, burning taste; they produce precipitates in solutions of neutral and basic plumbic acetate, cupric acetate, and many other metallic salts, and are precipitated by solutions of tannic acid, potassio-mercuric iodide, iodinized potassium iodide, and auric and platinic chlorides, but the aqueous solution affords no precipitate with chlorine-water (additional distinction from coniine); the alcoholic solution should yield no turbidity with diluted sulphuric acid (evidence of the absence of ammonia). The aqueous solution of nicotine, when applied to the eye, causes the pupil alternately to dilate (mydriasis) and to contract (stenocoriasis).

By careful oxidation with concentrated nitric acid or potassium permanganate, nicotine is converted into *nicotinic acid*, $C_6H_5NO_2$ (Pyridine-carbonic acid, $C_5H_4N{-}COOH$), which may be obtained from its silver salt by decomposing it with hydrogen sulphide. Nicotinic acid forms colorless, needle-shaped crystals, which are readily soluble in alcohol and in boiling water, but not in cold water or in ether; they melt at 225° C. (437° F.), and, when heated with soda-lime, yield the volatile organic base, *pyridine*, C_5H_5N.

For the separation of nicotine from other alkaloids, or from complex organic mixtures with which it may be associated, see page 108.

OLEUM AMYGDALÆ ÆTHEREUM.

OLEUM AMYGDALARUM AMARARUM ÆTHEREUM.

Volatile Oil of Bitter Almond.

Ger. Bittermandelöl; Fr Essence d'amandes amères;
Sp. Esencia de almendras amargas.

A thin, colorless, or golden-yellow liquid, of great refractive power, and of the odor of bitter almonds. Exposed to the air, it rapidly absorbs oxygen, with the formation of crystals of benzoic acid; its spec. grav. is from 1.060 to 1.070 at 15° C. (59° F.); or, after the removal of the hydrocyanic acid, 1.043 to 1.049; its boiling-point, 180° C. (356° F.).

When dropped into water, oil of bitter almonds sinks, but dissolves upon shaking, unless too much oil has been used, about 300 parts of water being required for solution. When a few drops of solution of potassium hydrate are added to its aqueous solution, and afterward one or two drops of a solution of a ferrous and a ferric salt, and finally, after agitation, a slight excess of hydrochloric acid, there will appear a blue coloration, and, after a while, a blue precipitate.

Oil of bitter almonds is miscible, in all proportions, with alcohol, ether, chloroform, carbon bisulphide, and essential and fatty oils; it is also soluble in concentrated nitric acid, without color, and without the evolution of nitrous fumes; with an equal volume of concentrated sulphuric acid the mixture assumes a red color, which gradually increases in intensity, but remains limpid and clear.

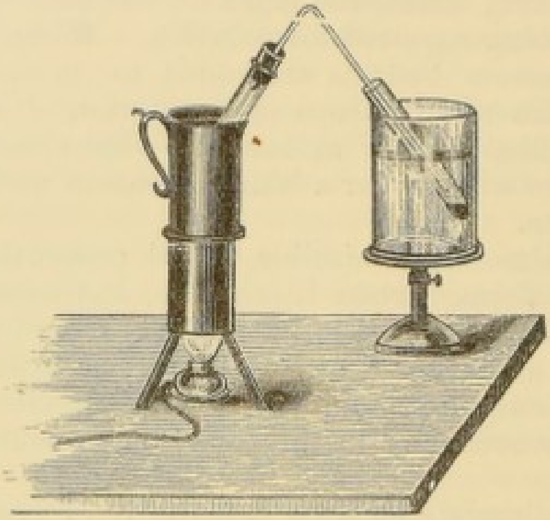
Oil of bitter almonds consists essentially of benz-aldehyde, or the aldehyde of benzoic acid, C_6H_5–COH, together with usually from 2 to 5 per cent. of hydrocyanic acid, which, in the process of distillation, combine to form a very unstable compound. From this compound the acid is gradually liberated, and becomes partially converted, by its decomposition, into ammonium cyanide and formic acid. The crude oil, obtained by distillation without further rectification, usually contains the largest proportion of hydrocyanic acid.

Examination:

Alcohol may be detected in oil of bitter almonds by agitating it with three times its volume of concentrated nitric acid, and subsequently warming the mixture by dipping the test-tube into hot water. No reaction takes place with pure oil; but, if it has an admixture of more than three per cent. of alcohol, effervescence will occur, with disengagement of yellowish nitrous vapors.

Chloroform, as well as *alcohol*, can be detected by submitting a small portion of the oil to distillation from a water-bath, cooling the receiving test-tube in ice-water (Fig. 139). The boiling-point of the oil being at 180° C. (356° F.), only admixtures volatile at or below the boiling-point of water will distil, with but small traces of the constituents of the oil. The obtained distillate is mixed with a little iodine-water; if chloroform be present, and no alcohol, it will absorb the iodine, and separate, with a rose-color. The colorless, aqueous liquid is decanted, and then warmed by dipping the test-tube in warm water; one drop of solution of iodinized potassium iodide is added, and then one drop of solution of potassium hydrate, or sufficient nearly to decolorize the liquid. If alcohol be present, minute yellow crystals of iodoform will be produced (Fig. 140), which, after subsiding, in a conical glass, may be recognized by the examination of the sediment under the microscope.

FIG. 139.



Nitrobenzol may be detected by adding 10 drops of the oil to a mixture of 5 cubic centimeters of alcohol and an equal volume of water, in a narrow test tube, closing the tube with the finger, and effecting the mixture by gently inverting the tube. If the oil is pure, a perfectly clear solution will at once be produced, whereas, if it contains but one per cent. of nitrobenzol, the liquid will appear turbid from the separation of oily drops, which, upon gentle agitation, aggregate, and are deposited at the bottom of the tube.

FIG. 140.

Another reliable test consists in adding to a portion of the oil, in a test-tube, a few fragments of metallic zinc, and a little diluted sulphuric acid. After standing for a couple of hours, or until the evolution of gas has ceased, the aqueous liquid is filtered through a wet filter, and to the filtrate a fragment of potassium chlorate and a drop of concentrated sulphuric acid are added; no coloration should be thereby produced; a violet color would indicate the presence of nitrobenzol through its reduction to aniline.

Essential Oils.—Adulteration with cheaper essential oils, as well as with nitrobenzol, may be detected by the property of oil of bitter almonds to dissolve in a concentrated aqueous solution of sodium bisulphite when added drop by drop and agitated; whereas such admixtures remain undissolved, floating upon the aqueous solution after dilution with a little tepid water.

Estimation of the Available Quantity of Hydrocyanic Acid in Oil of Bitter Almonds:

I. Five grams of the oil are mixed, in a beaker, with about 25 cubic centimeters of strong alcohol; then about 200 cubic centimeters of water and a few drops of solution of sodium chloride are added, and subsequently sufficient of a solution of potassium hydrate to render the liquid alkaline to test-paper. A decinormal solution of argentic nitrate (page 98) is then allowed to flow into the liquid from a burette until, with constant stirring, the precipitate ceases to be re-dissolved, and therefore a slight permanent turbidity occurs. The number of cubic centimeters of argentic nitrate solution employed, multiplied by the decimal 0.0054, will represent the amount of hydrocyanic acid contained in 5 grams of the oil, and has only to be subsequently multiplied by 20 to express the percentage.

II. Another method consists in adding to 1 gram of the oil, contained in a small flask, about five times its weight of strong alcohol, subsequently 45 cubic centimeters of distilled water, and finally a solution of 1 gram of pure crystallized argentic nitrate in an excess of dilute ammonia-water. The mixture is well agitated for a few moments, and subsequently pure nitric acid added until it acquires a slight acid reaction. The precipitated argentic cyanide is then carefully collected on a tared filter, thoroughly washed, and finally dried at 100° C. (212° F.) until of constant weight. The weight of dry argentic cyanide, when divided by 5, will represent the amount of hydrocyanic acid in 1 gram of the oil, and has, therefore, only to be subsequently multiplied by 100 in order to express the percentage.

OLEUM SINAPIS ÆTHEREUM.

OLEUM SINAPIS VOLATILE.

Volatile Oil of Mustard.

Ger. Ætherisches Senföl; Fr. Huile de moutarde; Sp. Aceite esencial de mostaza.

$$C_4H_5NS = (CS{=}N{-}C_3H_5);\ 99.$$

A colorless or pale-yellow liquid, of a most penetrating, pungent odor, and having the specific gravity 1.017 to 1.021 at 15° C. (59° F.); it boils at 148° C. (298.4° F.). When dropped into water, it sinks slowly, and dissolves in from 100 to 250 parts of it, the solubility of the oil in water apparently increasing with age; if to the aqueous solution a few drops of solution of argentic nitrate be added, and heated, a black precipitate of argentic sulphide will be produced.

Mustard oil is miscible with alcohol, ether, chloroform, carbon bisulphide, and benzol, and with fatty and essential oils; it suffers decomposition with concentrated nitric acid, with the evolution of nitrous vapors, and the formation of a resinous residue. When dropped into concentrated sulphuric acid, mustard oil dissolves, without color, and without the evolution of heat, and when mixed with concentrated sulphuric acid, in the proportion of one part of oil to three parts of acid, being careful that the mixture is kept cool, sulphurous acid is evolved, and, after twelve hours, a colorless or but slightly brown, thick liquid or crystalline mass is formed, devoid of the odor of mustard oil.

If 2 parts of mustard oil, 1 part of alcohol, spec. grav. 0.830, and 7 parts of ammonia-water, spec. grav. 0.960, be digested for several hours at a temperature of about 40° C. (104° F.), and subsequently concentrated on the water-bath, it is converted into *thiosinammine*, $C_4H_8N_2S$:

$$C_3H_5\text{-}CNS + NH_3 = C_4H_8N_2S.$$

The latter forms colorless and odorless, shining crystals, which possess a bitter taste, dissolve readily in water, alcohol, and ether, and fuse at 74° C. (165.2° F.).

Examination:

Admixtures of *essential* and *fatty oils*, *carbon bisulphide*, *nitrobenzol*, and *alcohol*, are indicated by becoming warm and dark-colored when about five or six drops of the oil are added to about 50 or 60 drops of concentrated sulphuric acid, in a dry test-tube; this is particularly the case when a mixture of 3 parts of concentrated sulphuric acid and one part of nitric acid is employed, being careful in the operation of mixing the acids to avoid elevation of temperature.

If an admixture of carbon bisulphide, chloroform, etc., is suspected, advantage may be taken of their relatively low boiling-points, and their separation from the mustard oil effected by distillation from the water-bath; to the distillate the respective special tests of identity, as described on pages 302 and 309, may then be applied.

Admixtures of *alcohol*, *benzol*, and other *hydrocarbons*, are also indicated when two or three drops of the oil are allowed to fall into a test-tube, about one-third filled with cold distilled water; the oil should sink slowly to the bottom, remaining clear and transparent, until, after gently inclining the tube two or three times, it becomes opalescent. When contaminated with only a few per cent. of the above adulterations, the drops lose their transparency, and become opalescent, as soon as they fall into the water.

Phenol (carbolic acid), *gaultheria oil*, and other similar bodies may readily be detected in the dilute alcoholic solution of the oil by the production of a violet color on the addition of a drop of solution of ferric chloride, whereas pure mustard oil remains unchanged.

PHOSPHORUS.

Phosphorus.

Ger. Phosphor ; Fr. Phosphore; Sp. Fósforo.

P; 31.

A translucent, slightly yellowish or nearly colorless solid, of a waxy lustre, and occurring usually in the form of cylindrical sticks. At ordinary temperatures it has about the consistence of wax, and may be easily cut with a knife, but at low temperatures is hard and brittle. It has a distinctive and disagreeable odor and taste, and the specific gravity 1.826 at 10° C. (50° F.); it melts at 44° C. (111.2° F.), forming a colorless or slightly yellow, strongly refractive liquid, which has the specific gravity 1.764; it boils in an atmosphere free from oxygen at 290° C. (554° F.), yielding a colorless vapor, but is slowly volatilized even at ordinary temperatures.

Phosphorus is nearly insoluble in water, but dissolves in 350 parts of absolute alcohol at 15° C. (59° F.), in 240 parts of boiling absolute alcohol, in 80 parts of ether, in about 50 parts of fatty oil, and very abundantly in carbon bisulphide; the latter dissolving twenty times its weight of the substance, forming a colorless solution, which, however, requires to be handled with the utmost caution, as a single drop of it, when allowed to fall upon paper, soon bursts into flame.

When exposed to the air, phosphorus emits white fumes, which are luminous in the dark, and have an odor somewhat resembling that of garlic; it is very inflammable, and must, therefore, be preserved under water in a cool place. It possesses strongly reducing properties, separating many metals, copper, lead, silver, etc., from solutions of their salts; by the action of direct sunlight, or by heating to 250° C. (482° F.), it is principally converted into the *red* or *amorphous* modification, which, among other characters, is distinguished from ordinary phosphorus by its insolubility in carbon bisulphide and other solvents, its unalterability by exposure to the air at ordinary temperatures, and its non-luminous and non-poisonous properties.

By treatment with nitric acid, phosphorus is converted into tri-basic or orthophosphoric acid.

Examination:

Arsenic and *Sulphur.*—Commercial phosphorus from its method of manufacture frequently contains small amounts of arsenic and sulphur, which, however, should not be present to any considerable extent. They may be recognized, and, if required, the amount quantitatively determined, by the following method. 1 part of phosphorus is digested with a mixture of from 6 to 8 parts of nitric acid and 6 parts of distilled water until it is completely dissolved. The solution is then evaporated until nitrous vapors cease to be evolved, subsequently diluted with water so as to weigh about 12 parts, and, being heated to about 70° C. (158° F.), hydrogen sulphide passed through the liquid for about half an hour, and finally, after the removal of the heat, until the liquid cools. The liquid is then set aside in a tightly corked flask for twenty-four hours, when any arsenic present, which should not be more than a trifling quantity, will become precipitated as yellow arsenic trisulphide. If the amount of the latter is to be quantitatively determined, it may be collected on a tared filter, washed first with water, and, after drying, with pure carbon bisulphide, in order to remove adhering sulphur, then dried at 100° C. (212° F.), and finally weighed: 100 parts of arsenic trisulphide, As_2S_3, correspond to 61 parts of metallic arsenic. Or the arsenic trisulphide may be converted into arsenic acid, by treatment with hydrochloric acid and a little potassium chlorate on the water-bath, and, by the addition of test magnesium mixture, precipitated as ammonio-magnesium arseniate; the latter, when collected on a tared filter, washed with dilute ammonia-water, and dried at 105° C. (221° F.), corresponds to the formula $MgNH_4AsO_4 + \frac{1}{2}H_2O$, and of which 100 parts correspond to 39.47 parts of metallic arsenic.

The filtrate from the original precipitate of arsenic trisulphide when tested with solution of barium chloride should not afford more than a slight opalescence; a white precipitate, insoluble in hydrochloric acid, will reveal the presence of *sulphur*, which, by the above treatment with nitric acid, becomes converted into sulphuric acid.

Separation and Detection of Phosphorus in Forensic Investigations.—In consideration of the extensive application of phosphorus in the preparation of lucifer matches, and of its employment in the form of a paste for the destruction of vermin, it is occasionally the object of search in cases of accidental or criminal poisoning, and a convenient and reliable method for its isolation and detection will therefore be briefly described.

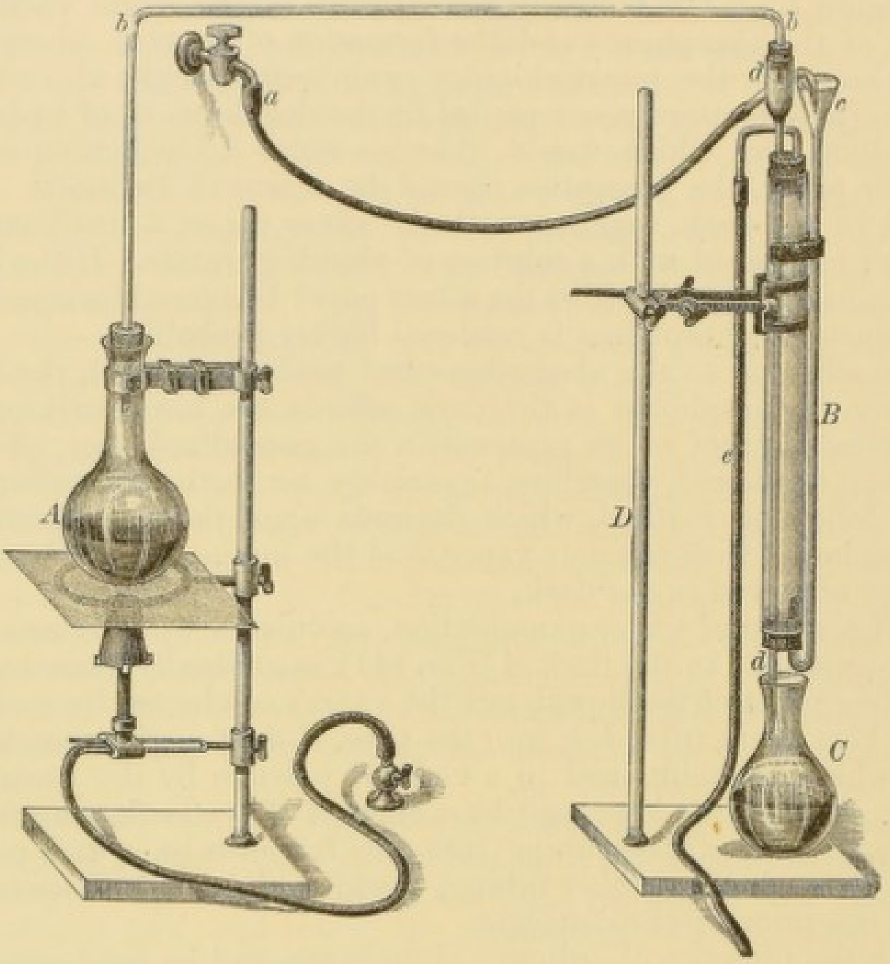
The substance under examination, which may consist of some article of food, the contents of a stomach, vomited matters, etc., is first examined by its odor, which will frequently reveal the presence of phosphorus, when existing in the free state. As a preliminary test, the substance is then brought into a glass flask, provided with a tightly fitting cork, and a small strip of paper moistened with a solution of argentic nitrate suspended from the cork, so as to project slightly into the interior of the flask. Sufficient water is then added to the mixture to form a thin liquid, and also a little tartaric acid, in order to insure a distinctly acid reaction, after which the contents of the flask are very gently heated. If phosphorus be present, the paper moistened with the silver solution will become blackened, either immediately or after standing for a few hours, in consequence of the slight volatilization of the phosphorus and the formation of argentic phosphide. As, however, the material under examination might also contain putrefying matters, accompanied by the development of hydrogen sulphide, etc., which would likewise cause a blackening of the silver paper, the precaution should be observed to insert in the cork of the flask, together with the silver paper, a small strip of paper moistened with a solution of plumbic acetate. If the latter remains unaffected, whilst the silver paper becomes blackened, the presence of phosphorus is rendered highly probable.

In addition to the above-described preliminary test, the luminosity of phosphorus in the dark affords the most striking and conclusive proof of its presence in the unoxidized state, and the substance should, therefore, invariably be further examined by the following method, which depends upon the volatilization of phosphorus with aqueous vapor, and the luminosity of the vapor when observed in the dark.

The material under examination, acidulated with tartaric acid, and contained in the flask *A* (Fig. 141), is gradually heated to the boiling-point of the liquid, and the vapors conducted by means of the bent glass tube, *b*, *b*, into the tube, *d*, *d*, of a glass condenser, *B*, which is maintained in a vertical position by the stative, *D*. The condenser is kept cool by a current of water flowing from *a* through the rubber tubing into the funnel-tube, *c*, and passing out through the rubber tubing, *e*, whilst the flask, *C*, serves for the reception of the distillate.

In the presence of ordinary phosphorus, and by conducting the distillation in a dark room, a luminous ring, which remains visible for a considerable time, will be observable in the cooled portions of the tube, *d*, *d*, while if considerable phosphorus be present, small particles of the latter will also frequently be found in the distillate. It should, however, be considered that the presence of alcohol and ether, as also of volatile oils, retard or prevent the luminosity of the vapor, but, as soon as these are volatilized, the characteristic reaction may at once be observed. If a quantitative determination of the phosphorus be required, the distillate, together with any particles of suspended phosphorus which it may contain, is mixed with a sufficient amount of good chlorine-water, and, after being allowed to stand for about twelve hours, evaporated to a small volume upon the water-bath. The phosphorous acid of the distillate is thereby converted into phosphoric acid, and, after supersaturation with ammonia-water, may be precipitated by test magnesium mixture as ammonio-magnesium phosphate; the latter is then collected upon a filter, washed with a little dilute ammonia-water, dried, and by ignition in a small porcelain crucible, converted into magnesium pyrophosphate,

Fig. 141.



$Mg_2P_2O_7$, and its weight finally determined: 100 parts of the latter compound correspond to 27.92 parts of phosphorus.

If in the above-described method for the detection of phosphorus it should also be necessary or desirable to take into consideration the possible presence of hydrocyanic acid, the same method of investigation may be pursued, reserving, however, the first portion of the distillate for examination for hydrocyanic acid, as described on page 162, or for other readily volatile substances by which it may be accompanied. The subsequent portion of the distillate may then be employed for the qualitative or quantitative determination of phosphorus, in the manner above described.

PHYSOSTIGMINÆ SALICYLAS.

PHYSOSTIGMINUM SALICYLICUM.

Salicylate of Physostigmine. Physostigmine Salicylate.

Ger. Salicylsaures Physostigmin; Fr. Salicylate de physostigmine; Sp. Salicilato de fisostigmina.

$C_{15}H_{21}N_3O_2.C_7H_6O_3$; 413.

Colorless or faintly yellowish, shining, acicular, or short columnar crystals, which by long exposure to air and light gradually assume a reddish color; when strongly heated on platinum-foil they are completely dissipated.

Physostigmine salicylate is soluble in 130 parts of water and in 12 parts of alcohol at 15° C. (59° F.); in 30 parts of boiling water, and very freely in boiling alcohol. The aqueous solution is neutral in its action upon litmus, and possesses a bitter taste; it is precipitated by the ordinary alkaloidal reagents, is rendered turbid by iodine-water, and yields with a drop of a dilute solution of ferric chloride a violet coloration; upon exposure to diffused light for one or two days it assumes a reddish color. The solution of the salt in concentrated sulphuric acid is at first colorless, but afterwards assumes a yellow color. If sodium bicarbonate be added to the aqueous solution of the salt, which is afterward shaken with ether, and the ethereal solution separated and allowed to evaporate spontaneously, an amorphous residue of physostigmine is obtained; the latter possesses a decidedly alkaline reaction, fuses at 45° C. (113° F.), and its aqueous solution, on exposure to the air, soon becomes red, or sometimes intensely blue, resulting from its partial decomposition; if sulphurous acid be added to such a solution, the color is discharged, but returns again on the evaporation of the acid. On concentrating the aqueous solution, which has been precipitated by sodium bicarbonate and shaken with ether, to a small volume, and supersaturating with sulphuric acid, a bulky white precipitate is obtained, which responds to the reactions of salicylic acid, page 181.

A solution of physostigmine, or any of its salts, when applied to the eye, strongly contracts the pupil.

PICROTOXINUM.

Picrotoxin.

Ger. Pikrotoxin; Fr. Picrotoxine; Sp. Picrotoxina.

$C_9H_{10}O_4$; 182.

Colorless, shining, prismatic crystals, which undergo no change by exposure to the air; they are odorless, possess an intensely bitter taste, and are neutral in their action upon litmus. On being heated to about 200° C. (392° F.) the crystals melt to a yellow liquid; when heated on platinum-foil they char, and at a strong heat are finally completely dissipated.

Picrotoxin is soluble in 150 parts of water and 10 parts of alcohol at 15° C. (59° F.), in 25 parts of boiling water and 3 parts of boiling alcohol; the latter solution forming upon cooling a mass of silky prisms. It is also soluble in about 2.5 parts of ether, and readily in amylic alcohol and chloroform; concentrated acetic acid likewise dissolves it, as do also the fixed alkalies and ammonia-water, and from the latter solutions it is precipitated unchanged on the addition of an acid.

If a little picrotoxin be placed in a capsule and mixed with four or five drops of concentrated sulphuric acid, the crystals dissolve with a golden-yellow color, which changes to saffron-yellow; on subsequently adding a trace of powdered potassium bichromate, a violet-green color is produced, and, upon dilution with water, a clear yellowish-green solution is formed. When a little picrotoxin is intimately mixed with 3 or 4 times its weight of potassium nitrate, and the mixture moistened with sulphuric acid, no change is observed, but on subsequently adding sufficient of a solution of potassium or sodium hydrate to impart a strongly alkaline reaction, it assumes an evanescent brick-red color.

The aqueous solution of picrotoxin, to which a few drops of a dilute solution of potassium or sodium hydrate have been added, reduces an alkaline solution of cupric tartrate on warming; in this respect resembling a solution of grape-sugar and many other indifferent organic substances, although its reducing properties are inferior in extent. It also resembles a solution of grape-sugar in that its alkaline solution becomes decomposed on warming; the solution becoming at first yellow, and then brick-red.

Picrotoxin being a perfectly neutral principle, and devoid of nitrogen, its solution is not affected by solutions of the salts of platinum, gold, and mercury, or by potassio-mercuric iodide, tannic acid, or other alkaloidal reagents, which thus distinguishes it from and indicates the absence of alkaloids. It is absorbed by ether from its acidulated aqueous solution, and may thus be separated from alkaloids and other complex organic principles with which it may be associated, as described on page 106.

PILOCARPINÆ HYDROCHLORAS.

PILOCARPINUM HYDROCHLORICUM SEU MURIATICUM.

Hydrochlorate of Pilocarpine. Pilocarpine Hydrochlorate.

Ger. Salzsaures Pilocarpin; Fr. Chlorhydrate de pilocarpine;
Sp. Hidroclorato de pilocarpina.

$C_{11}H_{16}N_2O_2.HCl$; 244.4.

Small, colorless, deliquescent crystals, without odor, but possessing a slightly bitter taste. When heated on platinum-foil they first melt, and at a strong heat are finally completely dissipated.

Pilocarpine hydrochlorate is readily soluble in water and in alcohol, but almost insoluble in ether, chloroform, benzol, and carbon bisulphide. The aqueous solution is neutral in its action upon litmus, and possesses a slightly bitter taste; when slightly acidulated it is not precipitated by ammonia-water, and solution of sodium hydrate produces only in a concentrated solution of the salt a slight turbidity; with solution of argentic nitrate the aqueous solution yields a white precipitate, which is insoluble in nitric acid, but soluble in ammonia water. With concentrated sulphuric acid the crystals of the salt yield a yellow, with nitric acid, spec. grav. 1.4, a faintly greenish-violet, and with sulphuric acid and potassium bichromate an emerald-green color.

An aqueous solution of pilocarpine, or any of its salts, when applied to the eye, strongly contracts the pupil.

PIPERINA.

Piperine.

Ger. Piperin; Fr. Piperine; Sp. Piperina.

$C_{17}H_{19}NO_3$; 285.

Colorless, or slightly yellowish, shining, four-sided prisms, belonging to the rhombic system, and permanent in the air; they are neutral in their action upon litmus, odorless, and almost tasteless when first placed on the tongue, but by prolonged contact produce a sharp, biting sensation. When heated to about 128° C. (262° F.), they melt to a clear, yellowish liquid, which, on cooling, congeals to a resinous mass; at a higher temperature they are decomposed, and, when strongly heated on platinum-foil, they take fire, and are finally completely dissipated.

Piperine is almost insoluble in either cold or hot water; it is soluble in 30 parts of alcohol at 15° C. (59° F.), in 1 part of boiling alcohol, and slightly soluble in ether, chloroform, benzol, and the volatile oils.

Concentrated sulphuric acid dissolves piperine with a dark blood-red color, which disappears on dilution with water. When treated with cold concentrated nitric acid it assumes a greenish-yellow color, which rapidly changes to orange and red, and gradually dissolves with a reddish color; on adding to this solution an excess of solution of potassium hydrate, the color is at first pale yellow, but, on boiling, it deepens to blood-red, while at the same time vapors of an alkaline reaction and of a peculiar odor (piperidine) are given off. On heating with soda-lime, or by prolonged boiling with an alcoholic solution of potassium hydrate, piperin is converted, by the absorption of a molecule of water, into *piperidine*, $C_5H_{11}N$, and crystallizable *piperic acid*, $C_{12}H_{10}O_4$:

$$C_{17}H_{19}NO_3 + H_2O = C_5H_{11}N + C_{12}H_{10}O_4.$$

Piperidine is a clear colorless alkaloid, having the odor of pepper and ammonia, and possessing strongly basic properties; it boils at 106° C. (222.8° F.), is soluble in all proportions in water and alcohol, and combines with acids to form well crystallizable salts.

Piperine is a very feeble base, being almost insoluble in the dilute mineral acids, and not combining with them, but forms well crystallizable double salts with the chlorides of platinum, mercury, and cadmium.

PLUMBI ACETAS.

PLUMBUM ACETICUM.

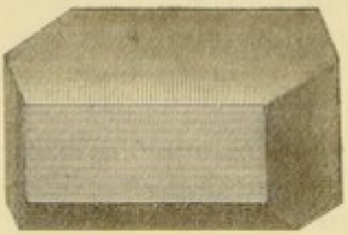
Acetate of Lead. Sugar of Lead. Plumbic Acetate.

Ger. Essigsaures Bleioxyd, Bleizucker; Fr. Acétate de plomb; Sp. Acetato de plomo.

$$Pb(C_2H_3O_2)_2+3H_2O; \quad 378.5.$$

Colorless, transparent, brilliant, monoclinic prisms or plates (Fig. 142), or, as generally met with, heavy, compact crystalline masses, somewhat resembling loaf-sugar, having an acetous odor and a sweet, astringent, afterwards metallic taste; they contain three molecules (14.21 per cent.) of water of crystallization, and effloresce slowly and absorb carbonic acid when exposed to the air; they become black when in contact with gaseous or dissolved hydrogen sulphide. When heated to 40° C. (104° F.) plumbic acetate loses its water of crystallization quickly and completely; it melts at 75° C. (167° F.) in its water of crystallization, with the loss of water and acetic acid, and is further decomposed at a higher temperature,

FIG. 142.



leaving a black residue, which is reduced, at a red heat, to plumbic oxide or to metallic lead.

Plumbic acetate is soluble in 1.8 parts of water and 8 parts of alcohol at 15° C. (59° F.), in 0.5 part of boiling water and 1 part of boiling alcohol, but insoluble in ether and in chloroform; its solution in water has generally a slightly turbid appearance from traces of plumbic carbonate, which, however, disappears upon the addition of acetic acid; the aqueous solution has a feeble acid reaction, forms white precipitates with the alkaline hydrates (soluble in excess of potassium and sodium hydrates), with the alkaline carbonates, and with sulphates and chlorides, a yellow one with iodides, and a black one with hydrogen sulphide and with sulphides. When completely precipitated by sodium chloride, the colorless filtrate will assume a deep-red tint with a few drops of solution of ferric chloride.

Examination:

Salts of the Alkalies, Alkaline-Earths, and *Zinc.*—An aqueous solution of the salt is acidulated with hydrochloric acid, filtered, and the lead completely precipitated by saturation with hydrogen sulphide. The filtrate, on evaporation, should leave no residue. If a residue is obtained, it may be dissolved in water, and a portion of the solution tested with sodium carbonate, when a white precipitate will indicate the presence of salts of *barium, calcium, magnesium,* or *zinc,* which may be distinguished by the appropriate tests; if the dissolved residue gives no precipitate with sodium carbonate, *potassium* or *sodium salts* will be indicated.

Copper may be detected by precipitating a solution of the salt with dilute sulphuric acid, and testing the filtrate with potassium ferrocyanide, or, by subsequent supersaturation with ammonia-water, a reddish-brown precipitate in the first instance, and a blue coloration of the liquid in the latter, will reveal the presence of copper.

PLUMBI CARBONAS.

PLUMBI SUBCARBONAS. PLUMBUM CARBONICUM. CERUSSA.

Carbonate or Subcarbonate of Lead. White Lead. Basic Plumbic Carbonate.

Ger. Basisch kohlensaures Bleioxyd, Bleiweiss; Fr. Carbonate de plomb;
Sp. Carbonato de plomo.

$$(PbCO_3)_2 + Pb(OH)_2;\ 773.5.$$

A heavy, white, opaque, and perfectly amorphous powder, or friable lumps, which are blackened by hydrogen sulphide. Heated upon charcoal before the blow-pipe, plumbic carbonate becomes yellow, fuses, and is finally reduced to soft, malleable metallic globules. It is insoluble in pure water, but somewhat soluble in water containing much carbonic acid or alkaline bicarbonates; it is wholly dissolved, with effervescence, by diluted acetic and nitric acids, affording colorless solutions, of a sweet, astringent taste; these solutions yield white precipitates with dilute sulphuric and hydrochloric acids, and with soluble sulphates and chlorides; they also give a white precipitate with solutions of potassium or sodium hydrate, soluble in an excess of the precipitant, a yellow one with potassium iodide, and a black one with hydrogen sulphide.

Examination:

Admixtures of *barium*, *calcium*, and *plumbic sulphates*, remain behind, upon solution of the white lead in dilute nitric acid. Their quantity may be ascertained by dissolving 100 parts of the sample in a sufficient quantity of warm diluted nitric acid, and collecting and washing the insoluble residue upon a tared filter; when completely dry, the weight indicates the percentage of such admixtures.

If the nature of the admixture has to be ascertained, the residue is intimately mixed with about three times its weight of anhydrous sodium carbonate, and strongly heated in a porcelain crucible. After being allowed to cool, the fused mass is lixiviated with water, filtered, and the filtrate supersaturated with nitric acid and tested with barium chloride, when a white precipitate will reveal the presence of *sulphate*. The residue, upon the filter, may then be dissolved in acetic acid, and tested with hydrogen sulphide for *lead*, when, after filtration, if necessary, the filtrate may be tested with potassium chromate for *barium*, and with ammonium oxalate for *calcium*.

Admixtures of *calcium carbonate* or *phosphate*, *barium carbonate*, and *oxide of zinc*, are also soluble in nitric acid. In order to detect and to distinguish them, the nitric-acid solution of the sample is freely diluted with water, and is subsequently saturated and completely precipitated with hydrogen sulphide; it is then filtered, and warmed, to expel the excess of gas, and a small portion of the solution is supersaturated with sodium carbonate; an ensuing white precipitate will confirm the presence of the above admixtures; in order to ascertain their nature, the remainder of the solution is nearly neutralized with a few drops of solution of potassium hydrate and then tested, in separate portions, with solution of calcium sulphate for *barium*, with oxalic acid, after the previous addition of a little sodium acetate, for *calcium*, and by the addition first of sodium acetate and subsequently of ammonium sulphide for *zinc*.

PLUMBI IODIDUM.

PLUMBUM IODATUM.

Iodide of Lead. Plumbic Iodide.

Ger. Jodblei; Fr. Iodure de plomb; Sp. Ioduro de plomo.

PbI_2; 459.7.

A bright-yellow, heavy, inodorous powder, when obtained by precipitation; or shining, golden-yellow, six-sided laminæ or prisms of the hexagonal system, when allowed to slowly crystallize from its solutions. Its specific gravity is 6.1. When heated in a dry test-tube, plumbic iodide becomes red, and fuses to a thick reddish-brown liquid, which congeals, on cooling, to a yellow crystalline mass; at a stronger heat, it is decomposed, with the evolution of violet vapors; and, when heated with exsiccated sodium carbonate, on charcoal, before the blow-pipe, it is entirely reduced to metallic globules.

Plumbic iodide is soluble in 2270 parts of water at 14° C. (57.2° F.), in 294 parts of boiling water, and also, to a slight extent, in alcohol; a hot saturated aqueous solution, on cooling, deposits the salt in brilliant yellow scales; it is readily soluble in acetic acid, in solution of potassium or sodium hydrate, in concentrated solutions of the alkaline or earthy iodides, in a warm solution of ammonium chloride, and in solution of sodium hyposulphite (thiosulphate), from all of which solutions hydrogen sulphide precipitates black plumbic sulphide.

When shaken with chlorine-water, plumbic iodide suffers partial decomposition, and yields a filtrate from which chloroform or carbon bisulphide will extract iodine, with a red color. When boiled with solutions of alkaline carbonates, it is decomposed, with the formation of an alkaline iodide and plumbic carbonate. When boiled with granular or powdered zinc and water, less readily with iron, plumbic iodide is likewise decomposed, forming soluble zinc or ferrous iodide and metallic lead.

Examination:

Plumbic chromate, which, in its physical characters, bears some resemblance to plumbic iodide, may readily be distinguished from the latter by triturating 1 part of the salt with 2 parts of ammonium chloride, in a porcelain mortar, and subsequently adding 2 parts of water, when a complete and colorless solution should be formed. If the solution be afterwards diluted with water, and the lead completely precipitated by hydrogen sulphide, the filtrate, on evaporation to dryness and subsequent ignition, should leave no residue, thus confirming the absence of other fixed impurities.

PLUMBI NITRAS.

PLUMBUM NITRICUM.

Nitrate of Lead. Plumbic Nitrate.

Ger. Salpetersaures Bleioxyd; Fr. Azotate de plomb; Sp. Nitrato de plomo.

$Pb(NO_3)_2$; 330.5.

Colorless, transparent or opaque, anhydrous, octahedral crystals, permanent in the air. Heated in a dry test-tube, the crystals decrepitate, emit yellow nitrous vapors, and leave a residue of plumbic monoxide. When thrown on red-hot charcoal, the salt detonates with brilliant sparks, and deflagrates when triturated with suiphur.

Plumbic nitrate is soluble in 2 parts of water at 15° C. (59° F.), and in 0.8 part of boiling water; it is almost insoluble in alcohol. Its aqueous solution has a sweet, astringent, afterwards metallic taste, and an acid reaction; it gives a white precipitate with sulphuric or hydrochloric acid, and with solutions of sulphates or chlorides, a yellow one with potassium iodide, and a black one with hydrogen sulphide. When triturated with concentrated sulphuric acid, and heated, the salt evolves red nitrous fumes.

Examination:

Salts of the Alkalies and *Alkaline Earths.*—An aqueous solution of the salt is acidulated with hydrochloric acid, filtered, and the lead completely precipitated by saturation with hydrogen sulphide. The filtrate, on evaporation, should leave no residue. If a residue is obtained, it may be dissolved in water, and a portion of the solution tested with sodium carbonate; an ensuing white precipitate would indicate the presence of *barium*, which may be confirmed by other tests. If the dissolved residue gives no precipitate with sodium carbonate, the presence of *potassium* or *sodium salts* will be indicated.

Copper may be detected, in the aqueous solution of the salt, by completely precipitating it with dilute sulphuric acid, and testing the filtrate with potassium ferrocyanide, or, by subsequent supersaturation with ammonia-water; a reddish-brown precipitate in the first instance, and a blue coloration of the liquid in the latter, will reveal the presence of copper.

PLUMBI OXIDUM.

PLUMBUM OXYDATUM FUSCUM. LITHARGYRUM.

Oxide of Lead. Litharge. Plumbic Monoxide.

Ger. Bleioxyd, Bleiglätte; Fr. Litharge; Sp. Litargirio.

PbO; 222.5.

A heavy, yellowish or reddish-yellow powder, or small, shining, rhombic scales of the same color, devoid of odor and taste. Its specific gravity is 9.36. It fuses at a red heat, assuming thereby a brownish-red tint, and solidifies on cooling to a crystalline mass; when heated on charcoal, before the blow-pipe, it is reduced to the metallic state.

Plumbic monoxide is but sparingly soluble in water, imparting thereto a feeble alkaline reaction; it is soluble in warm solutions of the fixed alkaline hydrates, and in diluted nitric and acetic acids, without effervescence or residue; it slowly absorbs carbonic acid from the atmosphere, and contains the more carbonate the longer it has been exposed to the air; from this cause, when very old, it becomes more or less effervescent with acids. The nitric-acid solution of plumbic monoxide yields white precipitates with dilute sulphuric and hydrochloric acids, with solutions of sulphates and chlorides, and with the alkaline hydrates, which latter, ammonia-water excepted, re-dissolve the precipitate, when added in excess; it gives a black precipitate with hydrogen sulphide, and, when neutral, a yellow one with potassium iodide.

Examination:

Plumbic carbonate and *red oxide* are detected, when a small quantity of the litharge is triturated with a little water, and the mixture is added, drop by drop, to concentrated nitric acid, in a test-tube; carbonate is recognized by effervescence; red oxide by a brown residue, insoluble in an excess of acid, with gentle warming, but soluble upon the addition of a little oxalic acid or sugar; if this residue, however, does not dissolve, an adulteration with powdered silicates, crude ferric oxide, etc., is indicated.

Silicates are also indicated by a white turbidity or a flocculent precipitate, occurring in the solution after the addition of the oxalic acid, in the preceding test.

Zinc oxide and *alkaline earths* may be detected by saturating the dilute nitric acid solution with hydrogen sulphide, so as to completely precipitate the lead, and filtering; the filtrate, on evaporation, should leave no residue. If a residue is obtained, it may be dissolved in a little water, and a portion of the solution tested with sodium carbonate; an ensuing white precipitate would indicate zinc, barium, or calcium oxides. In order to distinguish these, the remainder of the solution is tested, in separate portions, with ammonium sulphide for *zinc*, with solution of calcium sulphate for *barium*, and with ammonium oxalate for *calcium;* an ensuing white precipitate in either instance will indicate the respective impurities.

Copper may be detected by a blue coloration of the liquid, when the dilute nitric acid solution of the oxide is precipitated by sulphuric acid, and subsequently supersaturated with ammonia-water.

Metallic lead may be detected by its remaining undissolved when the oxide is boiled for a short time with acetic acid, or when digested with a warm solution of plumbic acetate or potassium hydrate. It may likewise be detected by digesting a small portion of the litharge with a solution of plumbic nitrate, at a gentle heat, and with occasional agitation, for about half an hour; a few drops of the decanted liquid are then diluted with a little water, a little mucilage of starch, and a few drops of dilute sulphuric acid and solution of potassium iodide added. If the sample contains even traces of metallic lead, this gives rise to the formation of plumbic nitrite, which will decompose the potassium iodide, with the liberation of iodine, and at once produce a blue color with the starch.

PLUMBI OXIDUM RUBRUM.

PLUMBUM OXYDATUM RUBRUM. MINIUM.

Red Oxide of Lead. Minium. Triplumbic Tetroxide. Plumbic Plumbate.

Ger. Rothes Bleioxyd, Mennige; Fr. Oxyde rouge de plomb;
Sp. Oxido rojo de plomo.

Pb_3O_4; 683.5.

A heavy, orange-red, crystalline powder, which becomes dark when heated, but regains its original color on cooling; at a red heat it loses oxygen and is converted into the monoxide. Heated upon charcoal, before the blow-pipe, it fuses, and is reduced to metallic globules. Its specific gravity varies from 8.6 to 9.1.

Red oxide of lead is almost completely soluble in twenty times its weight of warm glacial acetic acid, forming a colorless solution, which is not precipitated by the addition of a mixture of ether and alcohol; when treated with warm dilute nitric or acetic acid it only partially dissolves, leaving a brown residue of peroxide, which is soluble, however, upon the addition of a little oxalic acid or sugar. A slight remaining turbidity, of a whitish appearance, is due to silicic acid, with which red oxide of lead is generally more or less contaminated; any insoluble red or brown residue, however, would indicate impurities.

The impurities and admixtures which red oxide of lead is liable to contain, and the methods of detecting them, are the same as mentioned and described under litharge, on pages 457–458.

POTASSA SULPHURATA.

POTASSII SULPHURETUM. POTASSII SULPHIDUM. POTASSIUM SEU KALIUM SULFURATUM. HEPAR SULFURIS.

Sulphurated Potassa. Sulphuret of Potassium. Potassium Sulphide.

Ger. Schwefelleber ; Fr. Sulfure de potasse ; Sp. Súlfuro de potasio.

Solid, fused fragments, of a yellowish-brown color, when freshly prepared or recently broken ; on exposure to the air they assume a greenish appearance, and finally become of a dirty white, in consequence of gradual decomposition by the action of atmospheric moisture and oxygen, the sulphides being successively converted, with the evolution of hydrogen sulphide, into hyposulphite (thiosulphate), sulphite, and ultimately sulphate. When moistened with acids, sulphurated potassa evolves hydrogen sulphide.

Sulphurated potassa, which is usually a variable mixture of higher potassium sulphides with hyposulphite (thiosulphate), sulphite, and sulphate, and with undecomposed carbonate, is soluble in about 2 parts of water at 15° C. (59° F.), and is also soluble in alcohol, leaving behind in the latter case the oxygen salts; these solutions have an orange-yellow color, a nauseous, alkaline, bitter taste, and the odor of hydrogen sulphide, which is abundantly evolved, with the separation of sulphur, upon the addition of acids; they precipitate metallic sulphides from the solutions of most of the metallic salts. If a solution of 1 part of the salt in 20 parts of water be boiled with an excess of acetic acid until hydrogen sulphide ceases to be evolved, the solution filtered, and to the cold filtrate an excess of tartaric acid added, a white, crystalline precipitate will be produced.

The value of sulphurated potassa, when free from an undue proportion of carbonate, may be approximately estimated by the amount of crystallized cupric sulphate which is required to decompose it :

$$CuSO_4.5H_2O + K_2S_3 = CuS + S_2 + K_2SO_4 + 5H_2O.$$

In consideration of the amount of admissible foreign salts, the preparation should respond to the following test : 10 grams of the sulphurated potassa are triturated with 12.69 grams of crystallized cupric sulphate and 60 grams of water, and subsequently filtered;

the filtrate should be colorless, and afford no coloration or turbidity upon saturation with hydrogen sulphide (indicating the presence of at least 56 per cent. of true potassium sulphide).

POTASSII ACETAS.

POTASSIUM SEU KALIUM ACETICUM.

Acetate of Potassium. Potassium Acetate.

Ger. Essigsaures Kalium ; Fr. Acétate de potasse ; Sp. Acetato de potasa.

$KC_2H_3O_2$; 98.

A snow-white, very deliquescent salt, of a foliaceous or fibrous satiny appearance, or a white granular powder, unctuous to the touch, and of a warm, pungent, saline taste, and possessing a neutral or faintly alkaline reaction; it fuses at 292° C. (557.6° F.) without change, solidifying upon cooling to a crystalline mass, but is decomposed at a higher temperature with the evolution of empyreumatic, inflammable vapors, leaving behind a mixture of carbon and potassium carbonate.

Potassium acetate is soluble in 0.4 part of water, in 2.5 parts of alcohol, and in 3 parts of glycerin at 15° C. (59° F.); its dilute aqueous solution assumes a deep red color with one or two drops of solution of ferric chloride, and yields a white granular precipitate with a concentrated solution of sodium bitartrate or of tartaric acid. Potassium acetate disengages the vapor of acetic acid with concentrated sulphuric acid, and the vapor of acetic ether when heated with a mixture consisting of equal parts of alcohol and sulphuric acid.

Examination:

Metals are detected in the aqueous solution, previously acidulated with hydrochloric acid, by a dark coloration or precipitate with hydrogen sulphide, or, after neutralization with ammonia-water, by the addition of ammonium sulphide; if a precipitate is produced by these reagents, a portion of the acidulated solution of the salt may then be tested with potassium ferrocyanide; *copper* will be indicated by a reddish-brown coloration, *iron* by a blue one.

Tartrates, *sulphates*, and *chlorides* are indicated by the occurrence of a turbidity when a concentrated aqueous solution of the salt is dropped into strong or absolute alcohol; the latter two are also recognized in the diluted solution, acidulated with nitric acid, by white precipitates when tested in separate portions with argentic nitrate and barium nitrate respectively.

Carbonates, *silica*, and *alkaline earths* may be detected by dissolving a portion of the salt in water acidulated with hydrochloric acid; effervescence will indicate carbonates; upon evaporating the resulting solution to dryness, and treating the residue with water, the silica will remain undissolved; and the solution, after filtration, and the addition of sodium carbonate in slight excess, will yield a white precipitate, if alkaline earths be present.

Organic impurities will be indicated by a dark coloration when a little of the salt is strewn upon colorless concentrated sulphuric acid.

Estimation:

About 5 grams of the salt are accurately weighed, and ignited, at a strong heat, in a porcelain crucible, until inflammable vapors cease to be evolved; the residue is then dissolved in water, and the solution, contained in a beaker, after the addition of a few drops of a solution of litmus, is titrated with a standard solution of oxalic or sulphuric acid (page 82) until, with the application of a gentle heat to effect the complete removal of the disengaged carbonic acid gas, a slight excess of acid has been employed, and the liquid assumes a bright cherry-red color. The excess of acid is then inversely titrated with a standard solution of potassium or sodium hydrate (page 87) until a decided blue coloration of the liquid is just produced, when the number of cubic centimeters of alkali solution, subtracted from that of the acid first employed, will give the amount of the latter required for the exact neutralization of the salt. One cubic centimeter of the normal acid solution corresponding to 0.069 gram of potassium carbonate, or, as its equivalent, 0.098 gram of potassium acetate, the latter decimal, multiplied by the number of cubic centimeters of the normal acid solution employed for neutralization, will represent the amount of pure potassium acetate in the quantity under estimation.

By the employment of 4.9 grams of potassium acetate, and a strictly normal solution of oxalic or sulphuric acid, the number of cubic centimeters of acid required for the exact neutralization of the salt, after the above treatment, when multiplied by 2, will represent without further calculation the percentage purity of the salt under examination.

The United States Pharmacopœia requires that if 4.9 grams of potassium acetate are ignited until gases cease to be evolved, the alkaline residue should require, for complete neutralization, not less than 49 cubic centimeters of the volumetric solution of oxalic acid (corresponding to at least 98 per cent. of absolute potassium acetate).

POTASSII BICARBONAS.

POTASSIUM SEU KALIUM BICARBONICUM

Bicarbonate of Potassium. Potassium Bicarbonate. Hydrogen Potassium Carbonate.

Ger. Zweifach kohlensaures Kalium; Fr. Bicarbonate de potasse; Sp. Bicarbonato de potasa.

$KHCO_3$; 100.

Transparent, colorless, prismatic crystals, belonging to the monoclinic system, and having the specific gravity 2.153; they are permanent in dry air, odorless, of a saline and slightly alkaline taste, and a feebly alkaline reaction; when exposed to a red heat, they lose, in consequence of the elimination of water and carbonic acid gas, 31 per cent. of their weight, and are converted into the normal or neutral carbonate: $2KHCO_3 = K_2CO_3 + H_2O + CO_2$.

Potassium bicarbonate is soluble in 3.2 parts of water at 15° C. (59° F.), forming a slightly alkaline solution which effervesces with acids and evolves carbonic acid gas when heated to boiling; it gives a white granular precipitate with excess of tartaric acid, but no precipitate with magnesium sulphate unless when heated. It is almost insoluble in alcohol.

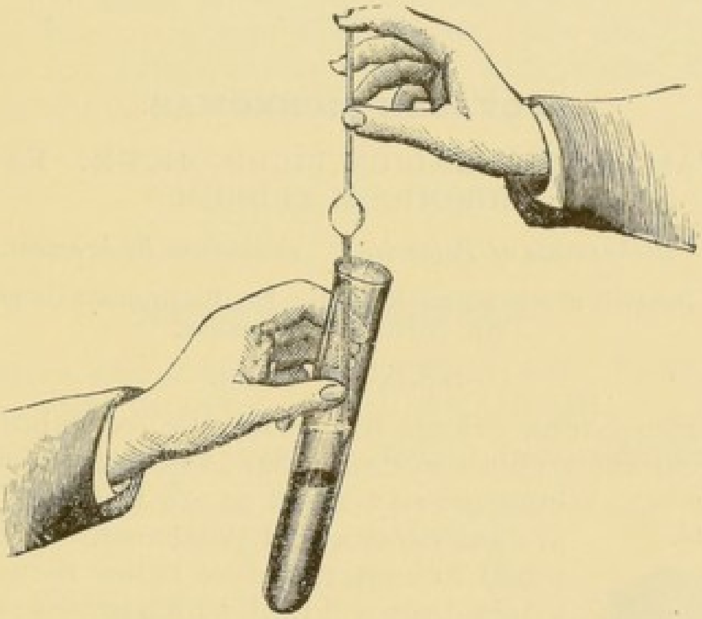
Examination:

Normal potassium or sodium carbonates will be indicated by a strongly alkaline reaction of the salt to test-paper, and may be detected in the cold aqueous solution by testing it, in separate portions, with a solution of magnesium sulphate and with mercuric chloride; a white precipitate with the first-named reagent, soluble upon the addition of ammonium chloride, and a brick-red one with the second, would indicate neutral carbonate. They may also be detected by carefully mixing, without agitation, equal volumes of a solution of 1 part of potassium bicarbonate in 200 parts of water with a solution of 1.22 parts of crystallized barium chloride in 200 parts of water; the immediate formation of a white precipitate will likewise reveal the presence of neutral carbonate.

Other Impurities.—The aqueous solution is slightly supersaturated with diluted nitric acid, evaporated to dryness, and the dried mass re-dissolved in water; a white insoluble residue would indicate *silicates;* the solution, if necessary, is filtered, and tested in separate portions with argentic nitrate for *chloride*, and with barium nitrate for *sulphate;* a white turbidity with argentic nitrate, gradually turning dark, would indicate *potassium hyposulphite* (thiosulphate); in this case, as a confirmatory test, a small portion of the potassium bicarbonate may be dissolved in about five times its weight of water, the solution slightly supersaturated with acetic acid, and then a few drops of mucilage of starch, and subsequently of solution of iodinized potassium iodide are added, drop by drop; the first drops of the latter reagent should at once produce the blue coloration which will not take place immediately if potassium hyposulphite be present in the salt.

Nitrates may be detected by dissolving a portion of the salt in cold concentrated sulphuric acid, and, after effervescence has ceased, carefully adding to the solution a concentrated solution of ferrous sulphate, so as to form two layers (Fig. 143); a dark coloration at the surface of contact of the two liquids will reveal the presence of nitrates.

FIG. 143.



Metals are detected by saturating a solution of the salt, previously acidulated with hydrochloric acid, with hydrogen sulphide, and, after the separation of any precipitate which may be thus formed, by the subsequent addition of ammonia-water and ammonium sulphide; a dark coloration or precipitate in either instance would indicate the presence of metallic impurities, which may be further examined as to their character by the methods of systematic analysis, as described on pages 51 to 61.

Estimation:

One hundred parts of potassium bicarbonate require for exact neutralization 70 parts of citric, or 75 parts of tartaric, acid.

The quantitative estimation of the salt may, however, be more conveniently accomplished volumetrically, by dissolving 5 grams of the salt in a small quantity of water, and titrating the solution, contained in a beaker, after the addition of a few drops of litmus solution, with a standard solution of oxalic or sulphuric acid (page 82). The liquid, during the addition of the acid, should be gently warmed, in order to completely expel the disengaged carbonic acid gas, and a slight excess of acid employed, which will be evident by the bright cherry-red tint of the liquid; the excess of acid being subsequently inversely titrated by means of a standard alkali solution (page 87). The number of cubic centimeters of normal acid which are thus required for the exact neutralization of 5 grams of the salt, when multiplied by 2, will represent the percentage purity of the salt under examination: One cubic centimeter of the normal acid corresponding to 0.1 gram of pure crystallized potassium bicarbonate.

POTASSII BICHROMAS.

POTASSIUM SEU KALIUM BICHROMICUM. KALIUM CHROMICUM RUBRUM.

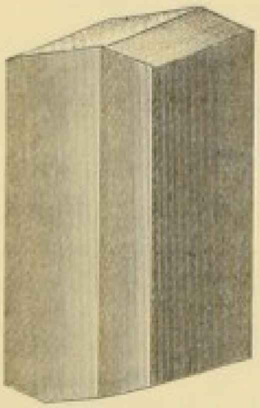
Bichromate of Potassium. Potassium Bichromate.

Ger. Doppelt chromsaures Kalium; Fr. Bichromate de potasse; Sp. Bicromato de potasa.

$K_2Cr_2O_7$; 294.8.

Large, transparent, orange-red, prismatic, or tabular crystals, belonging to the triclinic system (Fig. 144), and having the specific gravity 2.692 at 4° C. (39.2° F.). They are anhydrous, and permanent in the air; exposed to heat, they fuse below redness, forming a dark-brown liquid, which solidifies on cooling to a crystalline mass, and are decomposed at a red heat with the evolution of oxygen, leaving a residue consisting of green chromic oxide and yellow potassium chromate, which may be separated by the ready solubility of the latter in water.

FIG. 144.



Potassium bichromate is soluble in 10 parts of water at 15° C. (59° F.), and in 1.5 parts of boiling water, yielding an intensely orange-yellow solution, with a cooling, bitter, metallic taste, and an acid reaction; it is insoluble in alcohol. The aqueous solution becomes lemon-yellow with the alkaline hydrates and carbonates, and green or almost colorless, with the formation of a brown precipitate, when heated with reducing agents; it forms insoluble, colored bichromates and chromates with the solutions of most metallic salts. When the powdered salt is heated with hydrochloric acid, vapors of chlorine are evolved, and when heated with concentrated hydrochloric or sulphuric acid and a little alcohol, a vehement reduction takes place, and the liquid acquires a deep green color. A concentrated solution of the salt gives a white, granular precipitate with a concentrated solution of sodium bitartrate.

Examination:

Sulphate may be detected by heating to boiling a mixture of the aqueous solution with an equal volume of concentrated hydrochloric acid and a few drops of alcohol; when subsequently diluted with water and tested with barium chloride, a white precipitate will ensue if sulphate be present.

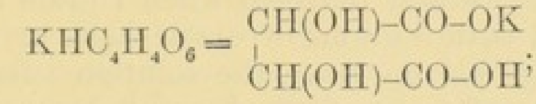
Chloride may be detected when the aqueous solution of the salt is mixed with about one-third of its volume of concentrated sulphuric acid, and when afterward a little alcohol is added; the mixture will become green, with spontaneous ebullition; it is then heated, and subsequently diluted with water, and tested with argentic nitrate for chloride.

POTASSII BITARTRAS.

POTASSIUM SEU KALIUM BITARTARICUM. TARTARUS DEPURATUS. CREMOR TARTARI.

Bitartrate of Potassium. Cream of Tartar. Potassium Bitartrate.

Ger. Saures weinsaures Kalium, Weinstein; Fr. Tartrate acide de potasse;
Sp. Bitartrato de potasa



$$KHC_4H_4O_6 = \begin{matrix} CH(OH)\text{-}CO\text{-}OK \\ | \\ CH(OH)\text{-}CO\text{-}OH \end{matrix}; \quad 188.$$

White, semi-transparent, hard, prismatic crystals, belonging to the rhombic system, or aggregated groups of crystals, or a white, somewhat gritty powder, permanent in the air, and having a spec. grav. of 1.957, a sour taste, and an acid reaction. When exposed to heat, in a porcelain crucible, potassium bitartrate is decomposed, with the evolution of empyreumatic, inflammable vapors, leaving a black residue of carbon and pure potassium carbonate; this residue, when dissolved in a little water, gives a filtrate which effervesces with acids, and forms a white, granular precipitate with an excess of tartaric acid.

Potassium bitartrate is soluble in 210 parts of water at 15° C. (59° F.), and in 15 parts of boiling water, but is very sparingly soluble in alcohol, and insoluble in absolute alcohol and ether; it dissolves wholly and readily in mineral acids, as also in solutions of citric and oxalic acids, in dilute solutions of the alkaline hydrates and carbonates, of boracic acid, and of sodium biborate. If the aqueous solution of the salt be exactly neutralized with a solution of potassium hydrate, and a few drops of solution of argentic nitrate added, a white precipitate is produced, which becomes black on boiling.

Examination:

Insoluble admixtures (such as *terra alba* or white clay, and similar crude adulterants) are indicated by a residue left when small samples of the powder are dissolved separately in a warm, diluted solution of potassium hydrate, and in dilute hydrochloric acid.

Sulphates and *chlorides* are detected by agitating a small portion of the salt with about ten times its weight of warm water, and by testing portions of the clear liquid, when cool, and after the addition of a few drops of nitric acid, with barium nitrate for sulphates, and with argentic nitrate for chlorides.

Alum.—An adulteration of powdered cream of tartar with alum is at once indicated by a greater solubility of the salt in water, by its intumescence upon incineration, and by the incomplete solubility of the fused residue in water, as also by the odor of ammonia, and the production of white fumes from a glass rod, moistened with acetic acid, when the powder is heated with a solution of potassium hydrate, and by the formation of a white precipitate, when a few drops of this alkaline solution are allowed to fall into a dilute solution of ammonium chloride.

Metallic impurities may be detected in the solution of the salt in ammonia-water, by a dark coloration or precipitate upon the addition of ammonium sulphide.

Calcium salts may be best detected when 1 gram of the salt is repeatedly agitated with 5 grams of acetic acid, at the ordinary temperature, during half an hour, the solution subsequently diluted with 25 grams of water, filtered, and 8 drops of solution of ammonium oxalate are added; a white turbidity, occurring either at once or within half a minute, will indicate the presence of more than 0.3 per cent. of such impurities.

Estimation:

The quantitative estimation of potassium bitartrate may readily be accomplished by its conversion into carbonate, and the estimation of the latter by means of a normal acid.

4.70 grams of the salt are ignited in a porcelain crucible, at a red heat, until gases cease to be evolved, and the residue subsequently dissolved in water, and filtered; the solution, together with the washings from the filter, contained in a beaker, after the addition of a few drops of litmus solution, is then titrated with a standard solution of oxalic or sulphuric acid (page 82) until, with the application of a gentle heat to expel the disengaged carbonic acid gas, a slight excess of acid has been employed, and the liquid assumes a bright cherry-red tint; the excess of acid is then inversely titrated with a standard solution of potassium or sodium hydrate (page 87) until the liquid just assumes a permanent blue color. If the salt be perfectly pure, 25 cubic centimeters of the normal acid solution will be required for the exact neutralization of the quantity indicated, or, the percentage purity of the salt will be determined, when, for the neutralization of the above stated amount, the number of cubic centimeters of normal acid employed are multiplied by 4; one cubic centimeter of the normal acid solution corresponding to 0.069 gram of potassium carbonate, or, as its equivalent, 0.188 gram of potassium bitartrate.

POTASSII BROMIDUM.

POTASSIUM SEU KALIUM BROMATUM.

Bromide of Potassium. Potassium Bromide.

Ger. Bromkalium; Fr. Brômure de potassium; Sp. Bromuro de potasio.

KBr; 118.8.

Anhydrous, colorless, semi-transparent, cubical crystals, sometimes elongated into prisms, or flattened to plates, permanent in the air, and of a spec. grav. of 2.69 at 4° C. (39.2° F.); when exposed to heat, they decrepitate, and fuse at a little below a red heat, without decomposition. When a few grains are triturated and subsequently heated, in a dry tube, with a little potassium bisulphate, yellowish-red vapors of bromine are evolved.

Potassium bromide is soluble in 1.6 parts of water and in 200 parts of alcohol at 15° C. (59° F.), in 1 part of boiling water, and in 16 parts of boiling alcohol; its aqueous solution has a strong saline taste, is neutral in its action upon litmus, and, when dropped into a very dilute solution of argentic nitrate, causes a yellowish-white, curdy precipitate, which is insoluble in dilute nitric acid, but soluble in a large excess of ammonia-water (distinction, in the latter instance, from argentic iodide); when dropped into a very dilute solution of mercuric chloride, no reaction takes place (additional distinction from potassium iodide): it gives a white, granular precipitate with a saturated solution of sodium bitartrate.

Potassium bromide and its solution may also be distinguished from the iodide by adding to the solution a little mucilage of starch, and subsequently a few drops of chlorine-water; the solution of the bromide becomes light yellow; that of the iodide will at once assume a deep-blue color.

Examination:

Moisture which may be contained in the crystals, as well as in the granular form of the salt, is recognized, and may be determined, by the loss of weight when the salt is dried at 100° C. (212° F.).

Potassium carbonate is detected by a white turbidity occurring upon the addition of a little of the concentrated solution of the salt to lime-water, as also by a decided alkaline reaction, when a few fragments of the salt are placed upon moistened red litmus-paper.

Sulphates may be detected, in the aqueous solution, acidulated with a few drops of diluted nitric acid, by a white precipitate with barium nitrate.

Potassium bromate is detected by placing a little of the powdered salt upon a piece of white porcelain, and subsequently adding one drop of dilute sulphuric acid; a yellow coloration of the moistened surface of the salt, or the developed odor of bromine, will reveal the presence of bromate. The presence of the latter, in an aqueous solution of the salt, may also be detected by the liberation of bromine upon the addition of a few drops of dilute sulphuric acid, imparting a yellow color, which, upon subsequent agitation of the solution with a few drops of carbon bisulphide, will be absorbed by the latter.

Potassium and *sodium chlorides* are distinguished from potassium bromide, and may be recognized by adding a few drops of chlorine-water to the aqueous solution of the salt; if this is bromide, the mixture assumes at once a yellow color, which, however, will be completely abstracted from the aqueous solution by chloroform, ether, or carbon bisulphide, when agitated therewith. This reaction does not take place with potassium or sodium chloride.

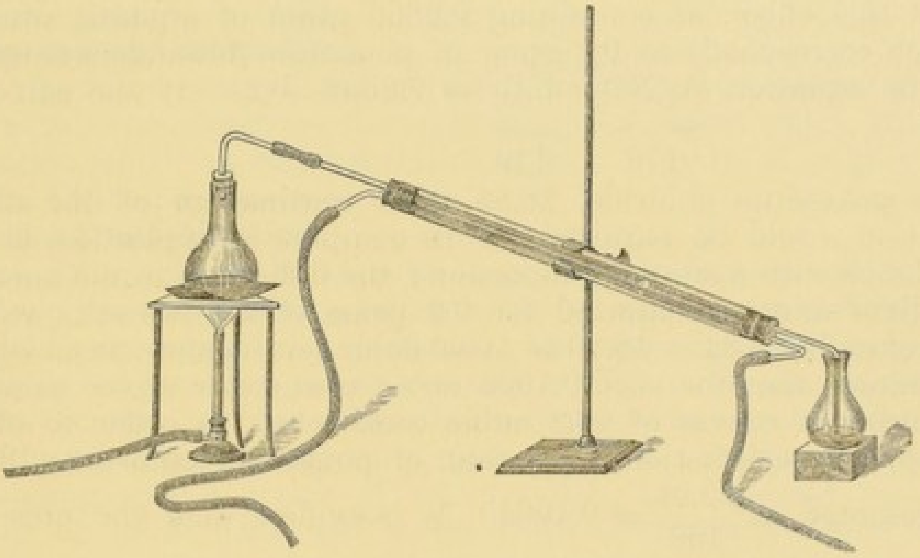
If an admixture of potassium chloride, or other salts, be suspected, the purity of the sample may be ascertained by preparing a solution of 1 gram of the dry, crystallized salt in about 10 times its weight of water, acidulated with a few drops of diluted nitric acid, and completely precipitating it with a solution of argentic nitrate; the precipitate is collected upon a moist, tared filter, is washed, dried, and, when completely dry, weighed. If the salt was pure potassium bromide, the obtained argentic bromide should weigh 1.58 grams; if it contained potassium or sodium chloride, the weight, provided the salt is free from other impurities, will be greater in proportion to the amount of those admixtures, since their molecular weights are lower; 1 gram of potassium chloride, for instance, would give 1.92 grams of argentic chloride.

The same test may also be used to indicate the purity of the bromide, by ascertaining the quantity of argentic nitrate required to precipitate completely a certain weight of potassium bromide, 1 gram of which requires 1.43 grams of argentic nitrate for precipitation.

The following additional methods for the detection of an admixture of chlorides may also be employed. A portion of the salt, dissolved in water, is completely precipitated by argentic nitrate, the washed and still moist precipitate digested for some time with a cold, saturated solution of ammonium carbonate, subsequently filtered, and the filtrate supersaturated with nitric acid; the production of a white, curdy precipitate will reveal the presence of chloride.

The presence of much smaller amounts of chloride, and less than that admitted in the officinal salt, may be detected as follows: 5 grams of the powdered and well-dried salt, together with 6 grams of pure powdered potassium bichromate, are introduced into a small flask, and 15 grams of concentrated sulphuric acid are added. The mixture is then submitted to distillation at a gentle heat, and the distillate collected in a receiver or flask containing a small quantity of ammonia-water (Fig. 145). Bromine distils over, and is dissolved by the ammonia-water without color; but, if chlorides are present, chlorochromic anhydride, CrO_2Cl_2, is produced, distils over, and forms ammonium chromate, which imparts a yellowish color to the distillate; by subsequently heating the latter with a little hydrochloric acid and alcohol, the bright green color of the chromic salt will be produced.

FIG. 145.



Nitrates may readily be detected, if the salt be free from bromate, by an ensuing intense yellow coloration, when a solution of a few fragments of the powdered salt in twenty times their weight of dilute sulphuric acid is heated to boiling. In the presence of bromate, nitrates will be indicated by the development of the odor of ammonia, when the salt, together with an equal weight of iron filings, zinc filings, and solid sodium or potassium hydrate, is gently heated, in a test-tube, with an equal volume of water. If, however, ammonium salts be originally present as an admixture, the ammonia must first be completely expelled, by heating a portion of the salt with a strong solution of potassium hydrate, after which, the iron and zinc filings may be added, and the test subsequently performed for nitrates, as above described.

Estimation:

The estimation of potassium bromide, or the amount of chloride which may be contained therein, is most readily accomplished volumetrically. Two grams of the potassium bromide, previously reduced to powder and carefully dried, are dissolved in water to the measure of 100 cubic centimeters. 10 cubic centimeters of this solution, corresponding to 0.2 gram of potassium bromide, are then brought into a beaker, diluted with about 50 cubic centimeters of water, and, after the addition of a few drops of a solution of potassium chromate, the solution is titrated with a decinormal solution of argentic nitrate (page 98) until a permanent reddish-brown coloration is produced. If the salt is pure potassium bromide, 16.8 cubic centimeters of the silver solution will be required to produce this effect, as containing 0.2856 gram of argentic nitrate, which corresponds to 0.2 gram of potassium bromide, according to the equation $\underbrace{AgNO_3}_{170} : \underbrace{KBr}_{119} = 0.2856 : 0.2$. If the salt was pure potassium chloride, 26.84 cubic centimeters of the silver solution would be required for its complete precipitation, in accordance with a similar proportion; the difference in the amount of silver solution, required for 0.2 gram of the two salts, would therefore be $26.84 - 16.80 = 10.04$ cubic centimeters; from which it follows, that for each 0.1004 cubic centimeter silver solution required in excess of 16.8 cubic centimeters, in order to effect complete precipitation, 1 per cent. of potassium chloride will be represented, as $\frac{10.04}{100} = 0.1004$. It is evident, that the presence of potassium iodide, or other alkaline chlorides or bromides, would influence the result in proportion to the quantity of the admixture.

The United States Pharmacopœia directs that if 3 grams of the well-dried salt be dissolved in distilled water to make 100 cubic centimeters, and 10 cubic centimeters of this solution be treated with a few drops of test-solution of potassium bichromate, and then volumetric solution of argentic nitrate be added, not more than 25.7 cubic centimeters of the latter should be consumed before the red color ceases to disappear on stirring (indicating the absence of more than 3 per cent. of chloride).

POTASSII CARBONAS CRUDUS.

POTASSIUM SEU KALIUM CARBONICUM CRUDUM.

Crude Carbonate of Potassium. Pearlash.

Ger. Rohes kohlensaures Kalium, Pottasche; Fr. Potasse impure;
Sp. Potasa ordinaria.

White, bluish-white, or reddish-white masses (the color being dependent upon the presence of small amounts of potassium manganate or ferric oxide), or a coarse granular powder intermingled with smaller lumps, somewhat deliquescent, and of a burning, alkaline taste and strong alkaline reaction. Water extracts from pearlash the potassium carbonate and hydrate, and the soluble impurities, the greater part of the impurities remaining behind (sulphates, chlorides, silicates, phosphates, and carbonates of calcium and aluminium); the filtered solution effervesces with acids, and yields a white, granular precipitate with an excess of tartaric acid.

The examination of pearlash consists in the determination of the quantity of soluble potassium carbonate and hydrate, or the available potassium oxide.

Approximate Estimation:

One hundred parts of commercial pearlash, when successively exhausted with about ten times its weight of warm water, afford a solution which should neutralize at least 58 parts of sulphuric acid of 1.843 spec. grav.

Volumetric Estimation:

The estimation of the amount of pure potassium carbonate in pearlash, when free from alkaline hydrates and sodium carbonate, is readily accomplished as follows. 34.5 grams of the pearlash are dissolved in water to the measure of 500 cubic centimeters. Of this solution, after the insoluble impurities have subsided and the liquid has become perfectly clear, 100 cubic centimeters (corresponding to 6.9 grams of the pearlash) are brought into a beaker or small flask, and a few drops of litmus solution are added. A standard solution of oxalic or sulphuric acid (page 82) is then allowed to flow into the liquid from a burette, until an excess of the acid has been employed, and the liquid, after being heated to boiling, in order to completely expel the liberated carbonic acid gas, assumes a cherry-red color. The excess of acid is then inversely titrated with a standard solution of potassium or sodium hydrate (page 87) until a permanent blue coloration of the liquid is produced. From the amount of acid required for the exact neutralization of the quantity of pearlash employed, the amount of pure potassium carbonate may be calculated: one cubic centimeter of the normal acid solution corresponding to 0.0692 gram of potassium carbonate; or, the number of cubic centimeters of the acid solution, if strictly normal, which is required for the neutralization of the above amount of the salt, will indicate at once its percentage purity in potassium carbonate.

If the pearlash contains potassium hydrate in addition to potassium carbonate, which will be indicated by an alkaline reaction of the solution of the salt after its complete precipitation by barium chloride and subsequent filtration, the hydrate will also be neutralized by the acid, and the estimation of the amount of carbonate would therefore be incorrect. In the latter case, the amount of potassium hydrate and carbonate may be separately estimated according to the following method: 100 cubic centimeters of the above solution (corresponding to 6.9 grams of the pearlash) are mixed with an excess of a solution of barium chloride, and to the unfiltered solution, containing the deposited barium carbonate, normal nitric acid is added from a burette, until a drop of the mixture no longer produces a brown stain upon turmeric paper. The number of cubic centimeters of the acid solution which are required to produce this reaction corresponds to the amount of potassium hydrate in the pearlash: one cubic centimeter of the normal nitric acid corresponding to 0.056 gram of potassium hydrate. The entire mixture, after the addition of a few drops of litmus solution, is then titrated, with the aid of heat, with an excess of normal nitric acid, until a cherry-red tint of the liquid is produced, and subsequently inversely titrated with a normal alkali until the red tint of the liquid is just changed to a permanent blue. The number of cubic centimeters of the normal nitric acid which are required in the last operation, after the deduction of the normal alkali solution subsequently employed, will correspond to the amount of potassium carbonate present in the salt: one cubic centimeter of normal nitric acid corresponding to 0.069 gram of pure potassium carbonate.

If sodium carbonate be also present in the pearlash, the results of the above methods of estimation will be influenced in proportion to its amount, and their correctness accordingly impaired. The estimation of the amount of sodium carbonate may also be quite readily accomplished by the following method: 10 grams of the pearlash are dissolved in 10 grams of hot water, the solution filtered, the filter with its contents of insoluble matter subsequently washed with 5 grams of water, and the entire filtrate finally supersaturated with acetic acid. The solution is then evaporated upon the water-bath to dryness, and the residue heated with 40 cubic centimeters of alcohol, of the spec. grav. 0.830, whereby the acetates of potassium and sodium pass into solution, and the sulphates, chlorides, phosphates, and silicates remain undissolved. To the solution thus obtained, a solution of 21 grams of tartaric acid in 20 parts of hot water is added until, after standing for some hours, no further precipitate of potassium bitartrate is produced. The mixture is then filtered, and the precipitate, contained upon the filter, washed with alcohol, until a few drops of the filtrate, after active agitation with a little potassium acetate, remain perfectly clear. The filtrate is subsequently evaporated to dryness, and gently ignited; a few drops of water are then added, and the operation repeated until, upon ignition, the mass becomes completely incinerated. The ignited mass is then dissolved in water, neutralized with hydrochloric acid, and again evaporated. The sodium chloride thus obtained is dissolved in a small amount of water, a little ammonium carbonate added, and again evaporated to dryness, in order to remove the iron and aluminium, as also traces of calcium and magnesium which may be present. The dried residue is then extracted with warm water, and the solution, which now contains pure sodium chloride, filtered, evaporated to dryness, ignited in a covered platinum crucible, and its weight finally determined. From the weight of the sodium chloride the amount of anhydrous sodium carbonate may readily be calculated: 100 parts of the former corresponding to 90.6 parts of the latter.

When the pearlash contains both potassium and sodium carbonates, and a determination of the relative amount of each is required, an estimation of the amount of carbonic acid contained in a weighed portion (about 2 grams) of the ignited soluble salt must be made, as described on page 86. From the total amount of carbonic acid, the amount corresponding to that of the sodium carbonate present in the salt may be deducted, when the remainder will correspond to the percentage of potassium carbonate, and should conform with the results of the volumetric estimation.

POTASSII CARBONAS DEPURATUS.

POTASSIUM SEU KALIUM CARBONICUM DEPURATUM.

Purified Carbonate of Potassium. Purified Pearlash.

Ger. Gereinigtes kohlensaures Kalium; Fr. Potasse purifiée;
Sp. Potasa refinada.

$2K_2CO_3.3H_2O$; 330.

A white, crystalline, or granular powder, permanent in a dry atmosphere, but deliquescent in a moist one, and possessing a strongly alkaline taste and reaction; when heated, on platinum wire, in the non-luminous flame, it communicates to the latter a violet color.

Purified pearlash is soluble in 1 part of water at 15° C. (59° F.), and in 0.7 part of boiling water, forming a strongly alkaline solution which frequently appears slightly turbid, and deposits gradually a flocculent or gelatinous sediment of silicic acid; it is insoluble in alcohol. Its aqueous solution is decomposed by acids, with effervescence, yields a white, amorphous precipitate with magnesium sulphate, and a white, crystalline one with an excess of tartaric acid.

Purified pearlash contains about 80 per cent. of potassium carbonate, and not more than 15 to 18 per cent. of water, which latter is lost by exposure to a red heat.

Examination:

Potassium hydrate is indicated in the solution of the salt, by an alkaline reaction after its complete precipitation with an excess of barium chloride, and subsequent filtration; its amount may be approximately estimated by agitating a few grams of the salt with absolute alcohol, filtering the solution, and evaporating the filtrate, together with the alcoholic washings therefrom, to complete dryness, in a tared porcelain capsule; the weight of the dried residue will indicate approximately the proportion of potassium hydrate contained in the salt.

Foreign Salts.—A small portion of the purified potassium carbonate is dissolved in an equal weight of water, in a test-tube; the solution should be complete and limpid, or nearly so; it is diluted with an equal volume of water, filtered, and supersaturated with hydrochloric acid; a gelatinous precipitate after a time would indicate *silicic acid;* the liquid is then filtered, and part of the filtrate supersaturated with ammonia-water, when a white turbidity would indicate *aluminium salts;* the other part of the filtrate is tested with barium chloride for *sulphate.*

Chloride and *phosphate* may be detected in the diluted solution of the salt, supersaturated with nitric acid, by testing it in two portions, with argentic nitrate for chloride, and by supersaturation with ammonia-water, and the subsequent addition of test magnesium mixture, for phosphate.

Sulphite and *hyposulphite* are detected in the filtered solution of the salt, slightly supersaturated with acetic acid, by adding a few drops of mucilage of starch, and subsequently two or three drops of diluted solution of iodinized potassium iodide; the first drop of the latter solution should produce a blue coloration at once, which will not occur before the addition of several drops, if the above impurities are contained in the salt.

Sodium carbonate may be detected by a white, crystalline precipitate, occurring at once or after some time, when a hot diluted solution of the potassium carbonate is nearly neutralized with acetic acid, and subsequently tested with potassium antimoniate.

Metallic impurities are detected in the filtered solution of the salt, by dividing it into two parts, one of which is supersaturated with hydrochloric acid; both are then saturated with hydrogen sulphide, when any coloration or precipitate in either of the liquids would indicate the presence of foreign metals.

Estimation:

Water.—The percentage of water contained in the salt may be determined by its loss of weight, upon ignition in a small porcelain crucible, at a red heat.

Potassium Carbonate.—About 3 grams of the salt, accurately weighed, and previously deprived of water, by ignition at a strong heat in a small porcelain crucible, are dissolved in about 20 cubic centimeters of water, in a beaker or small flask, and a few drops of litmus solution added; the solution having been heated to boiling, a standard solution of oxalic or sulphuric acid (page 82) is allowed to flow into the liquid from a burette until, with the continuance of the heat to expel the liberated carbonic acid gas, a slight excess of acid has been employed, and the liquid assumes a bright cherry-red tint; the excess of acid is then inversely titrated with a standard solution of potassium or sodium hydrate (page 87), until the red tint of the liquid is just changed to a permanent blue. From the number of cubic centimeters of acid solution required for the exact neutralization of the salt, the amount of pure potassium carbonate contained therein may be calculated: one cubic centimeter of the normal acid solution corresponding to 0.0692 gram of anhydrous, or 0.0825 gram of crystallized potassium carbonate, $2K_2CO_3.3H_2O$.

If alkaline hydrates or sodium carbonate be present in the salt, the above method of estimation must be modified, as described in the preceding article, on pages 471 to 473.

TABLE *of the amount of dry Potassium Carbonate contained in solutions of the salt of different specific gravities.*

Temperature 15° C. (59° F.).

Per cent. of K_2CO_3.	Specific gravity.	Per cent. of K_2CO_3.	Specific gravity.	Per cent. of K_2CO_3.	Specific gravity.	Per cent. of K_2CO_3.	Specific gravity.
1	1.00914	14	1.13199	27	1.26787	40	1.41870
2	1.01829	15	1.14179	28	1.27893	41	1.43104
3	1.02743	16	1.15200	29	1.28999	42	1.44338
4	1.03658	17	1.16222	30	1.30105	43	1.45573
5	1.04572	18	1.17243	31	1.31261	44	1.46807
6	1.05513	19	1.18265	32	1.32417	45	1.48041
7	1.06454	20	1.19286	33	1.33573	46	1.49314
8	1.07396	21	1.20344	34	1.34729	47	1.50588
9	1.08337	22	1.21402	35	1.35885	48	1.51861
10	1.09278	23	1.22459	36	1.37082	49	1.53135
11	1.10258	24	1.23517	37	1.38279	50	1.54408
12	1.11238	25	1.24575	38	1.39476	51	1.55728
13	1.12219	26	1.25681	39	1.40673	52	1.57048

POTASSII CARBONAS PURUS.

POTASSIUM SEU KALIUM CARBONICUM PURUM.

Pure Carbonate of Potassium. Salt of Tartar. Potassium Carbonate.

Ger. Kohlensaures Kalium; Fr. Carbonate de potasse;
Sp. Carbonato de potasa puro.

K_2CO_3; 138.

A white, deliquescent, granular powder, wholly soluble in an equal weight of water, forming a limpid alkaline liquid, which effervesces with acids, and gives a white, crystalline precipitate with an excess of tartaric acid. When exposed to a red heat, dry potassium carbonate loses about 16 per cent. of its weight. One hundred parts of the dry anhydrous carbonate require for complete neutralization 113 parts of citric, and 108.7 parts of tartaric, acid.

Examination:

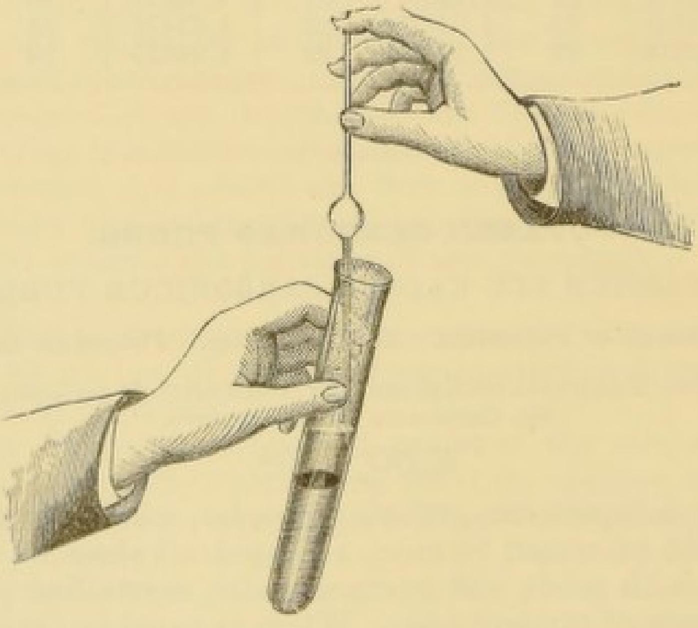
Bicarbonate.—A small portion of the salt is dissolved in an equal weight of water, aided by dipping the test-tube in hot water; the solution should be clear and complete, and remain so after cooling; the separation of a crystalline deposit would indicate potassium bicarbonate. The presence of the latter will also be indicated in a solution of one part of the salt in three parts of water, by the evolution of carbonic acid gas upon heating the solution to boiling.

Purified Pearlash.—A portion of the above-obtained solution is slightly supersaturated with diluted nitric acid, and allowed to stand in a corked test-tube for several hours; an ensuing gelatinous precipitate would indicate *silicic acid;* the solution, after filtering, if necessary, is then tested in separate portions, with argentic nitrate for *chloride*, and with barium nitrate for *sulphate*, which impurities would indicate the admixture or substitution of purified pearlash.

Metals.—Another portion of the above-obtained aqueous solution of the salt is tested with hydrogen sulphide in two test-tubes, the one after supersaturation with diluted hydrochloric acid. An ensuing dark coloration or precipitate in either of the fluids would indicate metallic impurities.

Potassium Nitrate.—The remainder of the concentrated solution of the salt is supersaturated with diluted sulphuric acid; the clear solution is decanted after a while, and divided into two parts, one of which is mixed with a little ferrous sulphate and then transferred, by means of a pipette, upon concentrated sulphuric acid in a test-tube (Fig. 146); an ensuing purple or brown

FIG. 146.



coloration, at the junction of the two strata of the liquids, would indicate nitrate; the other part is tinged slightly blue with solution of indigo, strongly acidulated with sulphuric acid, and heated; ensuing decoloration would confirm the presence of nitrate.

Nitrites may be detected by mixing a little of the aqueous solution of the salt with an excess of dilute sulphuric acid, and subsequently adding a few drops of a solution of potassium iodide and a little mucilage of starch; a blue coloration will reveal the presence of nitrite.

Potassium cyanide may be detected in the solution of the salt, by the addition of a few drops of a solution of ferrous sulphate and ferric chloride, gently warming, and subsequently slightly supersaturating the liquid with hydrochloric acid; the immediate or gradual formation of a precipitate of Prussian blue will confirm the presence of alkaline cyanide.

Calcium and *magnesium salts*, when present in the form of carbonates, will remain undissolved when the potassium carbonate is treated with twenty times its weight of water; they may be otherwise detected in the aqueous solution, previously neutralized with hydrochloric acid, by the addition of ammonia-water, ammonium chloride, and ammonium oxalate; a white precipitate will indicate the presence of calcium; the filtrate from the latter, or the clear liquid if no precipitate was produced, is then tested with sodium phosphate, when the formation of a white, crystalline precipitate will reveal the presence of magnesium.

Sodium salts will be indicated, by their property of imparting a persistent yellow color to the non-luminous flame; the *carbonate* may be specially tested for by supersaturating the aqueous solution of the salt with acetic acid, evaporating to dryness, and extracting the residue with absolute alcohol; the filtered alcoholic liquid is then evaporated to dryness, the residue dissolved in water, and a solution of potassium meta-antimoniate added; if sodium carbonate were present, a white, crystalline precipitate of sodium meta-antimoniate will be produced.

Estimation:

The estimation of pure potassium carbonate may readily be accomplished by the method described under purified pearlash, on pages 474–475.

The United States Pharmacopœia directs that to neutralize 3.45 grams of potassium carbonate should require not less than 40.5 cubic centimeters of the volumetric solution of oxalic acid (corresponding to at least 81 per cent. of pure, anhydrous potassium carbonate).

POTASSII CHLORAS.

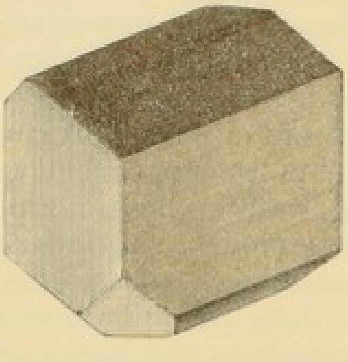
POTASSIUM SEU KALIUM CHLORICUM.

Chlorate of Potassium. Potassium Chlorate.

Ger. Chlorsaures Kalium; Fr. Chlorate de potasse; Sp. Clorato de potasa.

$KClO_3$; 122.4.

Fig. 147.



Colorless, transparent, monoclinic prisms or tables (Fig. 147), of a pearly lustre, anhydrous, and permanent in the air, and of a spec. grav. of 2.36 at 17.5° C. (63.5° F.); when thrown upon burning charcoal they deflagrate, as they also do more or less violently when triturated or heated with readily combustible substances, as sulphur, carbon, phosphorus, etc. Potassium chlorate melts at 334° C. (633.2° F.) without decomposition; at 352° C. (665.6° F.) it begins to decompose with the evolution of oxygen, and at 400° C. (752° F.) the entire amount of oxygen (39.2 per cent. by weight) is liberated, leaving behind a neutral residue of potassium chloride (60.8 per cent.), which is wholly soluble in water. The aqueous solution of this residue yields a white, crystalline precipitate with a concentrated solution of sodium bitartrate, and a white, curdy precipitate, soluble in ammonia-water, with argentic nitrate. When a little sulphuric acid is dropped on the crystals of the chlorate, they become first yellow and then orange-red; with concentrated hydrochloric acid the salt becomes likewise decomposed, with the liberation of chlorine and chlorine dioxide; the latter, in contact with an excess of acid, becoming subsequently decomposed into chlorine and water.

Potassium chlorate is soluble in 16.5 parts of water at 15° C. (59° F.), in 2 parts of boiling water, and in 120 parts of alcohol of 0.835 spec. grav. Its saturated aqueous solution has a cooling, saline, slightly acerb taste, and, when mixed with concentrated hydrochloric acid, produces a deep greenish-yellow coloration, with the evolution of chlorine gas. When a few drops of a concentrated solution of potassium chlorate, and subsequently a little concentrated sulphuric acid, are added to a little of a dilute solution of aniline sulphate, upon a watch-glass, the mixture assumes a brilliant deep-violet color. With solution of tartaric acid, the concentrated solution of potassium chlorate give a white granular precipitate.

Examination:

Potassium Nitrate.—A little of the powdered salt is heated in a porcelain crucible to a full red heat; the residue, when cool, is dissolved in a few drops of water, and the solution tested with turmeric-paper; a brown discoloration of the paper would indicate an admixture of potassium nitrate. As a confirmatory test, a few drops of the solution of the residue may be added to a solution of mercuric chloride; an ensuing yellow precipitate will confirm the presence of nitrate.

The presence of nitrate may also readily be detected by first heating a small portion of the salt, in a test-tube, with about twice its weight of solid potassium or sodium hydrate, and a little water, in order to ascertain the absence of ammonium salts, and subsequently adding a few iron and zinc filings, and again heating; if ammonium salts were found to be absent, or have been completely eliminated by the previous heating with caustic alkali, the odor of ammonia, developed upon the addition of the zinc and iron, will confirm the presence of nitrate.

Potassium chloride and *sulphate* are detected in the aqueous solution, acidulated with a few drops of diluted nitric acid, by the occurrence of a white precipitate, in the case of the former with argentic nitrate, of the latter with barium nitrate.

Most commercial potassium chlorate occasions a slight cloudiness with argentic nitrate.

Calcium salts may be detected in the dilute aqueous solution of the salt, by a white precipitate upon the addition of a few drops of a solution of ammonium oxalate.

Sodium chlorate will be indicated in the salt by its property of imparting a persistent yellow color to the non-luminous flame, as also by its much greater solubility in water and warm alcohol. It may be extracted by treating a portion of the salt with boiling alcohol, filtering, and adding to the filtrate a concentrated solution of tartaric acid; the potassium will thereby be precipitated, and, after its complete deposition, the filtrate may be further examined for sodium.

Metallic impurities may be detected in the aqueous solution of the salt, acidulated with hydrochloric acid, by a dark coloration or precipitate upon saturation with hydrogen sulphide, or, after neutralization with ammonia-water, by the addition of ammonium sulphide.

POTASSII CITRAS.

POTASSIUM SEU KALIUM CITRICUM.

Citrate of Potassium. Potassium Citrate.

Ger. Citronensaures Kalium; Fr. Citrate de potasse; Sp. Citrato de potasa.

$K_3C_6H_5O_7 + H_2O$; 324.

A white, granular powder, or transparent prismatic crystals, containing one molecule (5.55 per cent.) of water; it is deliquescent upon exposure to the air, odorless, of a slightly cooling and faintly alkaline taste, and neutral in its action upon litmus. When moderately heated, the salt loses its water, at a higher temperature it chars, and at a red heat becomes completely decomposed, with the evolution of empyreumatic, inflammable vapors, leaving a black residue, consisting of potassium carbonate and carbon, which strongly effervesces with acids.

Potassium citrate is soluble in 0.6 part of water at 15° C. (59° F.), and is very soluble in boiling water; it is very sparingly soluble in alcohol. Its aqueous solution yields a white, crystalline precipitate upon the addition of a concentrated solution of sodium bitartrate; upon the addition of a cold solution of calcium chloride the liquid remains clear, but, upon boiling, a white, granular precipitate is produced, which redissolves for the most part upon cooling.

Examination:

Potassium tartrate will be indicated by the separation of a white, crystalline precipitate, upon the addition of acetic acid to a concentrated aqueous solution of the salt.

Carbonates, *Sulphates*, and *Chlorides*.—The aqueous solution of the salt is slightly acidulated with nitric acid, when effervescence will indicate carbonates; the acidulated solution is then subsequently tested, in separate portions, with barium chloride for sulphates and with argentic nitrate for chlorides, when an ensuing white precipitate in either instance will reveal the presence of such impurities.

Metallic impurities may be detected in an aqueous solution of the salt, acidulated with hydrochloric acid, by a dark coloration or precipitate upon saturation with hydrogen sulphide, or, after supersaturation with ammonia-water, by the addition of ammonium sulphide.

Estimation:

Potassium citrate may be estimated volumetrically by its conversion into potassium carbonate, and the neutralization of the latter by means of a normal or standard acid. 5.4 grams of the salt are ignited in a porcelain crucible, at a red heat, until gases cease to be evolved; the soluble matter of the residue is then completely extracted with hot water, the solution filtered into a beaker or small flask, a few drops of litmus solution added, and a standard solution of oxalic or sulphuric acid (page 82) allowed to flow into the liquid from a burette until, after being heated to boiling, in order to completely expel the liberated carbonic acid gas, the liquid assumes a bright cherry-red tint. The excess of acid is then inversely titrated with a standard solution of potassium or sodium hydrate (page 87) until the red tint of the liquid is just changed to a permanent blue. If the above amount of the salt is employed, the number of cubic centimeters of normal acid which is required for its neutralization, when multiplied by 2, will represent without further calculation its percentage purity. With the employment of other quantities of the salt than that above indicated, the calculation may be made with the consideration that one cubic centimeter of normal acid corresponds to 0.108 gram of potassium citrate, $K_3C_6H_5O_7+H_2O$.

POTASSII CYANIDUM.

POTASSIUM SEU KALIUM CYANATUM.

Cyanide of Potassium. Potassium Cyanide.

Ger. Cyankalium ; Fr. Cyanure de potassium ; Sp. Cianuro de potasio.

KCN ; 65.

White, opaque, amorphous masses, or a white, granular, deliquescent powder, having a sharp, somewhat alkaline taste, and a strongly alkaline reaction. It is odorless when perfectly dry, but emits the odor of hydrocyanic acid upon exposure to a moist atmosphere, in consequence of the absorption of water and carbonic acid gas, and the liberation of hydrogen cyanide.

When exposed to a low red heat, with exclusion of the air, the salt is readily fusible without decomposition, and, upon slowly cooling, solidifies in the form of cubical crystals; when heated with exposure to the air, it absorbs oxygen, and becomes partially converted into potassium cyanate. It is decomposed by all acids, with the disengagement of hydrocyanic acid.

Commercial potassium cyanide is soluble in 2 parts of water at 15° C. (59° F.), and in its own weight of boiling water; it is but sparingly soluble in strong alcohol, but is quite freely soluble in boiling diluted alcohol, and crystallizes from the latter solution upon cooling. The aqueous solution has an alkaline reaction, exhales the odor of hydrocyanic acid, and becomes gradually decomposed by exposure to the air; upon boiling, it is rapidly decomposed, with the evolution of ammonia, and the formation of potassium formiate. The aqueous solution of potassium cyanide yields a white, crystalline precipitate upon the addition of a concentrated solution of sodium bitartrate; with argentic nitrate, it yields a white precipitate, which is soluble in an excess of potassium cyanide or of ammonia-water; and with a few drops of a solution of a ferrous and ferric salt, and the subsequent addition of hydrochloric acid in slight excess, a precipitate of Prussian blue is produced. It produces precipitates in solutions of the salts of most of the heavy metals, which, however, for the most part, are soluble in an excess of potassium cyanide, with the formation of crystallizable double salts.

The detection and isolation of potassium cyanide in subjects of forensic investigation depends upon the elimination of hydrocyanic acid in contact with stronger acids, and the same method is therefore to be pursued, and the same precautions observed, as described in detail under hydrocyanic acid, on pages 161 to 163.

Examination:

Potassium carbonate, which is usually present in small amount, will be indicated in the aqueous solution of the salt by effervescence upon the addition of dilute hydrochloric acid. The acidulated solution thus obtained may subsequently be tested with a drop of a solution of ferric chloride; a blue precipitate will indicate *ferrocyanide*, a deep blood-red coloration, *sulphocyanide*.

Estimation:

Since commercial potassium cyanide always contains a greater or less amount of impurities, and as its value depends upon the percentage amount of pure cyanide, the determination of the latter becomes necessary, and may be readily accomplished volumetrically by the following method, the principles of which have been explained on pages 100–101.

0.65 gram of the salt is dissolved in about 100 cubic centimeters of water, in a beaker, a few drops of a solution of potassium hydrate added, or sufficient to impart to the liquid a distinct alkaline reaction, and subsequently a few drops of a saturated solution of sodium chloride. A decinormal solution of argentic nitrate (page 98) is then allowed to flow into the liquid from a burette until, with constant stirring, a permanent cloudiness of the liquid is just produced. The number of cubic centimeters of silver solution which is required to produce this effect, with the employment of the above-stated amount of potassium cyanide, when multiplied by 2, will represent the percentage purity of the salt. With the employment of other amounts of the salt than that above stated, the calculation may be made with the consideration that one cubic centimeter of the decinormal silver solution, in accordance with the described process, corresponds to 0.013 gram of pure potassium cyanide.

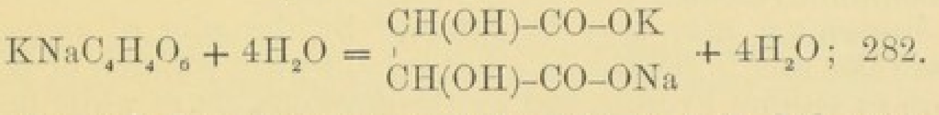
The United States Pharmacopœia directs that if 0.65 gram of potassium cyanide be dissolved in 12 cubic centimeters of water, and volumetric solution of argentic nitrate be gradually added, the precipitate first formed should dissolve on stirring, and a permanent precipitate should not appear until at least 45 cubic centimeters of the volumetric solution have been used (corresponding to at least 90 per cent. of pure potassium cyanide).

POTASSII ET SODII TARTRAS.

POTASSIUM ET SODIUM TARTARICUM. NATRIO-KALIUM TARTARICUM. SODIUM TARTARATUM. TARTARUS NATRONATUS.

Rochelle Salt. Seignette Salt. Potassium and Sodium Tartrate.

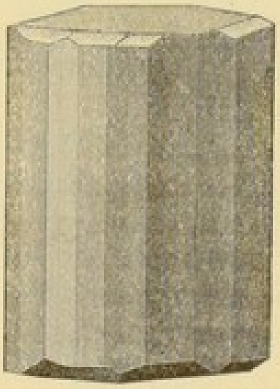
Ger. Weinsaures Kalium-Natrium; Fr. Tartrate de potasse et de soude; Sp. Tartrato de potasa y sosa.



$$KNaC_4H_4O_6 + 4H_2O = \begin{array}{l} CH(OH)\text{-}CO\text{-}OK \\ \mid \\ CH(OH)\text{-}CO\text{-}ONa \end{array} + 4H_2O;\ 282.$$

Large, colorless, transparent, prismatic crystals, belonging to the rhombic system, the faces of which are unequally developed (Fig. 148); they contain four molecules (25.53 per cent.) of water of crystallization, and are slightly efflorescent in dry air.

FIG. 148.



The salt occurs in commerce generally ground, as a snow-white powder. When quickly heated to about 75° C. (167° F.), it melts in its water of crystallization, and at 100° C. (212° F.) loses 3 molecules of water, the remaining molecule of water being eliminated at 130° C. (266° F.), at which temperature the salt begins to decompose; at a higher temperature it chars and is decomposed, with the evolution of inflammable vapors and the odor of burnt sugar, and, on moderate ignition, leaves a blackened residue, which consists of a mixture of potassium and sodium carbonates with carbon, and which colors turmeric-paper brown, effervesces with acids, and imparts a yellow color to the non-luminous flame when heated upon the looped end of a platinum wire (distinction from potassium tartrate).

Potassium and sodium tartrate is soluble in 2.5 parts of water at 15° C. (59° F.), and in much less than its own weight of boiling water, but is insoluble in alcohol; its aqueous solution is neutral, has a mild, cooling, saline taste, and forms a white, granular precipitate with acids and with solutions of acidulous salts. When dissolved in 8 parts of water, and dilute acetic acid is added to the liquid, a white, crystalline precipitate is gradually produced (distinction from sodium tartrate); with argentic nitrate it yields a white precipitate, which becomes black on boiling.

Examination:

A portion of the salt is dissolved in three times its weight of warm water; the solution should be clear and complete, and remain so after cooling; it should not act upon litmus-paper, nor effervesce upon the addition of hydrochloric acid (evidence of the absence of sodium carbonate or bicarbonate).

Chlorides and *sulphates* may be detected by a white precipitate when the diluted solution of the salt, acidulated with nitric acid, is tested in separate portions, with argentic nitrate for the former, and with barium nitrate for the latter. In case the solution separates granular potassium bitartrate upon the addition of the acid, sufficient hot water is added to redissolve the precipitate before adding the reagent.

Calcium salts are detected in the diluted solution, by means of ammonium oxalate.

Ammonium salts may be detected by the odor of ammonia, when the salt is heated, in a test-tube, with a solution of potassium or sodium hydrate, and by the development of white fumes, when a glass rod, moistened with acetic acid, is held over the mouth of the tube.

Metallic impurities are detected in the concentrated solution of the salt, acidulated with hydrochloric acid, and filtered, if necessary, by a dark coloration or precipitate upon saturation with hydrogen sulphide, or, after neutralization with ammonia-water, by the addition of ammonium sulphide.

Crystallized potassium and sodium tartrate, being in appearance somewhat similar to crystallized borax and alum, and therefore liable to incidental mistake, may readily be distinguished from either of these substances, in addition to its physical characters, by its taste, by its neutral reaction—alum being acid, borax alkaline, and by the black alkaline fuse upon incineration, while both borax and alum swell up to a porous mass, and yield a white or colorless fuse.

Estimation:

3.525 grams of the salt are ignited in a porcelain crucible, at a red heat, until gases cease to be evolved; the alkaline residue is then extracted with warm water, the solution filtered into a beaker, a few drops of litmus solution added, and titrated, by the aid of heat, with a standard solution of oxalic or sulphuric acid (page 82), as described under potassium carbonate, on page 474. The number of cubic centimeters of the normal acid solution which is thus required for the exact neutralization of the liquid, when multiplied by 4, will indicate, without further calculation, the percentage purity of the salt. By the employment of other quantities of the salt than precisely that above stated, the calculation may also readily be made with the consideration that one cubic centimeter of the normal acid solution corresponds to 0.141 gram of pure crystallized potassium and sodium tartrate.

POTASSII FERROCYANIDUM.

POTASSIUM SEU KALIUM FERROCYANATUM.

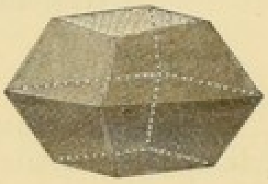
Ferrocyanide of Potassium. Yellow Prussiate of Potassium. Potassium Ferrocyanide.

Ger. Ferrocyankalium ; Fr. Cyanure de fer et de potassium ; Sp. Ferrocianuro de potasio.

$K_4Fe(CN)_6+3H_2O$; 421.9.

Large, translucent, yellow, tabular crystals, derived from an octahedron with a square base (Fig. 149); they cleave with facility in a direction parallel to the base of the octahedron, have a peculiar toughness and flexibility, and the specific gravity 1.83. The crystals contain three molecules (12.79 per cent.) of water of crystallization, and undergo no alteration in pure air at ordinary temperatures, but when heated to 60° C. (140° F.) they begin to lose their water of crystallization, which is completely eliminated at 100° C. (212° F.), leaving the anhydrous salt in the form of a white powder; the latter, upon exposure to a red heat, is decomposed with the evolution of nitrogen, leaving a residue consisting of ferric carbide and potassium cyanide. When heated with dilute sulphuric acid, hydrocyanic acid is evolved.

FIG. 149.



Potassium ferrocyanide is soluble in 4 parts of water at 15° C. (59° F.), and in 2 parts of boiling water; it is insoluble in alcohol. Its aqueous solution has a mild saline taste, gives a white, granular precipitate with a saturated solution of sodium bitartrate, and, when diluted, a blue one with ferric, a brick-red one with cupric, and a white one with ferrous and with plumbic salts; it is not acted upon by hydrogen sulphide or ammonium sulphide, by tannic acid, nor by the alkaline hydrates and carbonates. When the solution is exposed for some time to the action of light, Prussian blue is deposited, and, by long-continued boiling, with exposure to the air, ammonia is given off, and the liquid becomes alkaline.

Examination:

Foreign salts are indicated when the potassium ferrocyanide does not yield a complete and clear solution with four parts of water.

Carbonate is indicated by effervescence of the concentrated solution upon the addition of acetic acid, or upon placing fragments of a crystal in diluted sulphuric acid.

Sulphate is detected, in the diluted solution, acidulated with nitric acid, by a white turbidity with barium nitrate.

Chloride may be detected, when a mixture of 1 part of the exsiccated salt with 3 parts of potassium nitrate (free from chloride) and 10 parts of anhydrous sodium carbonate is heated nearly to redness in a porcelain crucible; when cool, the whole is dissolved in water, the filtered solution supersaturated with nitric acid, and tested with argentic nitrate, which will indicate chloride by a white precipitate.

POTASSII HYDRAS.

POTASSA. POTASSIUM SEU KALIUM HYDRICUM PURUM. KALI CAUSTICUM.

Pure Caustic Potash. Potassa. Potassium Hydrate.

Ger. Kaliumhydroxyd, Aetzkali; Fr. Potasse caustique;
Sp. Hidrato de potasa.

KOH; 56.

A white, opaque, granular powder, or, when fused, white, semi-transparent plates or cylindrical sticks, of a fibrous fracture; exposed to the air, it absorbs water and carbonic acid, and gradually deliquesces. It melts below a red heat to a clear oily liquid, and volatilizes unchanged, in the form of white vapors, when more strongly ignited; when introduced into the non-luminous flame, it imparts to the latter a violet color.

Potassium hydrate is soluble in 0.5 part of water and in 2 parts of alcohol at 15° C. (59° F.), with the evolution of heat, and is slightly soluble in ether; when the concentrated aqueous solution is cooled, the hydrate, $KOH + 2H_2O$, is deposited in transparent, colorless, acute rhombohedral crystals. Its aqueous solution has a soapy feel, a burning, corrosive taste, and a strong alkaline reaction; it gives a grayish-brown precipitate with argentic nitrate, soluble in ammonia-water, and precipitates from their solutions most metallic oxides, several of which are redissolved by an excess of the potassium hydrate; when dropped into solution of tartaric acid, it produces a white, crystalline precipitate, which is redissolved by an excess of the alkali; it decomposes ammonium salts with the evolution of ammonia.

Examination:

Potassium hydrate must afford a clear and nearly complete solution when treated with about five times it weight of alcohol; the insoluble residue will be in proportion to the amount of foreign salts present.

Sodium hydrate, although usually present in small amount, may be detected when contained in any considerable proportion by the following method. A weighed amount of potassium hydrate is dissolved in ten times its weight of water, the solution exactly neutralized with tartaric acid, and subsequently as much tartaric acid again added as was required for the neutralization of the alkali; the solution is then diluted with alcohol until the separation of potassium bitartrate no longer ensues, and finally filtered. The solution, which will contain the sodium in the form of bitartrate, is evaporated to dryness, the residue ignited, and the ignited mass, consisting of sodium carbonate and carbon, dissolved in water, and filtered. The filtered solution, after neutralization with nitric acid, will then afford upon evaporation rhombohedral crystals of sodium nitrate, which impart a yellow color to the non-luminous flame. The amount of sodium hydrate may also be quantitatively determined, by the neutralization of a definite amount of the sodium bitartrate solution with a normal solution of potassium or sodium hydrate (page 82). The number of cubic centimeters of normal alkali solution which is required for this purpose will be in direct proportion to the amount of sodium hydrate contained in the solution under examination.

Silicates, as also many foreign salts, will be indicated by a precipitate, or by the separation of a heavy aqueous layer, when a solution of the potassium hydrate in two parts of water is dropped into alcohol.

Carbonate may be detected when portions of a concentrated aqueous solution of the hydrate are dropped severally into acetic acid and into lime-water; effervescence with the acid, and a white turbidity with the lime-water, would indicate carbonate.

Nitrate is indicated by ensuing decoloration of the liquid when a little of the aqueous solution which has been mixed with an excess of dilute sulphuric acid, and tinted blue with one drop of indigo-solution, is gently heated.

Chloride and *sulphate* are detected in the diluted solution, supersaturated with dilute nitric acid, by testing it, in separate portions, with argentic nitrate for chloride, and with barium nitrate for sulphate.

Aluminium salts and *phosphoric acid* may be detected in the diluted solution, after supersaturation with hydrochloric acid, by the addition of ammonia-water in slight excess, and after filtering, if a precipitate be formed, by the subsequent addition of test magnesium mixture; a white, gelatinous precipitate with the ammonia-water would indicate aluminium salts, and a white, crystalline one with the latter reagent, occurring at once or after several hours, *phosphoric acid.*

Metallic impurities are detected by a dark coloration or turbidity of the solution, when saturated with hydrogen sulphide, and, in another portion of the solution, after previous supersaturation with hydrochloric acid.

Estimation:

2.8 grams of dry potassium hydrate are dissolved in about 20 cubic centimeters of water, in a beaker, a few drops of litmus solution added, and a standard solution of oxalic or sulphuric acid (page 82) allowed to flow into the liquid from a burette, until the blue tint of the liquid is just changed to a permanent pink. The number of cubic centimeters of normal acid solution which is thus required for the exact neutralization of the above amount of potassium hydrate, when multiplied by 2, will represent, without further calculation, its percentage purity. By the employment of other amounts of the hydrate, the calculation may readily be made, with the consideration that one cubic centimeter of the normal acid solution corresponds to 0.056 gram of pure potassium hydrate.

If the potassium hydrate contains carbonate, the above estimation will only be strictly correct, when in a weighed amount of the hydrate the amount of carbonic acid is determined, as described on pages 85–86; for 1 part of carbonic acid, 2.545 parts of potassium hydrate are deducted from the found amount of the latter, and the remainder then calculated as pure potassium hydrate.

For the determination of the strength of aqueous solutions of potassium hydrate, as based upon the specific gravity of the latter, see *Liquor Potassæ*, page 410.

POTASSII HYDRAS CRUDUS.

POTASSIUM SEU KALIUM HYDRICUM CRUDUM.

Crude Potash.

Ger. Rohes Aetzkali; Fr. Potasse caustique impure;
Sp. Hidrato de potasa ordinaria.

Fused, heavy, compact masses, of a stony appearance, fracture, and hardness, of a soapy feel, burning, corrosive taste, and a destructive action on vegetable and animal matters; its color is mostly greenish or brownish-gray; it is deliquescent, and rapidly absorbs water and carbonic acid. Heated to redness, it fuses, but remains unchanged; at a very high heat it is volatile.

Crude potash dissolves, for the most part, in water and in alcohol, with evolution of heat, leaving a more or less considerable residue of impurities; the decanted solution gives a grayish-brown precipitate with argentic nitrate, soluble upon the addition of ammonia-water.

The insoluble impurities of crude potash consist chiefly of carbonates, sulphates, silicates, chlorides, and ferric and manganic oxides.

Examination:

In order to ascertain the nature of the impurities, a portion of the crude potash is triturated and dissolved in twice its weight of tepid water, and the whole is allowed to subside in a conical glass vessel; the clear solution is then mixed with twice its volume of strong alcohol, and the mixture allowed to stand for several hours; the solution is then decanted from the precipitate, as far as practicable, and the latter dissolved in hot water; when cool, this solution is filtered, and the insoluble residue washed with a little water, and preserved upon the filter for further examination. The obtained aqueous solution may be examined as follows:

Carbonate and *silicate* are recognized on dropping a little of the solution into a test-tube containing a mixture of equal parts of water and concentrated nitric acid; the former will be indicated by effervescence, the latter by a white, gelatinous turbidity, ensuing at once or after some hours.

Sulphate and *chloride* may be detected, in separate portions of the solution, by supersaturating it with nitric acid, and subsequently testing with barium nitrate for sulphate, and with argentic nitrate for chloride.

Sulphite and *hyposulphite* are indicated by the occurrence of an insoluble residue, when a portion of the solution is precipitated with argentic nitrate, and the precipitate is treated with ammonia-water.

Nitrate is detected, in a portion of the solution, after the addition of an excess of dilute sulphuric acid and one drop of solution of indigo; the blue tint will disappear upon warming, if nitrate be present.

Phosphate may be detected by a white, crystalline precipitate, when the solution is supersaturated with hydrochloric acid, then mixed with an equal volume of ammonia-water, and subsequently tested with magnesium sulphate.

Metallic impurities are recognized by a dark coloration or precipitate, when both the alcoholic solution and the aqueous solution of the residue from the alcoholic one are tested separately with hydrogen sulphide, as also after having been previously supersaturated with hydrochloric acid.

The residue remaining from the solution in alcohol, and preserved upon the filter, is washed with a few drops of alcohol, then dissolved upon the filter in diluted hydrochloric acid, and subsequently neutralized with ammonia-water; this solution is then tested, in separate portions, with ammonium oxalate for *calcium*, and with barium chloride and a few drops of hydrochloric acid for *sulphate*.

The estimation of crude potash may be accomplished volumetrically by the method described for pure potassium hydrate, on pages 487–488.

POTASSII HYPOPHOSPHIS.

POTASSIUM SEU KALIUM HYPOPHOSPHOROSUM.

Hypophosphite of Potassium. Potassium Hypophosphite.

Ger. Unterphosphorigsaures Kalium; Fr. Hypophosphite de potasse;
Sp. Hipofósfito de potasa.

KH_2PO_2; 104.

White, opaque, crystalline masses, or hexagonal tables, or a white granular powder, very deliquescent, and neutral in its action upon litmus; when heated in a perfectly dry test-tube, the salt first loses adhering moisture, then evolves spontaneously inflammable hydrogen phosphide, and burns with a bright yellow flame; when evaporated to dryness, in contact with nitric acid, it detonates violently.

Potassium hypophosphite is soluble in 0.6 part of water, and in 7.3 parts of alcohol at 15° C. (59° F.); in 0.3 part of boiling water, and in 3.6 parts of boiling alcohol; but is insoluble in ether. The aqueous solution possesses a sharp, saline, and slightly bitter taste, and yields a white, crystalline precipitate on the addition of a concentrated solution of sodium bitartrate; with argentic nitrate it yields a white precipitate, which rapidly turns brown and black with the separation of metallic silver; when acidulated with hydrochloric acid, and added to excess of solution of mercuric chloride, it first produces a white precipitate of mercurous chloride (calomel), and, on further addition, metallic mercury is separated.

Examination:

Calcium salts will be detected by an ensuing white precipitate on the addition of ammonium oxalate to an aqueous solution of the salt.

Carbonates will be detected by effervescence of the solution on the addition of an acid.

Chlorides and *sulphates* will be detected in the aqueous solution of the salt, acidulated with nitric acid, by a white precipitate when tested, in separate portions, with argentic nitrate and barium chloride.

Phosphates will be indicated in the aqueous solution of the salt by the formation of a white crystalline precipitate, either at once or upon standing, on the addition of test magnesium mixture.

POTASSII IODIDUM.

POTASSIUM SEU KALIUM IODATUM.

Iodide of Potassium. Potassium Iodide.

Ger. Jodkalium; Fr. Iodure de potassium; Sp. Ioduro de potasio.

KI; 165.6.

Colorless, anhydrous, semi-transparent, or opaque crystals, cubical, or sometimes elongated in form, permanent in dry, but slightly deliquescent in moist, air, and having a spec. grav. of 2.97. When exposed to heat, potassium iodide decrepitates, and fuses below a red heat; on cooling, it solidifies into a crystalline, pearly mass, without loss of weight, except humidity; at a full red heat, it is slowly volatilized, without decomposition. When a few fragments of the salt are heated in concentrated sulphuric acid, or, in a dry test-tube, with a little potassium bisulphate, violet-colored vapors of iodine are evolved; and when dissolved in a little water, a few drops of chlorine-water added, and the mixture subsequently shaken with half its volume of chloroform or carbon bisulphide, these will acquire a purple or violet color.

Potassium iodide is soluble in 0.8 part of water, in 18 parts of alcohol, of 0.835 spec. grav., and in 40 parts of absolute alcohol at 15° C. (59° F.), in 0.5 part of boiling water, and in 6 parts of boiling alcohol, and is also very freely soluble in warm anhydrous glycerin. The aqueous solution possesses a pungent, saline taste, a neutral or feebly alkaline reaction, and gives, with an excess of tartaric acid, a white, granular precipitate; with argentic nitrate, a yellowish one, which is insoluble in diluted nitric acid, and almost insoluble in ammonia-water, but becomes white with the latter; and a vermilion-red precipitate with mercuric chloride, soluble in an excess of either the solution or the reagent; it gives a violet-blue color with a little mucilage of starch, upon the subsequent addition of a few drops of chlorine-water (distinction from potassium bromide and chloride), and a white, crystalline precipitate with a saturated solution of sodium bitartrate.

Examination:

Water, which may be contained as interstitial moisture in the crystals, is recognized, and may be quantitatively determined, by the loss of weight upon drying a known weight of the powdered salt at 100° C. (212° F.).

Impurities and Admixtures.—In order to obtain for examination an average representation of the iodide, several grams of smaller and larger crystals are selected from the bulk of the salt, and triturated to a granular powder, part of which may serve for the following tests: One gram of it is dissolved in an equal weight of water; the solution formed must be clear and complete, and remain so after the addition of several times its volume of strong or absolute alcohol; an ensuing turbidity or crystalline deposit would indicate foreign salts (carbonate, sulphate, iodate, nitrate); if this precipitate is considerable, it may be collected upon a filter, washed with a few drops of alcohol, and then dissolved in a few drops of warm water; the obtained solution may be tested for *carbonate* with turmeric-paper, or by allowing one or two drops of it to fall into concentrated hydrochloric acid; a brown coloration of the paper, and effervescence with the acid, will indicate the presence of carbonate; the rest of the solution is acidulated with a few drops of hydrochloric acid, and tested for *sulphate* with one drop of barium chloride, and subsequently, for *nitrate*, by the addition of a little sulphuric acid and a drop of indigo solution, and heating.

Potassium iodate may be detected in the aqueous solution of the salt, by adding a few drops of mucilage of starch, and then a few drops of a concentrated solution of tartaric acid, insufficient to cause a precipitate; if iodate be contained in the salt, a violet coloration of the liquid will occur at once. Or the aqueous solution, mixed with a few drops of concentrated solution of tartaric acid, may be shaken with a little chloroform, which will assume a red color when iodate is present.

Iodate may also be recognized in potassium iodide by dropping a crystal of tartaric acid into a strong solution of the iodide in previously boiled, distilled water, and allowing it to remain at rest for several minutes; if iodate be present, the crystal will be enveloped after that time in a yellowish-white zone.

Carbonate may be detected by a white turbidity when the aqueous solution of the potassium iodide is mixed with twice its volume of lime-water, and will also be indicated by a strongly alkaline reaction, when a few fragments of the salt are placed upon moistened red litmus paper.

Sulphate may be detected in the diluted solution of the iodide, previously acidulated with hydrochloric acid, by a white precipitate with barium chloride.

Nitrate may be detected in the aqueous solution, if the salt be free from iodate, by the addition of a few drops of mucilage of starch, and subsequently adding a little of this liquid to a mixture of zinc and dilute hydrochloric acid, in which the development of hydrogen is actively taking place; if any nitrate be present, the liquid will gradually assume a reddish-violet or blue color. If iodate be present, the presence of nitrate may also be determined by completely precipitating a solution of the salt with argentic sulphate, filtering, and adding to the filtrate, in a test-tube, a concentrated solution of ferrous sulphate, and afterwards concentrated sulphuric acid, so as to form two layers (Fig. 146, p. 476); a dark-brown coloration at the line of contact of the two liquids will then reveal the presence of nitrate.

Chloride and *bromide* are detected by dissolving 1 gram of the salt in 10 grams of ammonia-water, and agitating the solution with a solution of 1.1 grams of argentic nitrate in 20 grams of water; the mixture is then filtered, and the filtrate supersaturated with 8 grams of strong nitric acid; since ammonia-water dissolves only traces of argentic iodide, the transparency of the liquid must be not at all, or only slightly, impaired; a white turbidity, subsiding to a precipitate, would indicate the presence of more than about 0.5 per cent. of chloride or bromide. In order to distinguish these, the precipitate is collected upon a filter and washed with a little water, until this ceases to redden blue litmus-paper; the filter is then pierced by a glass rod, and the precipitate rinsed into a test-tube; after subsidence, the water is, as far as possible, decanted, and chlorine-water added and agitated with the precipitate; since chlorine decomposes argentic bromide, dissolving the disengaged bromine with a yellow color, bromide will be recognized by a more or less deep yellow color of the fluid, while argentic chloride remains unchanged. When chloroform or ether is then added to the fluid and agitated, it will absorb the bromine and the yellow color from the water.

A confirmatory test for the recognition of bromide is, to add to a solution of the salt an excess of solution of cupric sulphate, and subsequently so much of a saturated solution of sulphurous acid as to impart its strong odor to the mixture, and until the brownish color of the mixture has disappeared; the liquid is then filtered, a little chloroform added, and subsequently chlorine-water in very slight excess, in order to effect the oxidation of the sulphurous acid, and the mixture well agitated; after subsidence has taken place, a yellow color will have been imparted to the chloroform if bromide is contained in the salt.

Iron and *zinc* may be detected in the aqueous solution of the salt by the addition of a few drops of a solution of potassium ferrocyanide; a blue coloration will reveal the presence of iron, and a white precipitate that of zinc.

Estimation:

A quantitative estimation of the purity of potassium iodide may be made by dissolving 1 gram of the salt in 10 grams of ammonia-water, and adding to the solution a solution of not less than 1.1 grams of argentic nitrate in 20 grams of water; the mixture is then well agitated, filtered, and the precipitate of argentic iodide well washed with water, and finally dried at 100° C. (212° F.) until of constant weight. If the potassium iodide was pure, 1.415 grams of argentic iodide should be obtained, or, 100 parts of argentic iodide correspond to 70.65 parts of potassium iodide.

The estimation of the purity of potassium iodide may also be accomplished volumetrically by the following method: This is based upon the fact that mercuric chloride precipitates from a solution of potassium iodide, red mercuric iodide, which is soluble in an excess of a solution of potassium iodide with the formation of a soluble double salt, and the solution of the latter again yields upon the subsequent addition of mercuric chloride a precipitate of mercuric iodide.

$$
\begin{aligned}
& 2KI + HgCl_2 = HgI_2 + 2KCl \\
& HgI_2 + 2KI = HgK_2I_4 \\
\text{or}\quad & \underbrace{4KI}_{\substack{664 \\ (5)}} + \underbrace{HgCl_2}_{\substack{271 \\ (2.03)}} = HgK_2I_4 + 2KCl.
\end{aligned}
$$

2.03 grams of mercuric chloride are dissolved in water to the measure of 100 cubic centimeters, and 5 grams of the potassium iodide under examination are likewise dissolved in water to the measure of 100 cubic centimeters;* 10 cubic centimeters of the potassium iodide solution are then brought into a beaker, which is placed upon a sheet of white paper, and the above solution of mercuric chloride allowed to flow into the liquid from a burette until, with constant stirring, a permanent precipitate of mercuric iodide is just produced. The number of cubic centimeters of the mercuric chloride solution which are required to produce this reaction, when multiplied by 10, will represent the percentage amount of pure potassium iodide contained in the salt. The accuracy of the result of the estimation by the above method is not influenced by the presence of chloride or of considerable amounts of bromide.

POTASSII NITRAS.

POTASSIUM SEU KALIUM NITRICUM.

Nitrate of Potassium. Saltpetre. Nitre. Potassium Nitrate.

Ger. Salpetersaures Kalium, Salpeter; Fr. Azotate de potasse; Sp. Nitrato de potasa.

KNO_3; 101.

Long, striated, six-sided, prismatic crystals, belonging to the rhombic system (Fig. 150), colorless and transparent, and of a spec. grav. of 2.0; or a white, granular powder, permanent in the air. It melts at about 340° C. (642.2° F.) without decomposition, and solidifies on cooling to a white, opaque, crystalline mass; at a red heat, it is decomposed with the evolution of oxygen and nitrogen gases, and leaving a residue consisting principally of potassium nitrate, oxide, and dioxide, which emits nitrous vapors on the addition of sulphuric acid. When thrown upon burning coals,

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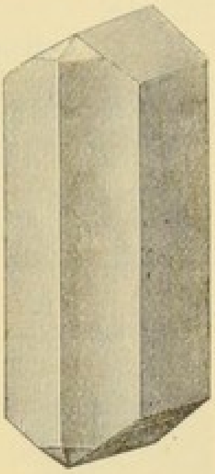
* The results attained by this method are rendered more accurate when, instead of dissolving the mercuric chloride and potassium iodide in water, alcohol of 17.5 per cent. by volume is employed. From the formula $x = \frac{17.5 \,.\, 100}{n}$, in which n represents the percentage strength of the alcohol to be diluted, the volume of alcohol may be calculated which must be added to the water in order to obtain 100 parts of alcohol of 17.5 per cent. by volume.

it deflagrates with bright scintillations, leaving an alkaline residue, which, when heated upon the looped end of a platinum-wire, imparts a violet color to the non-luminous flame.

FIG. 150.



Potassium nitrate is soluble in 3.8 parts of water at 15° C. (59° F.), and in 0.4 part of boiling water; it is far less soluble in glycerin, and almost insoluble in alcohol; its aqueous solution is neutral, has a cooling, saline taste, and forms a white, granular precipitate with a concentrated solution of sodium bitartrate; a few drops of it mixed with a solution of ferrous sulphate, and carefully placed upon concentrated sulphuric acid (Fig. 146, page 476), give rise to the formation of a dark coloration upon the line of contact between the two fluids.

Examination:

Chloride and *sulphate* are detected in the diluted solution of the salt, acidulated with nitric acid, by ensuing white precipitates when tested in two separate portions, with argentic nitrate for chloride, and with barium nitrate for sulphate.

Chlorate is indicated by a yellow coloration, and the evolution of chlorine, when a concentrated solution of the potassium nitrate is mixed and gently warmed with an equal volume of concentrated hydrochloric acid.

Calcium and *magnesium salts* are detected by a white turbidity when the diluted solution is warmed with dilute solution of sodium carbonate; they may be distinguished by adding a little ammonium chloride and ammonia-water to the dilute solution of the salt, and testing it, in separate portions, with ammonium oxalate for calcium, and, after filtration, if necessary, with sodium phosphate for magnesium.

Potassium nitrite may be detected by a violet or blue coloration, when to a solution of the salt a little mucilage of starch, a few drops of a solution of pure potassium iodide, and subsequently dilute sulphuric acid are added.

Sodium salts will be indicated by their property of imparting a persistent yellow color to the non-luminous flame, as also by a white, crystalline precipitate, occurring either at once or after several hours, when a concentrated cold solution of the salt is tested with a few drops of solution of potassium antimoniate. When thus indicated, the extent of such a contamination may be determined by repeatedly extracting a weighed amount of the powdered salt with boiling alcohol of the spec. grav. 0.890; the filtered liquid will then leave, upon evaporation, a residue, consisting principally of sodium nitrate with a little potassium nitrate. The residue is then dissolved in a little water, acidulated with hydrochloric acid, and the potassium completely precipitated by the addition of platinic chloride and a little alcohol; the liquid is subsequently filtered from the precipitate of potassio-platinic chloride, the excess of platinum removed by saturation with hydrogen sulphide, and, after filtration, evaporated to dryness, ignited at a gentle heat, and the residue finally weighed as sodium chloride: 100 parts of which correspond to 145.3 parts of sodium nitrate.

If potassium nitrate contains even a few per cent. of sodium nitrate, it will have a moist appearance, arising from the deliquescent character of the latter salt.

Metallic impurities will be indicated by a dark coloration or precipitate, when a solution of the salt, acidulated with hydrochloric acid, is tested with hydrogen sulphide, and, after filtration, if necessary, and neutralization with ammonia-water, by the subsequent addition of ammonium sulphide.

Estimation:

The proper amount of nitric acid contained in the salt may be conveniently determined by its ignition in a small porcelain crucible, at a red heat, with an equal weight of concentrated sulphuric acid, until it ceases to lose weight. One gram of the salt, if perfectly pure, will thus afford a residue of potassium sulphate, weighing 0.86 gram.

The determination of the proper amount of potassium in the salt, when free from sodium, may also readily be accomplished, as follows. A weighed amount (about 5 grams) of the potassium nitrate, contained in a porcelain capsule, is repeatedly evaporated with a solution of about 8 grams of oxalic acid to dryness, or until completely converted into potassium oxalate. The latter is then, by ignition, converted into potassium carbonate, which is dissolved in water, and, after the addition of a few drops of litmus solution, titrated with a standard solution of oxalic or sulphuric acid (page 82), as described under potassium carbonate, on page 474. The calculation may then be made with the consideration that one cubic centimeter of normal acid corresponds to 0.069 gram of potassium carbonate, or, as its equivalent, 0.101 gram of pure potassium nitrate.

TABLE *of the percentage strength of solutions of Potassium Nitrate of different specific gravities.*

Temperature 15° C. (59° F.).

Per cent. of KNO_3.	Specific gravity.	Per cent. of KNO_3.	Specific gravity.	Per cent. of KNO_3	Specific gravity.
1	1.00641	8	1.05197	15	1.09977
2	1.01283	9	1.05861	16	1.10701
3	1.01924	10	1.06524	17	1.11426
4	1.02566	11	1.07215	18	1.12150
5	1.03207	12	1.07905	19	1.12875
6	1.03870	13	1.08596	20	1.13599
7	1.04534	14	1.09286	21	1.14361

POTASSII PERMANGANAS.

POTASSIUM SEU KALIUM PERMANGANICUM SEU HYPERMANGANICUM.

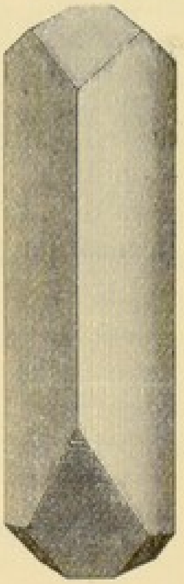
Permanganate of Potassium. Potassium Permanganate.

Ger. Uebermangansaures Kalium ; Fr. Permanganate de potasse ;
Sp. Permanganato de potasa.

$K_2Mn_2O_8$; 314.

Slender, dark-purple, prismatic crystals, belonging to the rhombic system (Fig. 151), of a metallic lustre, permanent in the air, and having a specific gravity of 2.71 ; they decrepitate when thrown upon burning coals, or when suddenly heated, and when mixed with sulphur or phosphorus, a mixture is obtained which takes fire or explodes violently on percussion or by heating; on exposure to a red heat, the salt gives off oxygen, and leaves a black residue of an alkaline reaction.

FIG. 151.



Potassium permanganate is soluble, with the exception of a slight brown residue, in 20 parts of water at 15° C. (59° F.), and in 3 parts of boiling water ; it is insoluble in alcohol, and is slowly decomposed in contact therewith. Its concentrated solution has a deep violet-red color, when highly diluted, a rose color, a sweet, astringent taste, is neutral, and becomes yellowish-brown when mixed and heated with alcohol.

Since permanganic acid is readily reduced, the solution of the salt is decomposed and decolorized by most organic substances, and by inorganic reducing agents—*e. g.*, sulphurous and oxalic acids, hydrogen sulphide, and all metallic subsalts. Potassium permanganate is, therefore, a powerful oxidizer, causing more or less violent reactions with many substances, and the combustion of inflammable bodies.

Examination:

The purity of the salt may readily be determined by the following simple test: 0.314 gram of the potassium permanganate is dissolved in water to the measure of one liter; another solution is then prepared by dissolving 0.63 gram of pure, crystallized oxalic acid in water, acidulated with sulphuric acid, to the measure of a liter ; if the potassium permanganate is pure, one cubic centimeter of the above permanganate solution will require for complete decoloration an equal volume, or exactly one cubic centimeter of the oxalic acid solution, and the amount of the latter, which is required to produce this reaction, will be, therefore, in direct proportion to the purity of the salt.

Nitrate and *Chloride.*—A portion of the decolorized liquid, as obtained by the preceding test, is carefully poured upon a cold solution of ferrous sulphate in strong sulphuric acid, when a dark-colored zone at the line of contact of the two liquids will indicate the presence of *nitrate:* another portion of the decolorized liquid is tested with a few drops of a solution of argentic chloride, when a permanent white turbidity or precipitate will reveal the presence of *chloride.*

Sulphate may be detected by boiling an aqueous solution of the salt with an excess of ammonia-water, until all the manganese is precipitated as hydrated oxide; the liquid is then filtered, and the colorless filtrate subsequently tested with barium chloride, when an ensuing white precipitate will reveal the presence of sulphate.

The United States Pharmacopœia directs that if 0.785 gram of the salt be dissolved in 50 cubic centimeters of boiling, distilled water, and 5 cubic centimeters of sulphuric acid be cautiously added, the solution so formed should require for complete decoloration not less than 24.7 cubic centimeters of the volumetric solution of oxalic acid (corresponding to at least 98.8 per cent. of pure potassium permanganate).

POTASSII SULPHAS.

POTASSIUM SEU KALIUM SULFURICUM.

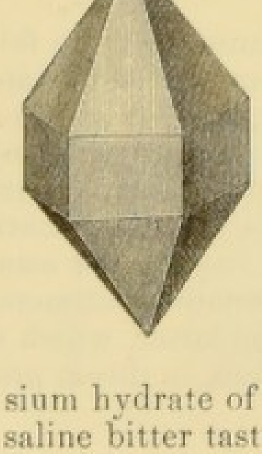
Sulphate of Potassium. Potassium Sulphate.

Ger. Schwefelsaures Kalium; Fr. Sulfate de potasse; Sp. Sulfato de potasa.

K_2SO_4; 174.

Hard, colorless, transparent, short, six-sided prisms, or pyramids, belonging to the rhombic system (Fig. 152), or a white, granular powder, anhydrous, and permanent in the air, and having a spec. grav. of 2.648; when heated, the crystals decrepitate strongly, and at a strong, red heat they fuse, without decomposition, solidifying again on cooling to a crystalline mass; at a white heat, they are to a slight extent volatilized. The salt, when heated on the looped end of a platinum-wire, imparts a violet color to the non-luminous flame.

FIG. 152.



Potassium sulphate is soluble in 9 parts of water at 15° C. (59° F.), in 4 parts of boiling water, sparingly soluble in glycerin, and insoluble in strong alcohol, and solution of potassium hydrate of the spec. grav. 1.35. Its aqueous solution has a saline bitter taste, is neutral, and forms white precipitates with tartaric acid or sodium bitartrate, and with solutions of salts of calcium, barium, or lead.

Examination:

Potassium bisulphate will be indicated by an acid reaction of the solution of the salt, and also by the loss of weight, when the salt, previously dried at 110° C. (230° F.), is heated nearly to redness in a covered porcelain crucible.

Sodium sulphate is indicated by the property of imparting a persistent yellow color to the non-luminous flame, and by a greater degree of solubility in cold water than that above stated; one part of the powdered salt, when dissolved in eight parts of boiling water, must, on cooling, give a crystalline deposit; otherwise sodium sulphate, or an admixture of more soluble salts, is indicated; in this case the solution may be tested with potassium metantimoniate for sodium, and, in another portion, after dilution with water and acidulation with nitric acid, by means of argentic nitrate for chloride. *Nitrate* will be detected in the aqueous solution of the salt, after the addition of a drop of indigo solution and a little concentrated sulphuric acid, by decoloration of the liquid upon heating.

Calcium and *Magnesium Salts.*—The aqueous solution of the salt is tested with ammonium oxalate, when a white precipitate will reveal the presence of *calcium;* after the removal of the latter, if present, by filtration, solution of ammonium chloride, ammonia-water, and sodium phosphate are added, when the formation of a white, crystalline precipitate will reveal the presence of *magnesium.*

Metallic impurities are detected in the warm aqueous solution, after acidulation with hydrochloric acid, by a dark coloration or turbidity upon saturation with hydrogen sulphide, or, after filtration, if necessary, and neutralization with ammonia-water, by the addition of ammonium sulphide. Potassium ferrocyanide should cause neither a blue (*iron*) nor a reddish (*copper*) coloration in the slightly acidulated solution.

POTASSII SULPHIS.

POTASSIUM SEU KALIUM SULFUROSUM.

Sulphite of Potassium. Potassium Sulphite.

Ger. Schwefligsaures Kalium; Fr. Sulfite de potasse; Sp. Sulfito de potasa.

$K_2SO_3 + 2H_2O$; 194.

Colorless, opaque, obliquely rhombic, octohedral crystals, or a white, crystalline powder, odorless, and somewhat deliquescent on exposure to a moist atmosphere; it contains two molecules (18.55

per cent.) of water of crystallization, which are lost by drying at a moderate heat; at a red heat it is decomposed, leaving an alkaline residue consisting of potassium sulphate, sulphide, and oxide, which imparts a brown color to moistened turmeric paper, and, on the addition of an acid, develops the odor of hydrogen sulphide.

Potassium sulphite is soluble in 4 parts of water at 15° C. (59° F.), and in 5 parts of boiling water, but is very sparingly soluble in alcohol. The aqueous solution possesses a bitter, saline, and sulphurous taste, a slightly alkaline reaction, and yields a white crystalline precipitate on the addition of a concentrated solution of sodium bitartrate; with argentic nitrate it yields a white precipitate, which becomes blackened on heating. On the addition of dilute hydrochloric or sulphuric acid to the solution of the salt, sulphur dioxide is liberated, which may be recognized by the odor of burning sulphur, but no turbidity is thereby produced in the liquid (distinction from hyposulphite).

Examination:

Sulphate may be detected in the dilute solution of the salt, strongly acidulated with hydrochloric acid, by a white precipitate on the addition of barium chloride.

Estimation:

About 0.3 gram of the salt is dissolved in 25 cubic centimeters of water, in a beaker, a little mucilage of starch added, and subsequently a decinormal solution of iodine (page 93) allowed to flow into the liquid from a burette until, with constant stirring, a permanent blue coloration of the liquid is just produced. The number of cubic centimeters of iodine solution required to produce this reaction, when multiplied by the decimal 0.0097, will represent the amount of pure, crystallized potassium sulphite, $K_2SO_3 + 2H_2O$, in the quantity employed, and therefrom its percentage purity may readily be calculated.

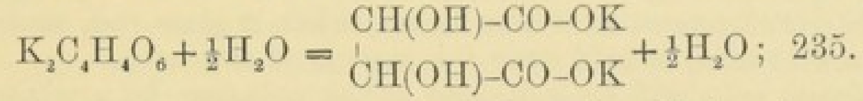
The United States Pharmacopœia directs that if 0.485 gram of the salt be dissolved in 25 cubic centimeters of water, and a little gelatinized starch added, at least 45 cubic centimeters of the volumetric solution of iodine should be required, until a permanent blue tint appears after stirring (corresponding to at least 90 per cent. of pure potassium sulphite).

POTASSII TARTRAS.

POTASSIUM SEU KALIUM TARTARICUM.

Tartrate of Potassium. Potassium Tartrate.

Ger. Weinsaures Kalium ; Fr. Tartrate de potasse ; Sp. Tartrato de potasa.



$$K_2C_4H_4O_6 + \tfrac{1}{2}H_2O = \begin{array}{l} CH(OH)\text{-}CO\text{-}OK \\ \mid \\ CH(OH)\text{-}CO\text{-}OK \end{array} + \tfrac{1}{2}H_2O;\ 235.$$

Colorless, semi-transparent, irregular, six-sided prisms, with dihedral summits, belonging to the monoclinic system, or a white, granular powder, of the specific gravity 1.96, and slightly deliquescent on exposure to a moist atmosphere. The salt contains one-half molecule (3.83 per cent.) of water of crystallization; when moderately heated, it melts, and, at a higher temperature, becomes charred and decomposed, with the evolution of empyreumatic vapors having the odor of burnt sugar; when strongly ignited at a red heat, it leaves a blackened alkaline residue, consisting of a mixture of carbon and potassium carbonate, which effervesces with acids, and imparts a violet color to the non-luminous flame.

Potassium tartrate is soluble in 0.7 part of water at 15° C. (59° F.), and in 0.5 part of boiling water, yielding a neutral solution, of a mild saline taste; it is but sparingly soluble in alcohol; its aqueous solution is decomposed by most acids and acidulous salts, forming, if not too dilute, a white, granular deposit of bitartrate, and yields with argentic nitrate a white precipitate, which becomes blackened on heating; the concentrated solution also produces with calcium, barium, and lead salts, white precipitates, which are soluble in dilute nitric acid.

Examination:

Potassium and Sodium Tartrate.—One part of the salt when shaken with an equal weight of water must afford a clear and complete solution; an incomplete solution may indicate an admixture of Rochelle salt. Such an admixture will also be indicated by a greater loss of weight on drying the salt at 100° C. (212° F.), pure Rochelle salt losing at this temperature 19.1 per cent. of its weight; and may be further ascertained by reducing a portion of the potassium tartrate, by ignition in a porcelain crucible, to carbonate, and then testing the residue in the non-luminous flame, when a persistent bright-yellow color will reveal the presence of sodium; the filtered solution of the residue may afterwards be tested by mixing it with an equal volume of solution of potassium metantimoniate; the occurrence of a white, crystalline deposit, at once or after several hours' standing, would indicate an adulteration with potassium and sodium tartrate.

Bicarbonate, *carbonate*, and *bitartrate* are recognized in the solution of the salt, the two former by effervescence on the addition of an acid, and by an alkaline reaction upon turmeric-paper; the latter by its relatively sparing solubility in cold water, and by an acid reaction upon blue litmus-paper.

Ammonium salts will be recognized by the development of the odor of ammonia, when a portion of the salt is heated, in a test-tube, with a strong solution of potassium or sodium hydrate, and by the development of white fumes, when a glass rod, moistened with acetic acid, is held over the mouth of the tube.

Calcium salts will be indicated in the solution by a white precipitate on the addition of solution of ammonium oxalate.

Sulphate and *chloride* may be detected in the dilute solution of the salt, when it is slightly acidulated with diluted nitric acid, and then tested, in separate portions, with argentic nitrate for chloride, and with barium nitrate for sulphate.

Metallic impurities are recognized in the concentrated solution of the salt, after acidulation with hydrochloric acid and subsequent filtration, by a dark coloration or turbidity upon saturation with hydrogen sulphide; or, after filtration, if necessary, by subsequent neutralization with ammonia-water, and the addition of ammonium sulphide.

Estimation:

2.938 grams of the salt are ignited in a porcelain crucible, at a red heat, until gases cease to be evolved; the alkaline residue is then extracted with warm water, the solution filtered into a beaker, a few drops of litmus solution added, and titrated, with the aid of a gentle heat, with a standard solution of oxalic or sulphuric acid (page 82), as described under potassium carbonate, on page 474. The number of cubic centimeters of normal acid solution which is thus required for the exact neutralization of the liquid, when multiplied by 4, will indicate, without further calculation, the percentage purity of the salt. By the employment of other quantities of the salt than precisely that above stated, the calculation may also readily be made, with the consideration that one cubic centimeter of the normal acid solution corresponds to 0.117 gram of pure crystallized potassium tartrate.

QUINIDINA.

CHINIDINUM SEU CONCHININUM.

Quinidine, Quinidia, or Conquinia.

Ger. Chinidin (Conchinin); Fr. Quinidine; Sp. Quinidina.

$C_{20}H_{24}N_2O_2 + 2H_2O$; 360.

Large, colorless, shining, four-sided prisms, containing 2 molecules (10 per cent.) of water of crystallization, and possessing a very bitter taste and a slightly alkaline reaction; when heated to 120° C. (248° F.), they lose their water of crystallization, and, when thus deprived of water, melt at 168° C. (334.4° F.), to a colorless liquid, which solidifies in a crystalline form upon cooling; at a higher temperature they are decomposed, and when strongly heated on platinum-foil, burn slowly away, leaving no residue.

Quinidine is soluble in 2000 parts of water at 15° C. (59° F.), and in 750 parts of boiling water, in 26 parts of alcohol, and 22 parts of ether at 20° C. (68° F.), and is also soluble in chloroform, carbon bisulphide, and benzol; it is freely soluble in water acidulated with sulphuric acid, and the solution displays a blue fluorescence. It neutralizes the acids, with the formation of neutral and acid salts, which are mostly well crystallizable. When exactly neutralized with diluted sulphuric acid, quinidine yields a solution which affords the same reactions as quinidine sulphate, and should respond to the tests for quality and purity, as described under the latter, on pages 503–504.

QUINIDINÆ SULPHAS.

CHINIDINUM SEU CONCHININUM SULFURICUM.

Sulphate of Quinidine, Quinidia, or Conquinia. Quinidine Sulphate.

Ger. Schwefelsaures Chinidin; Fr. Sulfate de quinidine;
Sp. Sulfato de quinidina.

$(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 2H_2O$; 782.

White, silky, prismatic needles or tufts, permanent in the air, and containing two molecules (4.6 per cent.) of water of crystallization, which are completely eliminated at 120° C. (248° F.); when strongly heated, they burn slowly away, leaving no residue.

Quinidine sulphate is soluble in 100 parts of water, and in 8 parts of alcohol at 15° C. (59° F.); in 7 parts of boiling water, and very soluble in boiling alcohol; it is freely soluble in acidulated water, and in 20 parts of chloroform at 15° C. (59° F.), but is almost insoluble in ether. The aqueous solution is neutral in its action upon litmus, possesses an intensely bitter taste, and, when acidulated with sulphuric acid, displays a blue fluorescence; with barium chloride it yields a white precipitate, insoluble in hydrochloric or nitric acid, and with chlorine water, followed by the addition of ammonia-water in slight excess, an emerald-green coloration is produced; if the addition of ammonia-water be preceded by a few drops of a solution of potassium ferrocyanide, the solution assumes a bright-red color. When to a solution of quinidine sulphate ammonia-water is added, a white precipitate of quinidine is produced, which is soluble in a considerable excess of the reagent, and in about thirty times its weight of ether. The neutral aqueous solution of quinidine sulphate yields upon the addition of a concentrated solution of potassium iodide a white granular precipitate of quinidine hydriodate, $C_{20}H_{24}N_2O_2.HI$, which is very sparingly soluble in water and in alcohol.

Examination:

Quinine, Cinchonine, and *Cinchonidine.*—These associate alkaloids of quinidine may readily be detected by the following simple test: 0.5 gram of the quinidine sulphate, together with an equal weight of neutral potassium iodide, is agitated with 10 cubic centimeters of water at about 60° C. (140° F.), the mixture allowed to cool, and stand for an hour, with frequent agitation, and filtered; to the filtrate one or two drops of ammonia-water are then added, when not more than a slight turbidity should be produced; a decided precipitate would reveal the presence of an undue proportion of the above-mentioned associate alkaloids.

In consequence of the previously existing confusion in the application of names, quinidine sulphate is liable to be confounded with the less valuable alkaloid cinchonidine. The admixture or substitution of the latter should therefore be the subject of a special test. It may be detected by its sparing solubility in chloroform, whereas quinidine sulphate is freely soluble in this liquid, and also by the following test: 0.5 gram of the salt is agitated for about half a minute with 30 cubic centimeters of water at 15° C. (59° F.), and immediately filtered; to the filtrate two or three cubic centimeters of a saturated solution of potassium and sodium tartrate (Rochelle salt) are added, when, if any considerable proportion of cinchonidine be present, a white, granular precipitate of cinchonidine tartrate, $(C_{19}H_{22}N_2O)_2C_4H_6O_6$, will gradually be formed.

Foreign Alkaloids or *Neutral Principles.*—An accidental admixture or substitution of foreign alkaloids, such as morphine, brucine, etc., or of neutral principles, such as salicin, may in most instances be detected by a coloration with concentrated sulphuric or nitric acid, whereas pure quinidine sulphate dissolves without color, or with the production of but a faint yellowish tint.

Inorganic impurities may be detected by a non-volatile residue when a little of the salt is ignited upon platinum-foil; or by an insoluble residue, when 0.5 gram of the salt is dissolved in a mixture of 3 cubic centimeters of chloroform and 2 cubic centimeters of absolute alcohol.

QUININA.

CHININUM. CHINIUM.

Quinine. Quinia.

Ger. Chinin; Fr. Quinine; Sp. Quinina.

$C_{20}H_{24}N_2O_2+3H_2O$; 378.

A snow-white, flaky, indistinctly crystalline powder, or minute, needle-like crystals, containing 3 molecules (14.28 per cent.) of water of crystallization, efflorescent on exposure to the air, and possessing an alkaline reaction. It melts at 57° C. (134.6° F.), and on the water-bath retains about 5.25 per cent. (about 1 molecule) of water of crystallization, which is completely expelled at 125° C. (257° F.); the anhydrous alkaloid then melts at 177° C. (350.6° F.), dissolves in hot water without previously fusing, and, on cooling, separates in needles; while the alkaloid, containing water of crystallization, first fuses in boiling water, and, on cooling, does not crystallize. When strongly heated on platinum-foil, it becomes charred and decomposed, and is finally completely dissipated.

Quinine is soluble in about 1600 parts of water at 15° C. (59° F.), in 700 parts of boiling water, in 6 parts of cold, or 2 parts of boiling, alcohol, in 22.7 parts of ether,* in about 5 parts of chloroform, and in 200 parts of glycerin; and is also soluble in carbon bisulphide, benzol, benzin, and ammonia-water; its solutions have a bitter taste, and a feebly alkaline reaction, and neutralize acids, with the formation of crystallizable salts. Quinine is freely soluble in diluted acids, forming solutions which exhibit an azure-blue fluorescence, caused by a change of refrangibility of the invisible chemical rays; this property is not displayed, however, by its solution in hydrochloric, hydriodic, or hydrobromic acids, and does not appear in such solutions by the subsequent addition of sulphuric acid; the fluorescence may likewise be made to disappear in solutions in which it has previously been produced, by the addition of the above-named acids, as also by solutions of chlorides, bromides, and iodides, with the exception of mercuric chloride and bromide. Concentrated sulphuric and nitric acids dissolve quinine without color, or with the production of but a slight yellowish tint.

Solutions of quinine and its salts are precipitated by the alkaline hydrates, carbonates, and bicarbonates, by calcium hydrate,

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* The solubility of quinine in ether differs according to the form of the alkaloid: requiring less when in the anhydrous or amorphous condition, as when freshly precipitated from its solution in acidulated water by ammonia-water, and directly shaken with ether, than in the crystalline or hydrated form, which it assumes when the precipitate is allowed to stand for several hours, previous to the addition of the ether.

by tannic and picric acids, by potassium ferrocyanide, potassio-mercuric iodide, iodinized potassium iodide, and most alkaloidal reagents; the precipitates with calcium, potassium, and sodium hydrates, and ammonia-water, are redissolved by a large excess of the precipitant.

Solutions of quinine and its salts, when mixed with chlorine-water, and afterwards with an excess of water of ammonia, assume a bright emerald-green color (thalleiochin); the green color passes into red upon the subsequent addition of potassium ferrocyanide; this characteristic reaction is most strikingly exhibited when, to the solution of quinine in chlorine-water, the solution of potassium ferrocyanide is first added, and subsequently the ammonia-water.

When a solution of quinine or its salts in acidulated water is precipitated with ammonia-water, and the turbid mixture is then divided into three portions in as many test-tubes, and these shaken severally with a little ether, chloroform, and benzol, the precipitate will be dissolved, and the liquids subside into two clear, colorless strata in each test-tube.

Examination:

The identity of quinine may be conclusively established by the above described physical characters, and its behavior towards reagents and solvents; it is also distinguished from many other alkaloids and crystallizable neutral principles, by affording no special coloration in contact with cold concentrated sulphuric or nitric acid.

Quinidine, *Cinchonine*, and *Cinchonidine*.—1 gram of the quinine is triturated in a mortar with 0.5 gram of ammonium sulphate and 5 cubic centimeters of distilled water, and the mixture thoroughly dried on the water-bath; the residue (which should be neutral to test-paper) is agitated with 10 cubic centimeters of distilled water, this mixture macerated at 15° C. (59° F.) for half an hour, then filtered, and to 5 cubic centimeters of the filtrate, in a test-tube, 7 cubic centimeters of ammonia-water, spec. grav. 0.960, are added, without shaking; on gently turning the test-tube, there should be formed, either at once, or after a short time, a clear liquid; an ensuing permanent precipitate would indicate an admixture of more than about 1 per cent. of cinchonidine and quinidine, and of more than traces of cinchonine. If the temperature during maceration was 16° C. (60.8° F.), 7.5 cubic centimeters of ammonia-water may be added, and if 17° C. (62.6° F.), 8 cubic centimeters may be employed.

Inorganic impurities may readily be detected by a non-volatile residue, when a small portion of the quinine is strongly heated on platinum-foil.

When dissolved in dilute sulphuric acid, quinine should respond to the tests of purity for quinine sulphate, as described under the latter, on pages 521–523.

Estimation of the Alkaloids in Cinchona-Barks:

The therapeutical value of the cinchona-barks is due to the alkaloids contained in the bark, of which the principal ones are *quinine*, *quinidine*, *cinchonine*, and *cinchonidine*. The estimation of the commercial value, therefore, depends upon the determination of the quantity of these alkaloids, and in particular of the first one, in a known weight of the bark. Of the numerous methods employed for this purpose, the following ones are simple, expeditious, and reliable:

I. Flückiger's Process:

From a large number of pieces of the bark, small fragments are cut and reduced to a fine powder, so as to represent as nearly as possible an average specimen of the bark to be examined; 20 grams of the powder, contained in a porcelain capsule, are moistened with ammonia-water, and, after standing for an hour, mixed with 80 grams of hot water; it is then allowed to cool, subsequently intimately mixed with milk of lime (prepared by triturating 5 grams of dry caustic lime with 50 grams of water), and the mixture evaporated upon the water-bath until it is uniformly converted into small, somewhat moist, crumb-like particles. This is then transferred to a cylindrical glass tube (Fig. 153), which at *A* is 2.5 centimeters (1 inch) wide, and from *A* to *B* 16 centimeters (6.4 inches) long. At *B* a small brass sieve is inserted, upon which a disk of filtering paper is secured by means of a bunch of loose cotton. The powder having been quite compactly adjusted upon the cotton, it is again covered at *A*, as in *B*, with a little cotton; the latter having been previously employed for removing the last traces of the powdered bark from the capsule. At *E* a tightly fitting cork is inserted, which is penetrated by the tube *R*, and connected with an inverted small glass condenser. The lower end of the apparatus, *C*, is tightly connected by means of a cork with the flask *K*, containing about 100 cubic centimeters of ether. The flask is then heated by means of a constant water-bath; and in the same degree as the vapors of ether are expelled through *D*, they become again condensed in the condenser, drop through the tube *R* upon the powder at *A*, penetrate the entire column of powder *A B*, and flow at *C*, saturated with alkaloid, into the flask *K*. To effect the complete exhaustion of the bark by the ether, the operation of displacement should be continued for nearly a day, but when once in progress it requires but little attention. In order to determine whether the bark is completely exhausted, a few drops of the ether, falling at *C*, are collected in a small test-tube, and tested with potassio-mercuric

FIG. 153.

iodide; which should afford no turbidity if the process of extraction has been sufficiently long continued. When this is accomplished, 36 cubic centimeters of one-tenth normal hydrochloric acid (3.65 grams HCl in 1 liter) are added to the ether in the flask *K*, the ether distilled off, and subsequently so much hydrochloric acid added as may be required to impart to the liquid an acid reaction. The liquid is then filtered from the separated mixture of fat, chinovin, and chlorophyll, and, after having become thoroughly cooled, 40 cubic centimeters of one-tenth normal sodium hydrate solution (4 grams NaOH in 1 liter) are added, and the whole allowed to repose until the precipitate has subsided, and the supernatant liquid has become perfectly clear. Sodium hydrate is then gradually added to the liquid as long as a precipitate continues to be produced, for which purpose a solution of the spec. grav. 1.3 is the most serviceable. The precipitated alkaloids are afterwards collected on a filter, and gradually washed with a little cold water until a few drops of the washings, when allowed to flow on the surface of a cold, saturated, neutral, aqueous solution of quinine sulphate, cease to produce a turbidity. The drained precipitate, contained on the filter, is then gently pressed between bibulous paper, and dried by exposure to the air; it may afterwards readily be removed from the paper without loss, and, after thoroughly drying upon a watch-glass over sulphuric acid, is finally dried at 100° C. (212° F.), and weighed; the weight of the precipitate, multiplied by 5, will give the total percentage of mixed alkaloids in the bark. If it be desired to establish the presence of quinine in the precipitate, a small portion of it may be dissolved in acidulated water, and subsequently tested with chlorine-water and ammonia, as described on page 506.

Separation of the Alkaloids.

When the separation and quantitative estimation of the respective alkaloids are required, the following method of De Vrij may be employed. The powdered mixed alkaloids are treated with ten times their weight of ether, and, after agitation, left at rest till the next day. By this operation the alkaloids are separated into two parts, viz., one (A) soluble in ether, and another (B) insoluble in that liquid. The part soluble in ether contains the quinine and the amorphous alkaloid, together with traces of quinidine, while the insoluble part contains the cinchonine, cinchonidine, and quinidine. These two parts are separated by filtration, the insoluble portion washed with a little ether, and the ethereal solution either directly evaporated, or the ether recovered by distillation.

A. Part Soluble in Ether.—The ether having been evaporated, and the residue dried at 100° C. (212° F.), this may in many cases be practically considered as consisting simply of quinine. If, however, the estimation of the quinidine and amorphous alkaloid is required, the residue is dissolved in sufficient acetic acid to afford a neutral solution, and an alcoholic solution of potassium iodide added, which will produce a sandy precipitate of quinidine hydriodate,* $C_{20}H_{24}N_2O_2.HI$. One part of this hydriodate, when dried at 100° C. (212° F.), represents 0.717 part of anhydrous quinidine. To the warmed filtrate from the latter precipitate ammonia-water is added until it ceases to produce a precipitate; the mixture is then shaken at once with ether, the ethereal solution allowed to evaporate, and the residue dried at 100° C. (212° F.). This residue will consist principally of quinine, accompanied possibly by amorphous alkaloid and quinamine. In order to exclude the latter bases, which are always only present in very small amount, the ethereal residue is dissolved in 10 parts of diluted alcohol, spec. grav. 0.915, the solution exactly neutralized with alcoholic sulphuric acid, and as much of the latter afterwards added as was required for neutralization. To this solution an alcoholic solution of iodine is carefully added until a precipitate ceases to be formed. If a considerable amount of quinine is present, there will appear immediately a black precipitate of quinine iodo-sulphate or *herapathite*, but if the amount of quinine is only very small, it may happen that no precipitate will be formed at once, and in the latter case only a small amount of iodine should be added, and the liquid, after having been well stirred with a glass rod, is left at rest till the next day. If quinine is really present, it will then be precipitated in the form of herapathite, which may be collected on a filter, washed with strong alcohol, and first dried upon bibulous paper and afterwards at 100° C. (212° F.). One part of the herapathite, when thus dried, represents, in accordance with the formula $(C_{20}H_{24}N_2O_2)_4+3H_2SO_4+2HI+4I$, 0.55 part of pure quinine.

To the liquid separated from the herapathite, a few drops of sulphurous acid are added, whereby the iodo-sulphate of amorphous alkaloid is converted into hydriodate, and the reddish-brown color of the solution disappears. The solution is then carefully neutralized with sodium hydrate, heated on the water-bath to expel the alcohol, and a solution of sodium hydrate in slight excess subsequently added, by which the amorphous alkaloid will be precipitated, including quinamine if present.

B. Part Insoluble in Ether.—This is converted into neutral acetate by the addition of a sufficient quantity of acetic acid, and to the solution potassium and sodium tartrate (Rochelle salt) in slight excess is subsequently added. After stirring with a glass

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* If only traces of quinidine be present, as is usually the case, no precipitate will be formed; but simply white striæ on the surfaces of the glass which have come in contact with the glass rod.

rod, the solution is left at rest for a day, when, if cinchonidine is present in appreciable quantity, its tartrate will be separated in a crystalline form, while the other tartrates remain dissolved. The cinchonidine tartrate is collected on a filter, washed with a little cold water, and, after first drying upon bibulous paper, is finally dried at 100° C. (212° F.), and weighed. One part of cinchonidine tartrate represents, in accordance with the formula $(C_{19}H_{22}N_2O)_2.C_4H_6O_6$, 0.796 part of pure cinchonidine.

To the filtrate from the latter precipitate, a solution of potassium iodide is added, and the whole well stirred with a glass rod. The quinidine will thus be precipitated as hydriodate, in the form of a sandy crystalline powder; it is collected on a filter, washed with a little cold water, and, after first drying on bibulous paper, is finally dried at 100° C. (212° F.), and weighed. One part of this hydriodate represents 0.717 part of pure anhydrous quinidine.

The filtrate from the quinidine hydriodate is finally precipitated with sodium hydrate, whereby the cinchonine is obtained; this is collected on a filter, washed with a little cold water, and, after first drying between bibulous paper, is finally dried at 100° C. (212° F.), and weighed.

II. Squibb's Process:

To 1.25 grams (19.29 grains) of well-burnt lime, contained in a 10-centimeter (4-inch) capsule, 30 cubic centimeters (1 fluidounce) of hot water are added, and, when the lime is slaked, the mixture is stirred, and 5 grams (77.16 grains) of the powdered cinchona are added, the mixture very thoroughly stirred, and digested in a warm place for a few hours, or over night. The mixture is then dried at a low temperature on a water-bath, rubbed to powder in the capsule, and transferred to a flask of 100 cubic centimeters (3.3 fluidounces) capacity, and 25 cubic centimeters (0.8 fluidounce) of amylic alcohol added. The flask is afterward corked, and digested in a water-bath at a boiling temperature and with frequent, vigorous shaking for four hours. It is then allowed to cool, and 60 cubic centimeters (2 fluidounces) of stronger ether, spec. grav. 0.728, added, and again shaken vigorously and frequently during an hour or more. The liquid is now filtered through a double filter of 10 centimeters (4 inches) diameter into a flask of 150 cubic centimeters (5 fluidounces) capacity, and the residue transferred to the filter. The flask is rinsed and the rinsings brought on to the filter with a mixture of 10 volumes of amylic alcohol and 40 volumes of stronger ether, and the residue on the filter percolated with 15 cubic centimeters (0.5 fluidounce) of the same mixture, added drop by drop from a pipette to the edges of the filter and surface of the residue. The residue is afterward returned to the flask from whence it came, 30 cubic centimeters (1 fluidounce) of the amylic alcohol and ether mixture added, shaken vigorously for five minutes or more, and the whole returned to the filter, and the residue again percolated with 15 cubic centimeters of the menstruum, applied drop by drop from a pipette, as before. The filter and residue are now put aside in order that it may be afterward tested in regard to the degree of exhaustion.

The ether is now boiled off from the filtrate in the flask by means of a water-bath, taking great care to avoid the ignition of the ether vapor, and also to avoid explosive boiling, by having a long wire in the flask. When boiled down as far as practicable in the flask, the remainder is transferred to a tared capsule of 10 centimeters (4 inches) diameter, and the evaporation continued on a water-bath until the contents are reduced to about 6 grams (92 grains). This is transferred to a flask of 100 cubic centimeters (3.3 fluidounces) capacity, rinsing the capsule with not more than 4 cubic centimeters (64 minims) of amylic alcohol, and adding the same to the contents of the flask. 6 cubic centimeters (96 minims) of water and 4 cubic centimeters (64 minims) of normal solution of oxalic acid are then added, and the mixture shaken vigorously and frequently during half an hour. The mixture, while intimately well mixed, is poured on to a well-wetted double filter of 12 centimeters (4.75 inches) diameter, and the aqueous solution filtered from the amylic alcohol into a tared capsule of 10 centimeters (4 inches) diameter. The filter and contents are washed with 5 cubic centimeters (80 minims) of water, applied drop by drop from a pipette to the edges of the filter and surface of the amylic alcohol. The amylic alcohol is then poured back into the flask over the edge of the filter and funnel, rinsing the last portion in with a few drops of water. 10 cubic centimeters (160 minims) of water and 1 cubic centimeter (16 minims) of normal solution of oxalic acid are now added, again shaken vigorously for a minute or two, and the whole returned to the wetted filter, and the aqueous portion filtered off into the capsule with the first portion. The amylic alcohol is again returned to the flask, and the washings repeated with the same quantities of water and normal oxalic acid solution. When this has drained through, the filter and contents are washed with 5 cubic centimeters (80 minims) of water, applied drop by drop from a pipette. The total filtrate in the capsule is evaporated on a water-bath, at a low temperature, until it is reduced to about 15 grams (241 grains) and this transferred to a flask of 100 cubic centimeters (3.3 fluidounces) capacity, rinsing the capsule with 5 cubic centimeters (80 minims) of water, and adding this to the contents of the flask. 20 cubic centimeters (0.66 fluidounce) of purified chloroform are now first added, and then 6.1 cubic centimeters (98 minims) of normal solution of sodium hydrate, and shaken vigorously for five minutes or more. While still intimately mixed by the shaking, the mixture is poured upon a filter of 12 centimeters (4.75 inches) diameter, well wetted with water. When the aqueous solution has passed through, leaving the chloroform on the filter, the filter and chloroform are washed with 5 cubic centimeters (80 minims) of water, applied drop by drop. The chloroform solution is then, by making a pin-hole in the point of the filter, transferred to another filter of 10 centimeters (4 inches) diameter, well wetted with chloroform, and placed over a tared flask of 100 cubic centimeters (3.3 fluidounces) capacity. The watery filter is washed through into the chloroform-wet filter with 5 cubic centimeters (80 minims) of purified chloroform, and, when this has passed through into the flask, the chloroform-wet filter is also washed with 5 cubic centimeters (80 minims) of chloroform, applied drop by drop to the edges of the filter. When the whole chloroform solution of alkaloids is collected in a flask, the chloroform is boiled off to dryness in a water-bath, when the alkaloids will be left in warty groups of radiating crystals, adhering over the bottom and sides of the flask. The flask is then placed on its side in a drying-oven, and dried at 100° C. (212° F.) to a constant weight. The weight of the contents, multiplied by 20, gives the percentage of the total alkaloids of the cinchona in an anhydrous condition, to within 0.1 or 0.2 per cent., if the process has been well managed.

Estimation of Quinine.

Into the flask containing the total alkaloids, after these have been weighed, are placed 5 grams (78 grains) of glass, which has been ground up in a mortar to a mixture of coarse and fine powder, and 5 cubic centimeters (80 minims) of stronger ether added. The flask is then corked, and shaken vigorously until, by means of the glass, all the alkaloids have been detached from the flask and ground up in the presence of the ether into fine particles. In this way the definite quantity of ether which is large enough to dissolve all the quinine that could possibly be present, becomes entirely saturated with alkaloids in the proportion of their solubility, and the solution will necessarily embrace all the very soluble ones as the quinine.

Two test-tubes are now marked at the capacity of 10 cubic centimeters (160 minims each), and a funnel and filter of 7 centimeters (2.8 inches) diameter placed over one of them. The filter is well wetted with ether, and the mixture of alkaloids, ether, and glass poured on to it from the flask. The flask is rinsed out two or three times on to the filter with fresh ether, the filter then washed, and the glass percolated with fresh ether, applied drop by drop from a pipette, until the liquid in the test-tube reaches the 10-cubic-centimeter (160-minim) mark. The funnel is then changed to the other test-tube, and the washing and percolation with ether continued until the mark on the second test-tube is reached by the filtrate. The contents of the two test-tubes are poured into two small tared capsules, evaporated to a constant weight, and weighed. The first capsule will contain what may be called the ether-soluble alkaloids, and if from the weight of these the weight of the residue in the second capsule be subtracted, the remainder will be the approximate weight of the quinine extracted from the 5 grams of bark. These weights, multiplied by 20, will give the percentage of ether-soluble alkaloids and of quinine.

III. Process of the United States Pharmacopœia:

1. *For Total Alkaloids.*

Twenty grams of the cinchona, in very fine powder, and fully dried at 100° C. (212° F.), are thoroughly mixed with 5 grams of lime which has previously been made into a milk with 50 cubic centimeters of distilled water, and the mixture completely dried at a temperature not above 80° C. (176° F.). The dried mixture is digested with 200 cubic centimeters of alcohol, in a flask, near the temperature of boiling, for one hour, and, when cool, the mixture poured upon a filter of about 15 centimeters (6 inches) diameter. The flask is rinsed and the filter washed with 200 cubic centimeters of alcohol, used in several portions, and allowing the filter to drain after the use of each portion. To the filtered liquid enough diluted sulphuric acid is added to render the liquid acid to test-paper, any resulting precipitate (calcium sulphate) allowed to subside, the liquid decanted, in portions, upon a very small filter, and the residue and filter washed with small portions of alcohol. The filtrate is then distilled or evaporated to expel all the alcohol, allowed to cool, passed through a small filter, and the latter washed with distilled water slightly acidulated with diluted sulphuric acid, until the washings are no longer made turbid by solution of sodium hydrate. To the filtered liquid, concentrated to the volume of about 50 cubic centimeters, when nearly cool, enough solution of sodium hydrate is added to render it strongly alkaline. The precipitate is collected on a wetted filter, allowed to drain, and washed with small portions of distilled water (using as little as possible), until the washings give but a slight turbidity with test solution of barium chloride, and the filter drained by laying it upon blotting or filter papers until it is nearly dry.

The precipitate is then carefully detached from the filter, and transferred to a weighed capsule; the filter is washed with distilled water acidulated with diluted sulphuric acid, the filtrate made alkaline with solution of sodium hydrate, and, if a precipitate results, this is washed on a very small filter, allowed to drain well, and also transferred to the capsule. The contents of the latter are now dried at 100° C. (212° F.) to a constant weight, cooled in a desiccator, and weighed. The number of grams, multiplied by 5, equals the percentage of total alkaloids in the cinchona.

2. *For Quinine.*

To the total alkaloids from 20 grams of cinchona, previously weighed, distilled water acidulated with diluted sulphuric acid is added, until the mixture remains for 10 or 15 minutes after digestion just distinctly acid to test-paper. It is then transferred to a weighed beaker, rinsing with distilled water, and adding of this enough to make the whole weigh 70 times the weight of the alkaloids. Solution of sodium hydrate, previously well diluted with distilled water, is now added, in drops, until the mixture is exactly neutral to test-paper, digested at 60° C. (140° F.), for 5 minutes, then cooled to 15° C. (59° F.), and maintained at this temperature for half an hour. If crystals do not appear in the glass vessel, the total alkaloids do not contain over 8 per cent. of their weight of quinine (corresponding to 9 per cent. of crystallized sulphate of quinine). If crystals appear in the mixture, the latter is passed through a filter not larger than necessary, prepared by drying two filter papers of 5 to 9 centimeters (2 to 3.5 inches) diameter, trimming them to an equal weight, folding them separately, and placing one within the other so as to make a plain filter four-fold on each side. When the liquid has drained away, the filter and contents are washed with distilled water of a temperature of 15° C. (59° F.), added in small portions, until the entire filtered liquid weighs 90 times the weight of the alkaloids taken. The filter is then dried, without separating its folds, at 60° C. (140° F.), to a constant weight, allowed to cool, and the inner filter and contents weighed, taking the outer filter for a counter-weight. To the weight of effloresced quinine sulphate so obtained, 11.5 per cent. of its amount is added (for water of crystallization), and 0.12 per cent. of the weight of the entire filtered liquid added (for solubility of the crystals at 15° C., or 59° F.). The sum in grams, multiplied by 5, equals the percentage of crystallized quinine sulphate equivalent to the quinine in the cinchona.

IV. Process of the Pharmacopoea Germanica:

Twenty grams of the finely powdered bark are repeatedly and actively agitated with a mixture of 10 grams of ammonia-water, spec. grav. 0.960, 20 grams of alcohol, spec. grav. 0.830 to 0.834, and 170 grams of ether, spec. grav. 0.724 to 0.728, and, after standing for a day, 120 grams of the liquid are poured off. After the addition of 3 cubic centimeters of normal hydrochloric acid (containing 36.5 grams HCl in 1 liter), the ether is removed by distillation or evaporation, and, if necessary, so much hydrochloric acid added as is required to acidulate the solution.* This is then

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* In consequence of the small amount of liquid obtained after the removal of the alcohol and ether, Prof. Flückiger suggests that the solution be evaporated

filtered, and the cooled liquid mixed with 3.5 cubic centimeters of normal solution of potassium hydrate (page 87). After the alkaloids have separated, solution of potassium hydrate is added to the clear supernatant liquid, until no further precipitate is produced. The entire precipitate is finally collected upon a filter, and gradually washed with a little water until the drops of liquid escaping from the filter, when allowed to fall upon the surface of a saturated neutral solution of quinine sulphate in cold water, no longer produce a turbidity. After being allowed to drain, the alkaloids are gently pressed between bibulous paper, then dried by exposure to the air sufficiently to admit of bringing them into a glass capsule, in which they are placed over sulphuric acid, and finally completely dried in a water-bath.

QUININÆ HYDROBROMAS.

CHININUM SEU CHINIUM HYDROBROMICUM SEU HYDROBROMATUM.

Hydrobromate of Quinine or Quinia. Quinine Hydrobromate.

Ger. Bromwasserstoffsaures Chinin; Fr. Hydrobromate de quinine;
Sp. Bromhidrato de quinina.

$C_{20}H_{24}N_2O_2.HBr + 2H_2O$; 440.8.

Colorless, lustrous, prismatic, or needle-shaped crystals, containing two molecules (8.16 per cent.) of water of crystallization; they are permanent in ordinary air, but efflorescent in a warm atmosphere; when exposed to a moderate heat the salt fuses, and, when strongly heated, burns slowly away, leaving no residue.

Quinine hydrobromate is soluble in about 16 parts of water, and in 3 parts of alcohol at 15° C. (59° F.); in 1 part of boiling water, and in less than 1 part of boiling alcohol; in 6 parts of ether, in 12 parts of chloroform, and moderately soluble in glycerine. The aqueous solution possesses a very bitter taste, is neutral in its action upon litmus, and, when acidulated with sulphuric acid, displays a blue fluorescence; if chlorine-water be added to the solution, and subsequently ammonia-water in excess, a bright emerald-green coloration is produced.

The aqueous solution of quinine hydrobromate, if not too dilute, yields with ammonia-water a white precipitate of quinine, which is readily dissolved by an excess of the precipitant, or when

to dryness, and the hydrochlorates of the alkaloids again taken up with 30 cubic centimeters of warm water, or, preferably, to apply originally 30 cubic centimeters of *decinormal* hydrochloric acid, and by distilling off the alcohol and ether to concentrate the liquid to 30 cubic centimeters In all cases the alcohol and ether should be completely removed before the addition of the potassa solution.

mixed and agitated with ether; with argentic nitrate it yields a white precipitate of argentic bromide, which, when collected, and washed with a little water, is insoluble in diluted nitric acid, or in a solution of ammonium carbonate.

Examination:

With reference to its mode of preparation, quinine hydrobromate should be examined for its possible contamination with quinine sulphate, or with barium bromide, by acidulating its aqueous solution with nitric acid, and subsequently testing, in separate portions, with barium chloride for the former, and with diluted sulphuric acid for the latter. If either of these impurities are found, it will, of course, exclude the presence of the other.

Water.—The presence of free water may be ascertained by the determination of the loss of weight upon drying 1 gram of the salt at the temperature of 100° C. (212° F.) until its weight remains constant. When dried at this temperature the residue should weigh not less than 0.918 gram, otherwise an undue percentage of water is indicated.

Quinidine, *Cinchonine*, and *Cinchonidine.*—One and one-half grams of the salt are dissolved in 15 cubic centimeters of hot distilled water, the solution stirred with 0.6 gram of crystallized sodium sulphate in powder, the mixture maintained at 15° C. (59° F.) for half an hour, and then drained through a filter just sufficiently large to contain it until 5 cubic centimeters of filtrate are obtained. Upon proceeding further, as directed under *Quinina*, on page 506, the results there stated should be obtained.

The further examination of quinine hydrobromate for other foreign organic or inorganic substances or alkaloids is the same as described under *Quininæ Sulphas*, on pages 522, 523.

QUININÆ BISULPHAS.

CHININUM BISULFURICUM. CHININUM SEU CHINIUM SULFURICUM ACIDUM.

Bisulphate of Quinine or Quinia. Acid Sulphate of Quinine. Quinine Bisulphate.

Ger. Saures Schwefelsaures Chinin; Fr. Sulfate acide de quinine; Sp. Bisulfato de quinina.

$$C_{20}H_{24}N_2O_2.H_2SO_4+7H_2O;\ 548.$$

Colorless, transparent, prismatic crystals, belonging to the rhombic system, or small needles, efflorescent, and assuming an opaque whiteness on exposure to the air. The salt contains 7 molecules (22.99 per cent.) of water of crystallization, which are lost by drying at 100° C. (212° F.); when thus deprived of water, and heated in a small porcelain capsule, it melts at 135° C. (275° F.), and is converted into quinicine bisulphate; at a higher temperature, it becomes yellow, then red, and is finally carbonized with the evolution of reddish vapors; when strongly heated on platinum-foil, it burns slowly away, leaving no residue.

Quinine bisulphate is soluble in about 10 parts of water and in 32 parts of alcohol at 15° C. (59° F.), and very freely soluble in boiling water and in boiling alcohol. Its aqueous solution possesses an intensely bitter taste and an acid reaction, and displays a vivid blue fluorescence; with barium chloride it gives a white precipitate, insoluble in hydrochloric acid, and with chlorine-water followed by the addition of ammonia, a bright emerald-green color is produced; when ammonia-water is added to the solution, a precipitate is produced which is readily soluble in an excess of the precipitant, as also when mixed and agitated with ether.

If to a solution of 1 part of quinine bisulphate in 20 parts of acetic acid and 5 parts of alcohol, a few drops of a saturated alcoholic solution of iodine are added, a precipitate of quinine iodosulphate, $(C_{20}H_{24}N_2O_2)_4 + 3H_2SO_4 + 2HI + 4I$, or *herapathite*, will be produced; this compound forms thin laminar crystals or groups of stellate needles, of a bright green color and metallic lustre, and is very sparingly soluble in water and in alcohol.

Examination:

Water.—The presence of free water may be ascertained by the determination of the loss of weight upon drying 1 gram of the salt at the temperature of 100° C. (212° F.) until its weight remains constant. When dried at this temperature, the residue of anhydrous quinine bisulphate so obtained should weigh not less than 0.77 gram, otherwise an undue percentage of water is indicated.

Quinidine, *Cinchonine*, and *Cinchonidine.*—One gram of quinine bisulphate, previously dried at 100° C. (212° F.), is agitated with 8 cubic centimeters of distilled water, the mixture made exactly neutral to test-paper by the cautious addition of ammonia-water, and the volume of liquid increased to the measure of 10 cubic centimeters by the addition of distilled water. The mixture is then macerated at 15° C. (59° F.) for half an hour, when, upon proceeding further as directed under *Quinina*, on page 506, the results there stated should be obtained.

The further examination of quinine bisulphate for other foreign organic or inorganic substances or alkaloids is the same as described under *Quininæ Sulphas*, on pages 522, 523.

QUININÆ HYDROCHLORAS.

QUINIÆ MURIAS. CHININUM SEU CHINIUM HYDROCHLORICUM SEU HYDROCHLORATUM

Hydrochlorate of Quinine or Quinia. Quinine Hydrochlorate.

Ger. Chlorwasserstoffsaures Chinin; Fr. Hydrochlorate de quinine; Sp. Clorhidrato de quinina.

$C_{20}H_{24}N_2O_2.HCl+2H_2O$; 396.4.

White, silky needles, or a crystalline powder, containing two molecules (9.08 per cent.) of water of crystallization; it is permanent at ordinary temperatures, but slightly efflorescent in a warm atmosphere; when heated to from 100 to 110° C. (212 to 230° F.) it loses its water of crystallization, fuses at a higher temperature, and, when strongly heated on platinum-foil, burns slowly away, leaving no residue.

Quinine hydrochlorate is soluble in 34 parts of water and in 3 parts of alcohol at 15° C. (59° F.); in 1 part of boiling water, and very soluble in boiling alcohol; and also soluble in 9 parts of chloroform, in the latter instance accompanied by the separation of water; if, however, the salt be previously rendered anhydrous by gently heating, it requires but its own weight of chloroform for solution. The salt is also freely soluble in acidulated water, and in diluted as well as in concentrated acids, without change of color; its aqueous solution is neutral, possesses a bitter taste, and, when sufficiently diluted, displays a slight blue fluorescence on the addition of dilute sulphuric acid; with chlorine-water, followed by the addition of ammonia-water in excess, it affords a bright emerald green coloration, and if the ammonia-water is preceded by the addition of a few drops of a solution of potassium ferrocyanide, a red color is produced; the aqueous solution, acidulated with nitric acid, yields a white, curdy precipitate with argentic nitrate, soluble in an excess of ammonia-water, and a white precipitate with ammonia-water, which, however, is dissolved by ether, alcohol, chloroform, or benzol, when added and agitated with the liquid.

Examination:

Water.—The presence of free water may be ascertained by the determination of the loss of weight upon drying 1 gram of the salt at the temperature of 100° C. (212° F.) until its weight remains constant. When dried at this temperature, the residue should weigh not less than 0.91 gram, otherwise an undue percentage of water is indicated.

Quinidine, *Cinchonine*, and *Cinchonidine*.—These associate alkaloids of quinine may readily be detected by *Hesse's* test, as described under *Quininæ Sulphas*, on page 521. In the application of the test, 0.5 gram of quinine hydrochlorate and 0.25 gram of crystallized sodium sulphate are added to 10 cubic centimeters of water at 50–60° C. (122–140° F.), contained in a test-tube; the mixture is well shaken several times, and, after standing for ten minutes, 5 cubic centimeters of the clear filtered solution are introduced into a graduated tube (Fig. 154, page 521), 1 cubic centimeter of ether is added, and subsequently 5 drops of ammonia-water, spec. grav. 0.960. The tube is now closed with a cork, is agitated gently, and allowed to stand for several hours. If the ethereal layer is now examined with a lens, it should show no evidence of crystals; the separation of crystals being evidence of the presence of more than traces of the above-mentioned associate alkaloids.

The detection of an admixture of the above-mentioned alkaloids may also be accomplished by the following method: 0.3 gram of the quinine hydrochlorate is agitated with 6 cubic centimeters of distilled water, the mixture macerated at 15° C. (59° F.) for half an hour, and filtered; 4 cubic centimeters of the filtrate are then diluted with 100 cubic centimeters of distilled water, and of the diluted solution 5 cubic centimeters are taken in a test-tube, and 7 cubic centimeters of ammonia-water, spec. grav. 0.960, added, without shaking; on gently turning the tube, closed by the finger, there should be formed, either at once, or after a short time, a clear liquid; an ensuing turbidity would indicate an admixture with the above-mentioned associate alkaloids of quinine.

In consequence of the occasional occurrence of an accidental admixture or substitution of morphine hydrochlorate, the latter salt may also be tested for. It may readily be detected in the aqueous solution of the salt, by agitating it with a few drops of a solution of iodic acid, when, if morphine be present, iodine will be liberated, and upon subsequent agitation with a few drops of chloroform or carbon bisulphide, the characteristic violet color will be imparted to these liquids. The same reducing action may also be shown, by adding to the solution of the salt a few drops of a solution of potassium ferricyanide and ferric chloride, and subsequently hydrochloric acid in slight excess, when, in the presence of morphine, a deep-blue coloration or precipitate will be produced.

The presence of morphine, as also of many other foreign alkaloids or neutral principles, will likewise be indicated by a red or dark coloration in contact with concentrated nitric or sulphuric acid, whereas pure quinine hydrochlorate affords no coloration, or but a pale yellowish tint is produced.

With reference to the method of its preparation, its aqueous solution needs, moreover, to be examined for contamination with quinine sulphate or with barium chloride, by acidulation with nitric acid, and subsequent testing, in separate portions, with barium nitrate for the former, and with diluted sulphuric acid for the latter. Either of these impurities, of course, excludes the presence of the other, without impairing the solubility of the salt.

The further examination of quinine hydrochlorate for quality and purity is the same as that of quinine sulphate, as described on pages 522, 523.

QUININÆ SULPHAS.

CHININUM SEU CHINIUM SULFURICUM.

Sulphate of Quinine or Quinia. Quinine Sulphate.

Ger. Schwefelsaures Chinin ; Fr. Sulfate de quinine ; Sp. Sulfato de quinina.

$$(C_{20}H_{24}N_2O_2)_2H_2SO_4+7H_2O;\ 872.$$

Fine, silky, slightly flexible, snow-white needles, interlaced among one another, or grouped in small, star-like tufts; the crystals contain seven molecules (14.45 per cent.) of water of crystallization, five of which (corresponding to 9.85 per cent.) are lost by long exposure to a warm and dry atmosphere, or more readily at a temperature of 50 to 60° C. (122 to 140° F.), while the remaining two molecules (4.6 per cent.) are slowly expelled at a temperature of 100 to 115° C. (212 to 239° F.), and are again rapidly absorbed by exposure to the air; at a higher temperature, crystallized quinine sulphate melts without decomposition, and, when strongly heated, becomes red, with the evolution of reddish vapors, becoming finally, upon ignition with access of air, slowly but wholly dissipated.

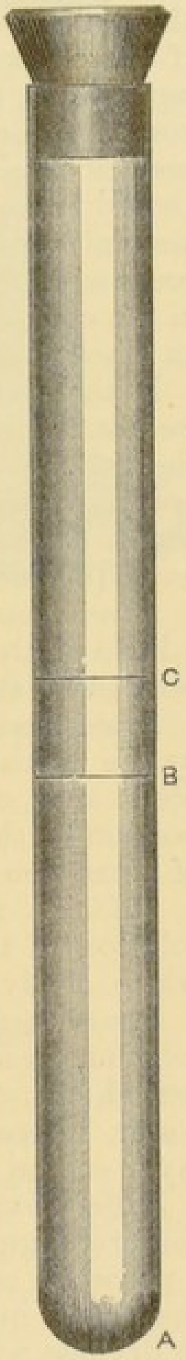
Quinine sulphate is soluble in 740 parts of water and in 65 parts of alcohol at 15° C. (59° F.); in about 30 parts of boiling water, and in about 3 parts of boiling alcohol; in 40 parts of glycerin, in 1000 parts of chloroform, and very sparingly soluble in ether; it is very freely soluble in dilute or strong acids, forming colorless, bitter solutions, and its solution in sulphuric acid, when diluted, exhibits a bright blue fluorescence.

Solutions of quinine sulphate are precipitated by the alkaline hydrates, carbonates, and bicarbonates, by lime-water, by tannic and picric acids, by potassium ferrocyanide, and by potassio-mercuric iodide. The precipitates with calcium hydrate and with the alkaline hydrates are soluble in an abundance of the precipitant. Its solution in dilute hydrochloric acid gives, upon the addition of a solution of barium chloride, a white precipitate of barium sulphate, insoluble in nitric or hydrochloric acids.

Like all quinine salts, quinine sulphate affords an emerald-green color, when to its dilute solution chlorine-water, and subsequently ammonia-water, in slight excess, are added; if the addition of ammonia-water be preceded by a few drops of a solution of potassium ferrocyanide, a red color will be produced.

If, to a solution of 5 parts of quinine sulphate in 250 parts of warm alcohol, 2 parts of dilute sulphuric acid, and subsequently a solution of 2 parts of iodine in 20 parts of alcohol are gradually added, a precipitate of quinine iodo-sulphate, or *herapathite*, $(C_{20}H_{24}N_2O_2)_4+3H_2SO_4+2HI+4I+3H_2O$, will be produced. This compound is almost insoluble in water or cold alcohol, and, when crystallized from boiling alcohol, forms small laminæ, with a green, metallic lustre.

FIG. 154.



Examination:

Water.—An undue proportion of water, with which the salt may have been moistened for the purpose of increasing its weight, may be detected by determining the loss of weight when dried at 100° C. (212° F.). One gram of the well-mixed salt, when dried at this temperature until the weight remains constant, should afford a residue weighing not less than 0.838 gram; a greater loss of weight will indicate the presence of more than 8 molecules of water.

Quinidine, *Cinchonine*, and *Cinchonidine Sulphates.*—These associate alkaloids of quinine may readily be detected by the application of *Hesse's* test, which is based upon the fact that water at 50–60° C. (122–140° F.) dissolves quinine sulphate but sparingly, while the sulphates of the other alkaloids are readily dissolved, and also that when the cooled solution, after supersaturation with ammonia-water, is shaken with a quantity of ether which is sufficient to dissolve all the quinine present, this quantity of ether is not sufficient to dissolve the other alkaloids if they exceed certain limits.

For executing this test a simple test-tube of the size represented in Fig. 154 may be employed. The internal diameter of the tube is about 1 centimeter, and its height 12 centimeters. It is provided with the marks *B* and *C*. The space below *B* (to *A* in the figure) has the capacity of 5 cubic centimeters, and the space between the lines *B* and *C* the capacity of 1 cubic centimeter. The application of the test is as follows:

0.5 gram of quinine sulphate and 10 cubic centimeters of water at 50–60° C. (122–140° F.) are shaken together in a test-tube several times. After standing for ten minutes, 5 cubic centimeters of the cooled and clear filtered solution are introduced into the graduated tube, 1 cubic centimeter of ether is added, and subsequently 5 drops of ammonia-water, spec. grav. 0.960. The tube is now closed with a tightly-fitting cork, is agitated gently, and allowed to stand for several hours; if the ethereal layer is now examined with a lens, it should show no evidence of crystals.

The absence of crystals under the conditions named is evidence of sufficient purity; but the salt may still contain 0.25 per cent. of cinchonine sulphate, 0.5 per cent. of quinidine sulphate, and about 1 per cent. of cinchonidine or homocinchonidine sulphates. If these alkaloids are present in larger quantities, crystals will separate in the ethereal layer, which are granular in the case of homocinchonidine or cinchonidine, and concentrically grouped needles if cinchonine or quinidine. The two former, homocinchonidine and cinchonidine, are most likely to be present in commercial quinine sulphate that is not intentionally adulterated, because of their liability to crystallize out along with the quinine in the course of manufacture, but they should not be present in an amount exceeding the above-named limits.

If the above-mentioned associate alkaloids are present in the free state, they will remain for the most part undissolved when the quinine sulphate is treated with thirty times its weight of boiling water, and will also be indicated by a strong alkaline reaction of the hot aqueous solution with litmus-paper, whereas pure quinine sulphate is neutral in its action upon litmus.

Mineral admixtures are detected by a residue left after igniting a little of the salt upon platinum-foil, or after dissolving a small portion of the salt in ten times its weight of boiling alcohol.

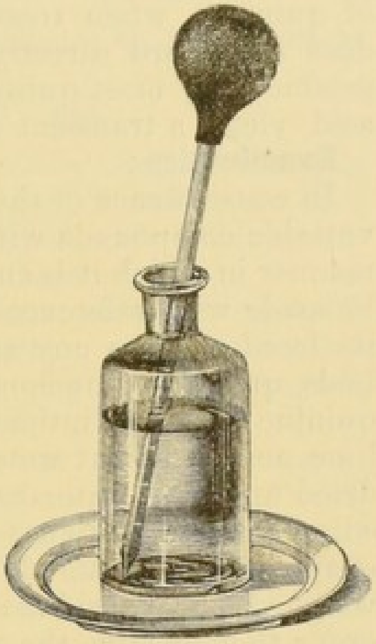
Ammonium salts are recognized by the odor of ammonia, and by the formation of white vapors from a glass rod moistened with acetic acid, when held in the orifice of a test-tube, wherein a small portion of the quinine sulphate is heated with a strong solution of potassium hydrate.

Chlorides and *hydrochlorates* may be recognized in the dilute solution of the salt in water, acidulated with nitric acid, by a white, curdy precipitate with argentic nitrate.

Stearic acid may be detected in the above-described alcoholic solution, by adding an equal volume of water; the liquid becomes turbid, but, on warming it gently, by dipping the test-tube in hot water, it becomes transparent again; the appearance of an oily layer on the surface would indicate the above fatty acid.

Salicin, *sugar*, and *mannite* may be detected in the solution of the preceding test, if free from fatty substances, by mixing it, in a porcelain capsule, with an amount of barium carbonate equal to that of the quinine sulphate employed, and evaporating the whole to dryness with constant stirring; the residue is triturated with a little water, and transferred upon a moist filter; the obtained filtrate is evaporated at a gentle heat, upon a watch-glass, and must leave no residue, or only a very small one; if a residue remains, it is divided, and placed upon two watch-glasses, with one drop of water upon each, and is again allowed to evaporate at a gentle heat; then, upon the one glass, a small drop of concentrated sulphuric acid is allowed to fall from a glass rod or from a small pipette (Fig. 155); a red color will be produced if *salicin* is present, a black one if *sugar;* mannite remains unchanged, and may be detected on the second watch-glass, by a few drops of alcohol, which dissolve the *mannite*, and leave it behind in small, acicular crystals upon spontaneous evaporation.

FIG. 155.



Since quinine sulphate dissolves without apparent change in strong sulphuric acid, even when gently warmed, this test may be directly applied for the detection of admixtures of sugar, mannite, or fatty acids. which will produce a black coloration; a red coloration might be indicative of the presence of salicin, but, since many other compounds produce a similar reaction, the following additional test may be employed for salicin:

A small portion of the quinine sulphate is dissolved, in a test-tube, in about ten times its weight of water, acidulated with a few drops of concentrated hydrochloric acid; the solution is boiled for a few minutes, when, if *salicin* be present, a white turbidity caused by the formation of saliretin will take place.

QUININÆ TANNAS.

CHININUM SEU CHINIUM TANNICUM.

Tannate of Quinine or Quinia. Quinine Tannate.

Ger. Gerbsaures Chinin; Fr. Tannate de quinine; Sp. Tanato de quinina.

$C_{20}H_{24}N_2O_2(C_{14}H_{10}O_9)_3+8H_2O$; 1449.

A yellowish-white, amorphous powder, which, when heated, becomes brown, fuses, and at a strong heat is wholly dissipated; it is only sparingly soluble in cold water, requiring 480 parts of it, but dissolves in about 50 parts of boiling water, forming a clear solution, which becomes turbid on cooling; the addition of acids increases the solubility to some extent; it is also quite sparingly soluble in boiling alcohol, ether, and chloroform, but quite readily soluble in warm glycerin; the alcoholic solution, when diluted with water, displays a slight blue fluorescence. The aqueous solution of quinine tannate has an astringent, bitter taste, and a feebly acid reaction; it is precipitated by metallic salts, and assumes a bluish-black color upon the addition of a few drops of solution of ferric chloride. In contact with the alkaline hydrates, quinine tannate assumes a fine red color, accompanied by the separation of quinine; when treated with chlorine-water and ammonia, it does not afford directly the characteristic green color which is produced by most quinine salts, but, in consequence of the tannic acid, yields a transient red color.

Examination:

In consequence of the capability of tannic acid of forming very variable compounds with quinine, according to the proportion or manner in which it is employed, an examination of the salt should be made with reference to the amount of contained quinine, and its freedom from any appreciable amount of the associate alkaloids, quinidine, cinchonine, and cinchonidine. One gram of the quinine tannate is intimately mixed with twice its weight of caustic lime and sufficient water to form a stiff paste, and the mixture dried upon the water-bath; the residue is then powdered, repeatedly extracted with hot chloroform, and the chloroformic solution evaporated in a tared beaker, dried at 120° C. (248° F.), and weighed. The residue should weigh not less than 0.22 gram. In order to determine the purity of the alkaloid thus obtained, the contents of the beaker are dissolved in a little water acidulated with a few drops of dilute sulphuric acid, filtered if necessary, and then shaken with 3 to 4 cubic centimeters of ether, and ammonia-water in excess. The two layers of liquid will remain clear if only quinine is present, while a greater or less turbidity is evidenced in the presence of the other alkaloids. The residue from the chloroformic solution is also adapted to the qualitative determination of quinine, by dissolving a small portion in chlorine-water, and subsequently adding a few drops of ammonia-water, when the characteristic emerald-green coloration will be produced; if the addition of ammonia-water be preceded by a few drops of a solution of potassium ferrocyanide, it assumes a bright red color.

Admixtures of *tannic* or *gallic acid*, *sugar*, *mannite*, or *dextrin* may be recognized by their ready solubility in cold water in comparison with that of quinine tannate.

Starch is detected by a blue color, when one drop of solution of iodinized potassium iodide is added to a little of the quinine tannate shaken with some boiling water, and subsequently allowed to cool.

QUININÆ VALERIANAS.

CHININUM SEU CHINIUM VALERIANICUM.

Valerianate of Quinine or Quinia. Quinine Valerianate.

Ger. Baldriansaures Chinin ; Fr. Valérianate de quinine ; Sp. Valerianato de quinina.

$C_{20}H_{24}N_2O_2.C_5H_{10}O_2+H_2O$; 444.

Thin, colorless, crystalline plates, of a pearly lustre, belonging to the triclinic system, having a faint odor of valerianic acid, and containing one molecule (4.04 per cent.) of water of crystallization; they are permanent in the air, fuse at about 90° C. (194° F.) to a colorless liquid, and lose their water of crystallization at 100° C. (212° F.), becoming thereby partially decomposed and incompletely soluble in water ; when strongly heated, they are entirely dissipated, emitting white, inflammable vapors.

Quinine valerianate is soluble in about 100 parts of water at 15° C. (59° F.), and in 40 parts of boiling water; in 5 parts of cold, and 1 part of boiling, alcohol, but only sparingly in ether ; diluted acids dissolve it freely, and strong sulphuric acid does so without color, if heat is not applied. The aqueous solution of the salt possesses a bitter taste, is neutral in its action upon litmus, and, when acidulated with sulphuric acid, displays a blue fluorescence with the development of the odor of valerianic acid; with ammonia-water it yields a white precipitate of quinine, which dissolves in a considerable excess of the reagent, as also readily upon agitation with ether. If chlorine-water be added to the solution, and subsequently ammonia-water in slight excess, an emerald-green color is produced; if the addition of ammonia-water is preceded by a few drops of a solution of potassium ferrocyanide, it assumes a bright red color.

Examination:

Stearic acid, *sugar*, and *salicin* are detected by agitating some of the quinine valerianate with strong sulphuric acid, in a test-tube; a black coloration would indicate one or both of the two former; a red one, salicin. In the case of a black coloration, a special test for *salicin* has to be made ; a little of the valerianate is agitated with cold water, the filtrate is then evaporated at a gentle heat to a small volume, and this is strongly acidulated with a few drops of concentrated hydrochloric acid, and heated; a white turbidity, taking place after a while, would indicate salicin.

Quinine hydrochlorate and *sulphate* may be detected, in the filtered aqueous solution of the salt, acidulated with a few drops of nitric acid, by testing portions of it with argentic nitrate for the former, and with barium nitrate for the latter. They will be indicated by a white precipitate with the respective reagent.

Zinc Valerianate or Acetate.—The absence of these or any other mineral salts, not readily volatilizable, may be ascertained by exposing the salt to a red heat, upon platinum-foil, whereby the organic matter is completely dissipated, leaving metallic oxides or carbonates behind, if such be present; if a residue remains which appears straw-yellow while hot and white when cold, it may be examined for zinc oxide by dissolving it, in a test-tube, in a few drops of diluted hydrochloric acid, supersaturating the solution with ammonia-water, and subsequently adding a little ammonium sulphide; an ensuing white precipitate will confirm the presence of *zinc.*

RESORCINUM.

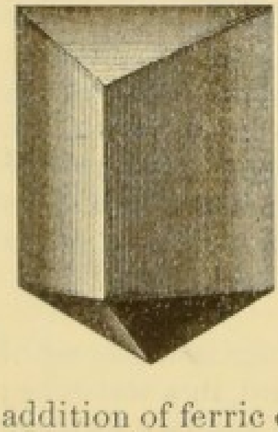
Resorcin. Meta-dioxybenzol.

Ger. Resorcin; Fr. Résorcine; Sp. Resorcina.

$$C_6H_6O_2 = C_6H_4(OH)_2;\ 110.$$

A crystalline powder, or short, thick prisms of the rhombic system (Fig. 156), odorless and colorless when perfectly pure, but on exposure to the air assuming a pinkish color. It melts at 104° C. (219.2° F.), and boils at 271° C. (519.8° F.), but becomes partially volatilized at a much lower temperature; when heated on platinum-foil, it burns with a bright flame, and is finally completely dissipated.

FIG. 156.



Resorcin is very readily soluble in water, alcohol, and ether, but is insoluble in chloroform and carbon bisulphide. Its aqueous solution is neutral in its action on litmus, possesses an intensely and disagreeably sweet taste, and assumes a dark violet color on the addition of ferric chloride, which disappears on the subsequent addition of ammonia; chlorinated lime also produces a transient violet coloration. Its solution with ammonia-water by exposure to the air becomes rose-red, then brown, by evaporation at a gentle heat, green, finally dark blue, and, on the addition of an acid, again dark red.

Resorcin reduces an ammoniacal solution of argentic nitrate and an alkaline cupric solution on boiling; upon the addition of bromine-water to its aqueous solution until a permanent turbidity is produced, small colorless needles of tribromresorcin, $C_6HBr_3(OH)_2$, are separated, which are sparingly soluble in cold water, more readily in hot water, and freely soluble in alcohol. With acetyl, benzol, and succinyl chlorides, resorcin combines to form ether-like compounds, in which the hydrogen atoms of the hydroxyl are replaced by acetyl, benzoyl, and succinyl groups, as, *e.g.*, $C_6H_4(O{-}C_2H_3O)_2$, $C_6H_4(O{-}C_6H_5{-}CO)_2$, etc. When heated with phthalic anhydride at 195° C. (383° F.), the phthalein of resorcin, or *fluorescein*, is produced, as follows:

$$\underbrace{2C_6H_6O_2}_{\text{Resorcin.}} + \underbrace{C_8H_4O_3}_{\substack{\text{Phthalic}\\ \text{anhydride.}}} = \underbrace{C_{20}H_{12}O_5}_{\text{Fluorescein.}} + 2H_2O.$$

From the solution of the melted mass in alcohol it is precipitated in white flakes by water, and crystallizes from alcohol in small, dark brown, crystalline crusts, which dissolve in ammonia-water, forming a red solution, and displaying an intense green fluorescence. From the fluorescein, by the action of bromine, tetra-brom fluorescein is produced, the potassium salt of which, *eosin*, $C_{20}H_6K_2Br_4O_5$, is remarkable for the rose-red color of its aqueous solution, accompanied by a green, or, when the solution is very dilute, yellow fluorescence. By the action of pure nitrogen tetroxide on resorcin in ethereal solution, diazo-resorcin is produced:

$$\underbrace{3C_6H_6O_2}_{\text{Resorcin.}} + N_2O_4 = \underbrace{C_{18}H_{10}N_2O_6}_{\text{Diazo-resorcin.}} + 4H_2O.$$

The latter forms brown, granular crystals, having a green metallic lustre, which are dissolved by alkalies with a magnificent blue-violet color.

A very characteristic test of resorcin is afforded by dissolving a small portion in fuming sulphuric acid; an orange-red solution is formed, which gradually darkens, and changes after a time, first to greenish-black, and then to pure blue, becoming purple-red on gently warming.

SALICINUM.

Salicin.

Ger. Salicin; Fr. Salicine; Sp. Salicina.

$C_{13}H_{18}O_7$; 286.

Small, colorless, needle-shaped crystals or laminæ, of a pearly lustre, without odor, but having a very bitter taste. When heated to 198° C. (388.4° F.) they melt to a colorless liquid, which, upon further heating, becomes yellow, with the development of white vapors having the odor of salicylous acid, and becomes finally carbonized; when strongly heated on platinum-foil they burn entirely away, leaving no residue.

Salicin is soluble in 28 parts of water and in 30 parts of alcohol at 15° C. (59° F.), in 0.7 part of boiling water, and in 2 parts of boiling alcohol, and is quite freely soluble in aqueous solutions of the alkaline hydrates and in acetic acid, but insoluble in ether and chloroform. The aqueous solution is neutral in its action upon litmus, possesses a bitter taste, and is precipitated by none of the ordinary reagents.

With cold concentrated sulphuric acid, salicin affords a solution having a fine red color; upon the subsequent addition of water the solution becomes colorless, and deposits a dark red powder, insoluble in water and in alcohol; when cautiously heated with diluted sulphuric or hydrochloric acid, it is decomposed by absorption of water into glucose and *saligenin:*

$$\underbrace{C_{13}H_{18}O_7}_{\text{Salicin.}} + H_2O = C_6H_{12}O_6 + \underbrace{C_7H_8O_2.}_{\text{Saligenin.}}$$

The latter is a handsomely crystallizable substance, readily soluble in hot water, alcohol, and ether, and its aqueous solution assumes, on the addition of a drop of a solution of ferric chloride, an indigo-blue color. By long-continued heating with dilute acids, saligenin is converted, by the elimination of a molecule of water, into *saliretin*, C_7H_6O, a white or yellowish, resinous body, which is insoluble in water, but soluble in concentrated acetic acid, alcohol, and ether, and is dissolved by concentrated sulphuric acid with a red color.

The purity of salicin may be sufficiently determined, in connection with the above described reactions, by its leaving no residue upon ignition, and by affording a clear, colorless solution when 1 gram of the salicin is agitated with a mixture of 22 parts of water and 5 parts of solution of potassium hydrate. It is also distinguished from the alkaloids, by its aqueous solution affording no turbidity or precipitate with tannic or picric acids, potassio-mercuric iodide, or an ammoniacal solution of argentic nitrate.

SANTONINUM.

Santonin.

Ger. Santonin ; Fr. Santonine ; Sp. Santonina.

$C_{15}H_{18}O$; 246.

Small, flat, rhombic prisms, transparent, without odor or color, and of a slightly bitter taste; they fuse at 170° C. (338° F.), and solidify on cooling to an amorphous mass, which, however, in contact with a minute quantity of any of its simple solvents, again assumes the crystalline form; at a stronger heat, they volatilize in dense, white, irritating, inflammable vapors, which condense in part unaltered on cooling, forming a white crystalline sublimate; at a red heat, with free access of air, they burn away without residue.

Santonin is permanent in the air, and assumes a straw-yellow color when exposed to solar light, without, however, undergoing any chemical change. When moistened with concentrated sulphuric acid, it remains unchanged and colorless for a while (evidence of the absence of salicin, which at once assumes a deep red color); the mixture does not assume a bluish color upon the addition of a little powdered potassium bichromate (evidence of the absence of strychnine*), nor does it afford any coloration with concentrated nitric acid. When a few drops of a mixture consisting of equal volumes of a very dilute solution of ferric chloride and concentrated sulphuric acid are added to a crystal of santonin, and the whole gently warmed, a fine red color is developed, which changes to purple and finally to violet.

Santonin is almost insoluble in cold water, requiring 5000 parts of the latter for solution, and is not much more freely soluble in acidulated water or in dilute acids; when agitated with the latter and filtered, the filtered liquid has only a feebly bitter taste, and affords no precipitate with tannic acid, potassio-mercuric iodide, or with trinitrophenol (picric acid), either before or after the addition of a little solution of sodium acetate (further evidence of the absence of salicin, and of cinchonine, and other bitter alkaloids). Boiling water dissolves $\frac{1}{250}$th part of santonin. It is, however, readily soluble in diluted solutions of the alkaline hydrates, but is reprecipitated upon supersaturation with an acid, or upon the addition of acidulous salts.

Santonin is also soluble in 40 parts of cold, and in 3 parts of boiling, alcohol, in 160 parts of cold, or 42 parts of boiling ether, in 4 parts of chloroform (distinction from cinchonine, which is almost insoluble in chloroform), and more or less freely in benzol, and in essential and fatty oils. The alcoholic solution possesses an intensely bitter taste, is neutral in its action upon litmus, and burns with a pale yellow flame (evidence of the absence of an adulteration with boric acid); it becomes transiently carmine-red upon the addition of a few drops of a concentrated solution of potassium hydrate.

Santonin is the anhydride of *santoninic acid*, $C_{15}H_{20}O_4$, forming with the alkalies soluble, and, in part, well crystallizable salts.

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* Santonin and strychnine have some similarity in their appearance, and this fact has repeatedly been the cause of incidental mistakes and sad accidents. They may, however, at once be distinguished, besides their difference in taste, by the solubility of *strychnine* in diluted acids, by its insolubility in ether and in solution of potassium hydrate, and by its reaction with concentrated sulphuric acid, in which it dissolves without color, but produces, upon the addition of a minute crystal of potassium bichromate, a bluish-violet color, which successively changes to violet, to red, and finally to yellow.

From the sodium salt, by the addition of dilute hydrochloric acid, and direct agitation with ether, the free santoninic acid may be obtained; it forms white, rhombic crystals, unalterable by exposure to light, and sparingly soluble in cold water, but readily soluble in alcohol, and which, at 120° C. (248° F.), are decomposed into santonin and water. The same decomposition takes place upon the addition of sulphuric acid to the aqueous solution of the salt, or when the latter is warmed with dilute hydrochloric acid.

The purity of santonin may, in most instances, be sufficiently determined by the above described physical characters, and its deportment with the simple solvents. An admixture of *stearic acid*, or other crystallizable fatty acids, may be detected by their lower fusing points, and by the production of a greasy stain, when a little of the santonin is warmed upon a piece of glazed paper at a temperature not exceeding 100° C. (212° F.).

SODII ACETAS.

SODIUM SEU NATRIUM ACETICUM.

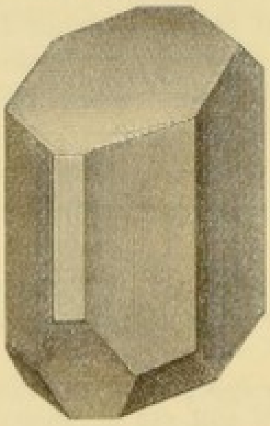
Acetate of Sodium. Sodium Acetate.

Ger. Essigsaures Natrium; Fr. Acétate de soude; Sp. Acetato de sosa.

$NaC_2H_3O_2 + 3H_2O$; 136.

Large, colorless, transparent, monoclinic prisms (Fig. 157), containing three molecules (39.70 per cent.) of water of crystallization; they are efflorescent in a dry, warm atmosphere, liquefy at 75° C. (167° F.), and lose their water of crystallization at 123° C. (253.4° F.), leaving the anhydrous salt as a white powder.

FIG. 157.



The anhydrous salt melts at about 300° C. (572° F.), without decomposition, and solidifies on cooling in a crystalline form; at temperatures above 315° C. (599° F.) it is decomposed, with the evolution of empyreumatic, inflammable fumes, leaving a black residue of carbon and sodium carbonate, which imparts to the flame a yellow color, changes moistened red litmus-paper to blue, and effervesces with acids.

Sodium acetate is soluble in 3 parts of water and in 30 parts of alcohol at 15° C. (59° F.), and in 1 part of boiling water and 2 parts of boiling alcohol; its aqueous solution is neutral or nearly so, has a cooling, saline taste, is not precipitated when dropped into strong alcohol, nor when mixed with a diluted solution of sodium carbonate, or with a concentrated solution of sodium bitartrate; it assumes a red color upon the addition of a few drops of solution of a ferric salt, evolves the vapor of acetic acid, when warmed with concentrated sulphuric acid, and that of acetic ether, when heated with a mixture of alcohol and sulphuric acid.

Examination:

Sodium chloride and *sulphate* are detected, in the solution of sodium acetate, acidulated with a few drops of diluted nitric acid, by testing it, in separate portions, with argentic nitrate and barium nitrate; a white precipitate with the first reagent would indicate *chloride*, and with the second one, *sulphate*.

Carbonates, *silica*, and *alkaline earths* may be detected by dissolving a portion of the salt in water acidulated with hydrochloric acid; effervescence will indicate carbonates; upon evaporating the resulting solution to dryness, and treating the residue with water, the silica will remain undissolved; and the solution, after filtration, and the addition of sodium carbonate in slight excess, will yield a white precipitate if alkaline earths be present.

Organic impurities will be indicated by a dark coloration when a little of the salt is strewn upon colorless concentrated sulphuric acid.

Metallic impurities may be detected in the aqueous solution of the salt, acidulated with hydrochloric acid, by a dark coloration or precipitate upon saturation with hydrogen sulphide, or, after neutralization with ammonia water, by the addition of ammonium sulphide.

Estimation:

About 5 grams of the dry but uneffloresced crystals of the salt are accurately weighed and ignited at a strong heat, in a porcelain crucible, until inflammable vapors cease to be evolved; the residue is then dissolved in water, and the solution, contained in a beaker, after the addition of a few drops of solution of litmus, is titrated with a standard solution of oxalic or sulphuric acid (page 82) until, with the application of a gentle heat to effect the complete removal of the disengaged carbonic acid gas, a slight excess of acid has been employed, and the liquid assumes a bright cherry-red color. The excess of acid is then inversely titrated with a standard alkali solution (page 87) until a decided blue coloration of the liquid is just produced, when the number of cubic centimeters of alkali solution, subtracted from that of the acid first employed, will give the amount of the latter required for the exact neutralization of the salt. One cubic centimeter of the normal acid solution corresponding to 0.053 gram of sodium carbonate, or, as its equivalent, 0.136 gram of crystallized sodium acetate, the latter decimal, multiplied by the number of cubic centimeters of normal acid solution employed for neutralization, will represent the amount of pure sodium acetate in the quantity under estimation.

By the employment of 6.8 grams of crystallized sodium acetate, and a strictly normal solution of oxalic or sulphuric acid, the number of cubic centimeters of acid required for the exact neutralization of the salt after the above treatment, when multiplied by 2, will represent without further calculation the percentage purity of the salt under examination.

SODII ARSENIAS.

SODIUM SEU NATRIUM ARSENICUM.

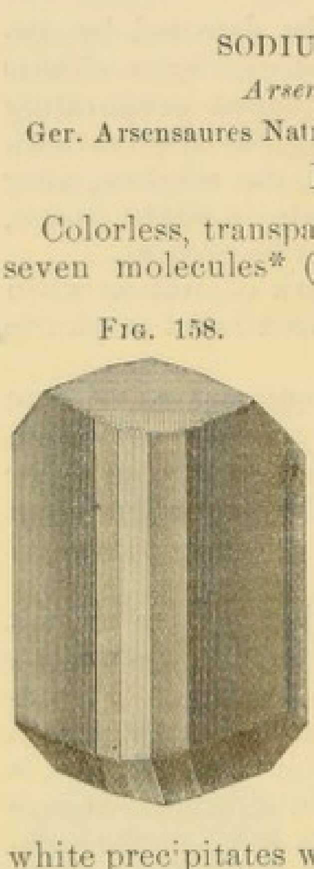
Arseniate of Sodium. Sodium Arseniate.

Ger. Arsensaures Natrium ; Fr. Arséniate de soude ; Sp. Arseniato de sosa.

$Na_2HAsO_4+7H_2O$; 311.9.

Colorless, transparent, monoclinic prisms (Fig. 158), containing seven molecules* (40.38 per cent.) of water of crystallization; they effloresce slightly in a dry atmosphere, and, when gently heated, lose 5 molecules (28.84 per cent.) of water, becoming converted into a white powder, which still contains two molecules (11.54 per cent.) of water; these, however, are expelled at 148° C. (299.4° F.), when the salt fuses.

FIG. 158.



Sodium arseniate is soluble in 4 parts of water at 15° C. (59° F.), but is very sparingly soluble in cold alcohol; it is very freely soluble in boiling water, and in 60 parts of boiling alcohol. Its aqueous solution possesses a mild, feebly saline taste, and a slightly alkaline reaction; it gives white precipitates with barium and calcium salts, and with magnesium and zinc sulphates, and a brick-red one with argentic nitrate, all of which are soluble in nitric acid; it suffers no immediate alteration by hydrogen sulphide, either in its alkaline solution or when this is acidulated with acids; the latter mixture, however, becomes turbid upon warming, separating white sulphur first, and subsequently yellow arsenic trisulphide. Fused upon charcoal, before the blow-pipe, sodium arseniate gives the garlic-like odor of arsenic, and imparts a yellow color to the flame; heated, in a narrow tube, with a little potassium cyanide, it forms a metallic mirror.

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* When crystallized from a cold solution, the salt contains 12 molecules of water of crystallization, but readily loses 5 molecules of water at ordinary temperatures, becoming converted, without change of form, into a salt of the above composition.

SODII BENZOAS.

SODIUM SEU NATRIUM BENZOICUM.

Benzoate of Sodium. Sodium Benzoate.

Ger. Benzoësaures Natrium; Fr. Benzoate de soude; Sp. Benzoato de sosa.

$$NaC_7H_5O_2 + H_2O = C_6H_5\text{–CO–ONa} + H_2O;\ 162.$$

Colorless, needle-shaped crystals, or a white, semi-crystalline powder, containing one molecule (11.11 per cent.) of water of crystallization, and efflorescent on exposure to the air. The salt is odorless, or possesses but a faint odor of benzoin; on being heated, it first melts, with the evolution of irritating, inflammable vapors, then chars, and finally leaves a blackened residue of an alkaline reaction, which effervesces with acids and imparts an intense yellow color to the non-luminous flame.

Sodium benzoate is soluble in 1.8 parts of water and in 45 parts of alcohol at 15° C. (59° F.), in 1.3 parts of boiling water, and in 20 parts of boiling alcohol. The aqueous solution possesses a sweetly astringent taste, and is neutral in its action upon litmus; on the addition of a few drops of a dilute solution of ferric chloride, a flesh-colored precipitate of basic ferric benzoate is produced, and with hydrochloric acid it yields a crystalline precipitate of benzoic acid, which, upon subsequent agitation with ether or chloroform, becomes readily dissolved.

Examination:

Sulphates and *chlorides* may readily be detected in the diluted aqueous solution of the salt, acidulated with nitric acid, by testing it, in separate portions, with barium chloride for the former, and with argentic nitrate for the latter; a white precipitate with either of these reagents, insoluble in nitric acid, will reveal the presence of such impurities.

Chloro-benzoic acid may be detected by the addition of hydrochloric acid to a concentrated solution of the salt, washing the precipitated benzoic acid thoroughly with water, and subsequently heating a small portion of it, together with a little recently ignited and moistened cupric oxide, on the looped end of a platinum wire in the non-luminous flame; if a green or bluish-green color is imparted to the oxide, the presence of chloro-benzoic acid will be indicated.

The presence of the latter impurity, in case other chlorides are absent, may also be detected by mixing 1 gram of the salt with a few drops of a solution of sodium hydrate, allowing the mixture to dry slowly, and subsequently igniting; the residual mass is then extracted with water, filtered, and the filtrate, after supersaturation with nitric acid, tested with argentic nitrate, when a white, curdy precipitate will indicate an admixture or substitution of sodium chloro-benzoate.

Organic impurities will in many instances be indicated by a dark coloration when a little of the salt is added to concentrated sulphuric acid; the mixture may subsequently be diluted with twice its volume of water, a small crystal of potassium bichromate added, and gently heated, when neither a green color nor the development of the odor of bitter almonds should be produced; in the latter case the presence of cinnamic acid will be indicated.

SODII BICARBONAS.

SODIUM SEU NATRIUM BICARBONICUM.

Bicarbonate of Sodium. Sodium Bicarbonate.

Ger. Doppelt kohlensaures Natrium; Fr. Bicarbonate de soude;
Sp. Bicarbonato de sosa.

$NaHCO_3$; 84.

White, opaque masses, or crystalline crusts, consisting of monoclinic tables, or a snow-white powder, permanent in dry air, and having the specific gravity 2.22. When heated to 100° C. (212° F.), the salt rapidly loses water and carbonic acid gas, amounting to 36.9 per cent. of its weight, and leaves a strongly alkaline residue of normal sodium carbonate, which melts at a red heat: $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$.

Sodium bicarbonate is soluble in 11.3 parts of water at 15° C. (59° F.), and is insoluble in alcohol. The solution possesses a mild alkaline taste and reaction, but does not change the color of turmeric paper; when heated, effervescence takes place, and at the boiling-point of the solution the salt is completely converted into normal sodium carbonate, Na_2CO_3. Solution of sodium bicarbonate affords no precipitate upon the admixture of a concentrated solution of sodium bitartrate, of tartaric acid, or of magnesium sulphate.

Examination:

Normal sodium carbonate will be indicated by a strongly alkaline reaction of the salt to test-paper, and may be recognized in the cold aqueous solution by the production of a white precipitate on the addition of a solution of magnesium sulphate, as also by the following simple tests. 2 grams of the salt are dissolved with as little agitation as possible, in a closed vessel, in 30 parts of cold water, and the solution added at once to 5 grams of a cold solution of 1 part of mercuric chloride in 20 parts of water; after standing for three minutes, only a slight white turbidity should have occurred; a reddish-brown turbidity or a reddish deposit will indicate the presence of more than 4 per cent. of normal carbonate. By the employment of 6 grams of the mercuric chloride solution, the occurrence of a reddish-brown turbidity within three minutes will indicate 3 per cent., with 6.5 grams, 2 per cent., with 7 grams, 1 per cent., and with 7.5 grams, 0.16 per cent. respectively of normal sodium carbonate. To insure the accuracy of the above test, however, the absence of sodium chloride must be previously established, as the latter has the property of dissolving the red mercuric oxychloride, and its precipitation would thereby be prevented.

Another method for determining the presence of normal carbonate in bicarbonate depends upon the conversion of calomel in a concentrated solution of sodium carbonate into black mercurous oxide, whereas it is not affected by a solution of bicarbonate. About 0.5 gram of calomel, 1 gram of the sodium bicarbonate, and 1.5 grams of water are mixed, in a test-tube, and the mixture well agitated for one minute; if the bicarbonate be free from normal carbonate, the calomel will remain white, even after standing for twenty-four hours, whereas, with an admixture of 0.25 per cent. of carbonate, a slight grayish coating will be observed within about twenty minutes, with 0.5 per cent. of carbonate it will appear gray within fifteen minutes, and with one per cent. will become whitish-gray in a few minutes, and gradually increase in intensity of color.

Sodium chloride and *sulphate* are detected in the solution of the salt, when supersaturated with diluted nitric acid, by testing it in separate portions, with argentic nitrate for chloride, and with barium nitrate for sulphate.

Sodium sulphite and *hyposulphite* (thiosulphate) may be detected in the aqueous solution of the salt, supersaturated with sulphuric acid, by warming with a little potassium bichromate, when a green coloration will be produced. The hyposulphite may also be specially tested for, by supersaturating the solution of bicarbonate with acetic acid, and subsequently adding a little solution of argentic nitrate; a white precipitate, gradually changing to brown, will indicate hyposulphite; if chlorides also be present, the resulting precipitate may be digested with ammonia-water, when the argentic chloride will become dissolved, leaving brown argentic sulphide if hyposulphite were present.

Ammonium salts may be detected by the odor of ammonia, when a little of the salt is heated, in a test-tube, with a concentrated solution of potassium hydrate, and by the formation of white fumes, when a glass rod, moistened with acetic acid, is held over the mouth of the tube.

Calcium and *Magnesium Salts.*—A small portion of the salt is dissolved in diluted acetic acid, and subsequently tested with ammonium oxalate, when a white precipitate will reveal the presence of *calcium;* to the filtrate, ammonium chloride, ammonia-water, in slight excess, and solution of ammonium phosphate are then successively added, when the formation of a white, crystalline precipitate will indicate *magnesium*.

Silica, Metallic Impurities, etc.—A small portion of the salt is dissolved in an excess of diluted hydrochloric acid, the solution evaporated to dryness, and the dry mass treated with water acidulated with hydrochloric acid; a white insoluble residue will indicate *silica*. The acid solution is then tested for metals, *copper*, *iron*, *aluminium*, etc., by saturating with hydrogen sulphide, and, after filtration, if necessary, by supersaturation with ammonia-water, and the addition of ammonium sulphide; a dark coloration or a precipitate with these reagents would indicate one or the other of the above-mentioned impurities, which may be further examined as to its nature by the methods of systematic analysis, as described on pages 51 to 59.

Estimation:

One hundred parts of sodium bicarbonate require for exact neutralization 83.33 parts of citric, or 89.29 parts of tartaric, acid. The quantitative estimation of the salt may, however, be more conveniently and accurately accomplished by igniting a weighed portion, and determining its loss of weight, which, if the salt be pure, will amount to 36.9 per cent. The residue may then be dissolved in water, and the amount of pure sodium carbonate estimated volumetrically by means of a standard solution of oxalic or sulphuric acid (page 82), as described under sodium carbonate, on page 545; one cubic centimeter of the normal acid corresponding to 0.053 gram of anhydrous sodium carbonate, or, as its equivalent, 0.084 gram of sodium bicarbonate. If desired, the accuracy of the result of the above estimation may be verified by determining the amount of carbonic acid contained in a weighed portion of the salt, as described on page 86; 100 parts of carbon dioxide, CO_2, corresponding to 190.9 parts of pure sodium bicarbonate.

The U. S. Pharmacopœia directs that to neutralize 4.2 grams of sodium bicarbonate should require not less than 49.5 cubic centimeters of the volumetric solution of oxalic acid, and to neutralize the same amount of the commercial salt, should require not less than 47.5 cubic centimeters of the volumetric solution of oxalic acid; corresponding, in the first instance, to at least 99 per cent., and, in the second instance, to at least 95 per cent., of pure sodium bicarbonate.

SODII BISULPHIS.

SODIUM SEU NATRIUM BISULFUROSUM.

Bisulphite of Sodium. Sodium Bisulphite. Acid Sodium Sulphite.

Ger. Doppelt schwefligsaures Natrium ; Fr. Bisulfite de soude ;
Sp. Bisúlfito de sosa.

$NaHSO_3$; 104.

Small, opaque, prismatic crystals, having the odor of sulphurous acid, an unpleasant, sulphurous taste, and an acid reaction. On exposure to the air, the salt readily loses sulphur dioxide, and becomes converted into sodium sulphate; when strongly heated, it decrepitates, and is resolved into sulphur and sodium sulphate; and when introduced, on a platinum-wire, into the non-luminous flame, it imparts to the latter a persistent yellow color.

Sodium bisulphite is soluble in 4 parts of water and in 72 parts of alcohol at 15° C. (59° F.), in 2 parts of boiling water and in 49 parts of boiling alcohol. If hydrochloric acid be added to the aqueous solution of the salt, it is decomposed, with the evolution of vapors of sulphur dioxide, but without the separation of sulphur (distinction from hyposulphite).

Examination:

The dilute aqueous solution of the salt, acidulated with hydrochloric acid, should not afford more than a slight cloudiness upon the addition of a few drops of solution of barium chloride; a white precipitate would indicate the presence of an undue amount of sulphate.

Estimation:

About 0.2 gram of the salt is dissolved in a small portion of water, in a beaker, a little mucilage of starch added, and subsequently a decinormal solution of iodine (page 93) allowed to flow into the liquid from a burette until, with constant stirring, a permanent blue tint is just produced. One cubic centimeter of the decinormal iodine solution corresponding to 0.0052 gram of sodium bisulphite, $NaHSO_3$, the number of cubic centimeters of iodine solution required to produce this reaction will indicate, by simple calculation, the amount of the pure salt in the specimen under examination.

The United States Pharmacopœia directs that if 0.26 gram of the salt be dissolved in 10 cubic centimeters of water, and a little gelatinized starch added, at least 45 cubic centimeters of the volumetric solution of iodine should be required before a permanent blue tint appears after stirring (corresponding to at least 90 per cent. of pure sodium bisulphite).

SODII BORAS.

SODIUM SEU NATRIUM BORICUM SEU BIBORICUM.

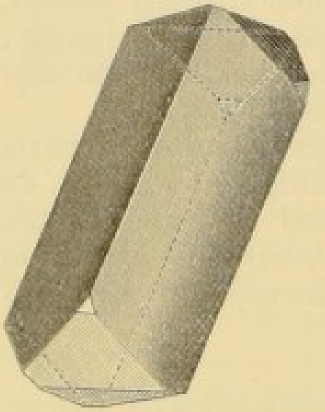
Borate or Biborate of Sodium. Borax. Sodium Borate. Sodium Pyroborate.

Ger. Borax; Fr. Borate de soude; Sp. Borato de sosa.

$Na_2B_4O_7 + 10H_2O$; 382.

Colorless, transparent, hard, monoclinic prisms (Fig. 159), having a specific gravity of 1.72, and containing 10 molecules (47.12 per cent.) of water of crystallization; they are ordinarily permanent, but slightly efflorescent in dry and warm air; when heated, they undergo aqueous fusion with intumescence and the elimination of the water of crystallization, and form a white porous mass, which fuses at a red heat into a glass, which is a powerful solvent for the metallic oxides, forming colored fluxes. When powdered borax is mixed in a porcelain capsule with diluted sulphuric acid and subsequently with alcohol, and the mixture ignited, the alcohol burns with a greenish flame.

FIG. 159.



Borax is soluble in 16 parts of water at 15° C. (59° F.), in half its weight of boiling water, and, at 80° C. (176° F.), in its own weight of glycerin, but insoluble in alcohol; its aqueous solution has an alkaline, sweetish taste, and an alkaline reaction upon litmus and especially upon turmeric paper; it forms precipitates of insoluble or sparingly soluble borates with the solutions of most earthy and metallic salts, and acts upon salts of gold, silver, mercury, and others, almost like potassium hydrate, precipitating their oxides.

When added to mucilage of gum-arabic or Iceland-moss, or to other similar vegetable mucilages, solution of borax thickens them considerably, unless they contain an addition of grape or cane-sugar.

Examination:

A portion of the powdered borax, when dissolved in twenty times its weight of warm water, should yield a complete and clear solution, remaining so after cooling; this solution may serve for the following tests:

Sodium carbonate is indicated by effervescence, or the rise of gas-bubbles, when a portion of the solution is added to concentrated hydrochloric acid.

Calcium and *aluminium salts* (alum) will be indicated by a white precipitate with solution of sodium carbonate. The presence of alum may further be confirmed, when tested with ammonium sulphide, by the production of a white precipitate of aluminium hydrate, soluble in a solution of potassium hydrate.

Chloride and *sulphate* may be detected in the solution, after dilution with three times its volume of water and acidulation with diluted nitric acid, by the formation of white precipitates when tested, in separate portions, with argentic nitrate for chloride, and with barium nitrate for sulphate.

Phosphate may be detected by a white granular precipitate, upon the addition of test magnesium mixture.

In order to ascertain the absence of arsenic acid or an arseniate, which would afford the same reaction with test magnesium mixture, the precipitate may be collected, washed, and dried, and then tested by heating a portion of it, mixed with a little exsiccated sodium carbonate, upon charcoal, and another portion, with a little potassium cyanide, in a narrow glass tube; a garlic-like odor in the first test, and a metallic mirror in the second, would indicate an incidental contamination with an arseniate.

The presence of phosphate may also be definitely determined by heating the solution of borax with a solution of ammonium molybdate, acidulated with nitric acid, when a yellow, crystalline precipitate of ammonium phospho-molybdate will be produced.

Nitrate will be indicated in the solution, strongly acidulated with sulphuric acid, and tinged slightly blue with indigo solution, by ensuing decoloration upon heating.

Metallic impurities may be detected in the solution of the salt, acidulated with a few drops of hydrochloric acid, by a coloration or turbidity upon saturation with hydrogen sulphide, or, after filtration, if necessary, and supersaturation with ammonia-water, by the addition of ammonium sulphide.

SODII BROMIDUM.

SODIUM SEU NATRIUM BROMATUM.

Bromide of Sodium. Sodium Bromide.

Ger. Bromnatrium; Fr. Brômure de sodium; Sp. Bromuro de sodio.

$NaBr$; 102.8.

Small, colorless or white, anhydrous, cubical crystals, or a crystalline powder, permanent in dry air. On exposure to a dull-red heat, the salt melts without losing weight, and, at a full red heat, it is slowly volatilized without decomposition. A fragment of the salt imparts an intense yellow color to the non-luminous flame.

Sodium bromide is soluble in 1.2 parts of water and in 13 parts of alcohol, at 15° C. (59° F.), in 0.5 part of boiling water, and in 11 parts of boiling alcohol. The aqueous solution possesses a saline, faintly bitter taste, and a neutral or slightly alkaline reaction; with argentic nitrate it yields a yellowish-white, curdy precipitate of argentic bromide, which is insoluble in nitric acid, but soluble in a large excess of ammonia-water (distinction from argentic iodide); when dropped into a very dilute solution of mercuric chloride, no reaction takes place (additional distinction from sodium iodide), nor does it afford any precipitate on the addition of a concentrated solution of tartaric acid or sodium bitartrate (distinction from potassium bromide).

Sodium bromide may also be distinguished from the iodide by adding to the solution a little mucilage of starch, and subsequently a few drops of chlorine-water; the solution of the bromide becomes yellow or yellowish-brown, while that of the iodide assumes a deep blue color. If carbon disulphide be poured upon a solution of the salt, then chlorine-water added, drop by drop, and the whole agitated, the disulphide should acquire a yellow or yellowish-brown color, without a violet tint.

Examination:

Moisture, which may be contained in the crystals, as well as in the granular form of the salt, is recognized, and may be quantitatively determined by ascertaining the loss of weight upon drying at 100° C. (212° F.).

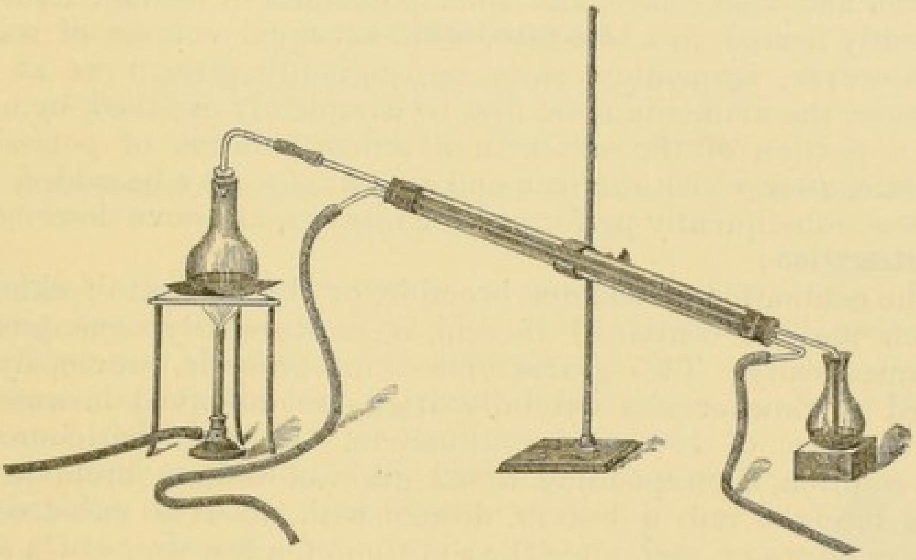
Sodium carbonate will be indicated by a strongly alkaline reaction, when a few fragments of the salt are placed upon moistened red litmus-paper, and may be recognized by the occurrence of a white turbidity, when a little of the concentrated solution of the salt is added to lime-water.

Sulphates may be detected, in the dilute aqueous solution, acidulated with a few drops of nitric acid, by a white precipitate on the addition of a few drops of solution of barium nitrate or chloride.

Bromate is detected by placing a little of the powdered salt upon a piece of white porcelain, and subsequently adding one drop of dilute sulphuric acid; a yellow coloration of the moistened surface of the salt, or the developed odor of bromine, will reveal the presence of bromate. The presence of the latter, in an aqueous solution of the salt, may also be detected by the liberation of bromine upon the addition of a few drops of dilute sulphuric acid, imparting a yellow color, which, upon subsequent agitation of the solution with a few drops of carbon bisulphide, will be absorbed by the latter.

Chlorides may be detected, in the solution of the salt, by completely precipitating it with argentic nitrate, digesting the washed and still moist precipitate for some time with a cold, saturated solution of ammonium carbonate, subsequently filtering, and supersaturating the filtrate with nitric acid; the production of a white, curdy precipitate will reveal the presence of chloride. The presence of smaller amounts of chloride. and less than that admitted in the officinal salt, may be detected as follows. 5 grams of the powdered and well-dried salt, together with 6 grams of pure powdered potassium bichromate, are introduced into a small flask, and 15 grams of concentrated sulphuric acid are added. The mixture is then submitted to distillation at a gentle heat, and the distillate collected in a receiver or flask, containing a small quantity of ammonia-water (Fig. 160). Bromine distils over, and is dissolved by the ammonia-water without color; but, if chlorides are present, chloro-chromic anhydride, CrO_2Cl_2, is produced, distils over, and forms ammonium chromate, which imparts a yellowish color to the distillate; by subsequently heating the latter with a little hydrochloric acid and alcohol, the bright green color of the chromic salt will be produced.

FIG. 160.



If sodium chloride or other salts are indicated by the above tests, the extent of such an admixture may be approximately ascertained by preparing a solution of 1 gram of the dry, crystallized salt in about 10 times its weight of water, acidulated with a few drops of diluted nitric acid, and completely precipitating it with a solution of argentic nitrate; the precipitate is collected upon a moist, tared filter, is washed, dried, and, when completely dry, weighed. If the salt was pure sodium bromide, the obtained argentic bromide should weigh 1.824 grams; if it contained sodium or potassium chloride, the weight will be greater in proportion to the amount of the admixture, since their molecular weights are lower; 1 gram of sodium chloride, for instance, would give 2.45 grams of argentic chloride.

The same test may also be employed to indicate the purity of the bromide, by ascertaining the quantity of argentic nitrate required to completely precipitate a definite weight of sodium bromide; 1 gram of which requires 1.65 grams of argentic nitrate for precipitation.

Nitrates may readily be detected, if the salt be free from bromate, by an ensuing intense yellow coloration, when a solution of a few fragments of the powdered salt in twenty times their weight of dilute sulphuric acid is heated to boiling. In the presence of bromate, nitrates will be indicated by the development of the odor of ammonia, when the salt, together with an equal weight of iron and zinc filings, and solid potassium or sodium hydrate, is gently heated, in a test-tube, with an equal volume of water. If, however, ammonium salts be originally present as an admixture, the ammonia must first be completely expelled, by heating a portion of the salt with a strong solution of potassium hydrate, after which the iron and zinc filings may be added, and the test subsequently performed for nitrates, as above described.

Estimation:

The estimation of sodium bromide, or the amount of chloride which may be contained therein, is most readily accomplished volumetrically. Two grams of sodium bromide, previously reduced to powder and carefully dried, are dissolved in water to the measure of 100 cubic centimeters. 10 cubic centimeters of this solution, corresponding to 0.2 gram of sodium bromide, are then brought into a beaker, diluted with about 50 cubic centimeters of water, and, after the addition of a few drops of a solution of potassium chromate, a decinormal solution of argentic nitrate (page 98) is allowed to flow into the liquid from a burette until, with constant stirring, a permanent reddish-brown coloration is produced. If the salt is pure sodium bromide, 19.4 cubic centimeters of the silver solution will be required to produce this effect, as containing 0.33 gram of argentic nitrate, which corresponds to 0.2 gram of sodium bromide, according to the equation $\underbrace{AgNO_3}_{170} : \underbrace{NaBr}_{103} = 0.33 : 0.2$. If the salt was pure sodium chloride, 34.18 cubic centimeters of the silver solution would be required for its complete precipitation, in accordance with a similar proportion; the difference in the amount of silver solution, required for 0.2 gram of the two salts, would therefore be $34.18 - 19.4 = 14.78$ cubic centimeters; from which it follows, that for each 0.1478 cubic centimeter of silver solution required in excess of 19.4 cubic centimeters, in order to effect complete precipitation, 1 per cent. of sodium chloride will be represented, as $\frac{14.78}{100} = 0.1478$. It is evident that the presence of sodium iodide, or other alkaline chlorides or bromides, would influence the result in proportion to the extent of the admixture.

The United States Pharmacopœia directs that if 3 grams of the well-dried salt be dissolved in distilled water to the measure of 100 cubic centimeters, and 10 cubic centimeters of this solution be treated with a few drops of test-solution of potassium bichromate, and then volumetric solution of argentic nitrate be added, not more than 29.8 cubic centimeters of the latter should be consumed before the red color ceases to disappear on stirring (indicating the absence of more than 3 per cent. of chloride).

SODII CARBONAS.

SODIUM SEU NATRIUM CARBONICUM.

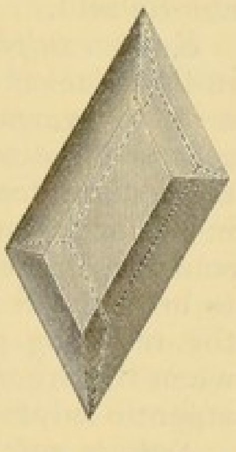
Carbonate of Sodium. Sodium Carbonate.

Ger. Kohlensaures Natrium ; Fr. Carbonate de soude ; Sp. Carbonato de sosa.

$$Na_2CO_3 + 10H_2O;\ 286.$$

Large, colorless, transparent, monoclinic prisms (Fig. 161), having the specific gravity 1.440, and containing 10 molecules (62.85 per cent.) of water of crystallization ; they effloresce in dry air, losing readily 5 molecules of water, and falling into a white powder, which, when heated to about 45° C. (113° F.), suffers a further loss of water, and is converted into a salt of the composition $Na_2CO_3 + H_2O$ (*Sodii Carbonas Exsiccatus*) ; the latter salt, when heated to about 80° C. (176° F.), loses the remaining molecule of water, and becomes anhydrous. The crystals, when heated, undergo aqueous fusion at 34° C. (93.2° F.), and, after the evaporation of the water, the anhydrous salt fuses at a red heat, without undergoing further change.

FIG. 161.



Crystallized sodium carbonate is soluble in 1.6 parts of water at 15° C. (59° F.), and in 0.25 part of boiling water; or in other words, 100 parts of water dissolve, at 14° C. (57.2° F.), 60.4 parts, at 36° C. (96.8°) 833 parts, and at 104° C. = 219.2° F. (the boiling-point of the saturated solution), 445 parts, of crystallized sodium carbonate.* The salt is insoluble in alcohol. Its aqueous solution has a strong alkaline taste and reaction; dropped into solution of tartaric acid, it produces no precipitation; it effervesces with acids and acidulous salts, and decomposes the soluble salts of the earthy and heavy metals, forming, with most of them, insoluble or sparingly soluble

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* Sodium carbonate, with ten molecules of water of crystallization, is altered in its solution, at near the boiling-point, into a salt with only one molecule of water of crystallization, which is less soluble, and gives rise to the anomaly in the solubility of sodium carbonate. A similar instance is met with in sodium sulphate and several other salts.

carbonates or hydrates. The salt imparts an intense yellow color to the non-luminous flame.

Examination:

Sodium hydrate is indicated in the solution of the salt by an alkaline reaction after complete precipitation with a slight excess of barium chloride, and subsequent filtration; it may be approximately estimated by agitating a few grams of the salt with absolute alcohol, filtering the solution, and evaporating the filtrate, together with the alcoholic washings therefrom, to complete dryness in a tared porcelain capsule; the weight of the dried residue will indicate approximately the amount of sodium hydrate contained in the salt.

Chloride and *sulphate* are readily detected in the solution of the salt, slightly supersaturated with nitric acid, by testing it, in separate portions, with argentic nitrate for the former and with barium nitrate for the latter; a white precipitate in either case will reveal the presence of such impurities.

Sodium sulphide will be indicated by a black precipitate, when a solution of the salt is tested with plumbic acetate or argentic nitrate, and may also be recognized by the development of the odor of hydrogen sulphide upon the addition of a little hydrochloric acid.

Sodium sulphite and *hyposulphite* (thiosulphate) may be detected in the aqueous solution of the salt, supersaturated with sulphuric acid, by warming with a little potassium bichromate, when a green coloration will be produced. The hyposulphite may also be specially tested for, by supersaturating the solution of the carbonate with acetic acid, and subsequently adding a few drops of solution of argentic nitrate; a white precipitate, gradually changing to brown, will indicate hyposulphite; if chlorides also be present, the resulting precipitate may be digested with ammonia-water, when the argentic chloride will become dissolved, leaving brown argentic sulphide if hyposulphite were present.

Sodium sulphocyanide and *ferrocyanide* will be detected in the solution of the salt, slightly supersaturated with hydrochloric acid, by the addition of a few drops of solution of ferric chloride; a blood-red coloration will indicate sulphocyanide, a blue coloration or precipitate, the presence of ferrocyanide.

Calcium and *Magnesium Salts.*—A small portion of the salt is dissolved in acetic acid, and subsequently tested with ammonium oxalate, when a white precipitate will reveal the presence of *calcium;* to the filtrate, ammonium chloride, ammonia-water, in slight excess, and solution of ammonium phosphate are then successively added, when the formation of a white, crystalline precipitate will indicate *magnesium.*

Silica, *Iron*, and *Alumina.*—A small portion of the salt is dissolved in an excess of diluted hydrochloric acid, the solution evaporated to dryness, and the dry mass treated with water acidulated with hydrochloric acid; a white insoluble residue will indicate *silica*. The slightly acid solution may then be tested for iron by the addition of a few drops of solution of potassium ferrocyanide, and, after supersaturation with ammonia-water, an ensuing white, flocculent precipitate will indicate the presence of *alumina*.

Arsenic.—A small quantity of the crystallized salt is dissolved in about four times its weight of water, the solution is slightly supersaturated with hydrochloric acid, filtered, if necessary, and then warmed to about 60 to 70° C. (140 to 158° F.); while still warm, hydrogen sulphide is allowed to pass into the solution until it is nearly cooled, the flask is then corked, and allowed to stand for twelve hours, when a flocculent, yellow precipitate would indicate the presence of arseniate.

Estimation:

One hundred parts of crystallized sodium carbonate require for exact saturation 48.95 parts of citric, or 52.44 parts of tartaric, acid. The quantitative estimation of the salt may, however, be more conveniently and accurately accomplished volumetrically, as follows. 26.5 grams of the crystallized salt are dissolved in water to the measure of 500 cubic centimeters. Of this solution, after the insoluble impurities have subsided and the liquid has become perfectly clear, 100 cubic centimeters (corresponding to 5.3 grams of anhydrous sodium carbonate) are brought into a beaker or small flask, and a few drops of litmus solution are added. A standard solution of oxalic or sulphuric acid (page 82) is then allowed to flow into the liquid from a burette, until an excess of the acid has been employed, and the liquid, after being heated to boiling, in order to completely expel the liberated carbonic acid gas, assumes a cherry-red color. The excess of acid is then inversely titrated with a standard alkali solution (page 87) until a permanant blue coloration of the liquid is produced. From the amount of acid required for the exact neutralization of the solution of sodium carbonate employed, the amount of the pure salt contained therein may be calculated: one cubic centimeter of the normal acid solution corresponding to 0.053 gram of anhydrous, or 0.143 gram of crystallized sodium carbonate.

If desired, the accuracy of the above result may be verified by determining the amount of carbonic acid contained in the salt, according to the method described on page 86, from which the equivalent amount of anhydrous or crystallized salt may readily be calculated: 100 parts of carbon dioxide corresponding to 240.91 parts of anhydrous, or 650 parts of crystallized, sodium carbonate.

The United States Pharmacopœia directs that to neutralize 7.15 grams of sodium carbonate should require not less than 49 cubic centimeters of the volumetric solution of oxalic acid (corresponding to at least 98 per cent. of pure, crystallized sodium carbonate; and to neutralize 2.65 grams of dried sodium carbonate (*Sodii Carbonas Exsiccatus*) should require not less than 36.3 cubic centimeters of the volumetric solution of oxalic acid (corresponding to at least 72.6 per cent. of anhydrous sodium carbonate).

TABLE *of the amount of crystallized and anhydrous Sodium Carbonate contained in* 100 *parts of the solution of the salt of different specific gravities* (*Schiff*).

Specific gravity.	Per cent. of $Na_2CO_3+10H_2O$.	Per cent. of Na_2CO_3.	Specific gravity.	Per cent. of $Na_2CO_3+10H_2O$.	Per cent. of Na_2CO_3.
1.0038	1	0.370	1.1035	26	9.635
1.0076	2	0.741	1.1076	27	10.005
1.0114	3	1.112	1.1117	28	10.376
1.0153	4	1.482	1.1158	29	10.746
1.0192	5	1.853	1.1200	30	11.118
1.0231	6	2.223	1.1242	31	11.488
1.0270	7	2.594	1.1284	32	11.859
1.0309	8	2.965	1.1326	33	12.230
1.0348	9	3.335	1.1368	34	12.600
1.0388	10	3.706	1.1410	35	12.971
1.0428	11	4.076	1.1452	36	13.341
1.0468	12	4.447	1.1494	37	13.712
1.0508	13	4.817	1.1536	38	14.082
1.0548	14	5.188	1.1578	39	14.453
1.0588	15	5.558	1.1620	40	14.824
1.0628	16	5.929	1.1662	41	15.195
1.0668	17	6.299	1.1704	42	15.566
1.0708	18	6.670	1.1746	43	15.936
1.0748	19	7.041	1.1788	44	16.307
1.0789	20	7.412	1.1838	45	16.677
1.0830	21	7.782	1.1873	46	17.048
1.0871	22	8.153	1.1916	47	17.418
1.0912	23	8.523	1.1959	48	17.789
1.0953	24	8.894	1.2002	49	18.159
1.0994	25	9.264	1.2045	50	18.530

SODII CHLORAS.

SODIUM SEU NATRIUM CHLORICUM.

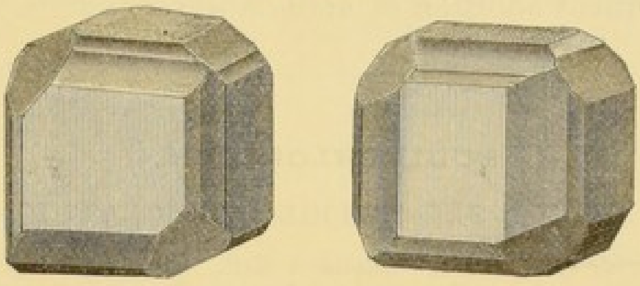
Chlorate of Sodium. Sodium Chlorate.

Ger. Chlorsaures Natrium; Fr. Chlorate de soude; Sp. Clorato de sosa.

$NaClO_3$; 106.4.

Colorless, transparent crystals of the regular system, presenting the form of a cube with dodecahedral and tetrahedral surfaces (Fig. 162), and deviating the plane of polarization either to the right (*a*), or to the left (*b*). They are anhydrous, and permanent in dry air; when thrown upon burning charcoal they deflagrate, and when triturated or heated with readily oxidizable or combustible substances, such as sugar, sulphur, etc., a more or less violent explosion ensues. On being heated the salt melts, and afterwards gives off oxygen, leaving finally, when strongly heated, a neutral residue of sodium chloride, amounting to 54.88 per cent. of its weight, and completely soluble in water; this residue imparts an intense yellow color to the non-luminous flame, and its aqueous solution yields with argentic nitrate a white, curdy precipitate, insoluble in nitric acid, but readily soluble in ammonia-water.

FIG. 162.



a b

Sodium chlorate is soluble in 1.1 parts of water and in 40 parts of alcohol at 15° C. (59° F.), in 0.5 part of boiling water, and in 43 parts of boiling alcohol. Its aqueous solution possesses a cooling, saline taste, and is neutral in its action upon litmus; when mixed with concentrated hydrochloric acid, a deep greenish-yellow color is produced, and the odor of chlorine is evolved.

Examination:

Potassium chlorate, when present as an admixture or substitution, will remain principally undissolved when the salt is treated with three times its weight of cold water, and may be detected in the saturated aqueous solution of the salt, by the formation of a white, crystalline precipitate on the addition of a concentrated solution of tartaric acid or sodium bitartrate.

Nitrates may be detected by first heating a portion of the salt, in a test-tube, with about twice its weight of solid potassium or sodium hydrate, and a little water, in order to ascertain the absence of ammonium salts, and subsequently adding a few iron and zinc filings, and again heating; if ammonium salts were found to be absent, or, if present, have been completely eliminated by the previous heating with caustic alkali, the odor of ammonia, developed upon the addition of the zinc and iron, will confirm the presence of nitrates.

Chlorides and *sulphates* are detected in the aqueous solution of the salt, acidulated with nitric acid, by white precipitates, when tested with argentic nitrate for the former, and with barium chloride for the latter.

Calcium salts may be detected in the dilute aqueous solution of the salt, by an ensuing white precipitate on the addition of a few drops of solution of ammonium oxalate.

Metallic impurities will be recognized in the aqueous solution of the salt, acidulated with hydrochloric acid, by a dark coloration or precipitate upon saturation with hydrogen sulphide, or, after filtration, if necessary, and neutralization with ammonia-water, by the subsequent addition of ammonium sulphide.

SODII CHLORIDUM.

SODIUM SEU NATRIUM CHLORATUM.

Chloride of Sodium. Common Salt. Sodium Chloride.

Ger. Chlornatrium, Kochsalz; Fr. Chlorure de sodium; Sp. Cloruro de sodio.

$NaCl$; 58.4.

Anhydrous, colorless, transparent, cubical crystals, often agglomerated into hollow, quadrangular pyramids, or a white, granular powder, having a spec. grav. of 2.15; the salt is permanent in the air, but slightly deliquescent when containing traces of magnesium and calcium chlorides. When exposed to heat, sodium chloride decrepitates, from the presence of interstitial moisture, melts at a red heat, and volatilizes with partial decomposition at a high temperature. It imparts a yellow color to the flame, and evolves vapors of hydrochloric acid, when heated with strong sulphuric acid.

Sodium chloride is almost equally soluble in water at all temperatures: 100 parts of water dissolve at 0° C. (32° F.) 35.52 parts, at 14° C. (57.2° F.) 35.87 parts, at 25° C. (77° F.) 36.13 parts, at 40° C. (104° F.) 36.64 parts, at 80° C. (176° F.) 38.22 parts, at 100° C. (212° F.) 39.61 parts, and at 110° C. (230° F.), the boiling-point of the saturated solution, 40.35 parts, of the salt; it is also soluble in glycerin, but not perceptibly soluble in absolute alcohol, in ether, or in chloroform, but its solubility in alcohol increases with the quantity of water contained therein. Its aqueous solution is neutral, and remains colorless upon the addition of chlorine-water (distinction from the alkaline bromides and iodides); it forms white precipitates with the solutions of those metallic salts whose chlorides are quite or almost insoluble in water—for instance, with the salts of silver, bismuth, and lead, and with the subsalts of mercury.

Examination:

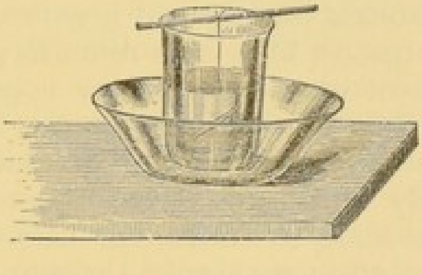
Water.—The amount of water, which may be present as interstitial moisture, is readily determined by drying a small portion of the salt at 150° C. (302° F.) until its weight remains constant.

Potassium chloride will be indicated in the concentrated aqueous solution of the salt, from which a portion of the sodium chloride has been separated by crystallization, by the formation of a yellow crystalline precipitate with an excess of solution of platinum chloride, and the subsequent addition of one-fifth of its volume of alcohol; with the employment of a weighed quantity of the salt, the precipitate of potassio-platinic chloride thus obtained, after washing upon a filter with a mixture of alcohol and ether, and drying at 100° C. (212° F.) until of constant weight, may be finally weighed, and therefrom the amount of potassium chloride calculated: 100 parts of potassio platinic chloride, K_2PtCl_6, corresponding to 30.50 parts of potassium chloride.

Nitrates.—To a little of the solution of the salt, contained in a test-tube, a drop of solution of indigo is added, so as to impart to the liquid a bluish tint, subsequently a few drops of concentrated sulphuric acid, and the mixture gently heated; if nitrates be present, decoloration of the liquid will ensue.

A confirmatory and still more sensitive test is to dip a bright zinc rod into a test-tube, or to suspend it in a small beaker (Fig. 163), containing a little diluted sulphuric acid, to which a few drops of a solution of pure potassium iodide, a little mucilage of starch, and subsequently twice the volume of the liquid of a solution of the salt, has been added; if nitrate be present, a bluish coloration, emanating from the zinc, will be produced in the liquid.

Fig. 163.



Iodides and Bromides.—A portion of the finely powdered salt is digested with about ten times its weight of warm alcohol, and the liquid, after being allowed to cool, is filtered, and evaporated to dryness at a gentle heat. The residue thus obtained is dissolved in a little water, a little mucilage of starch added, and subsequently chlorine-water, drop by drop, the liquid being gently stirred with a glass rod. The presence of even minute traces of iodide will cause a bluish coloration of the fluid; when iodide alone is present, the blue color will gradually become purple upon the continued addition of the chlorine-water, and decrease, until it finally disappears; but, when bromide also is present, the blue color will not change to purple, but become successively brownish, then orange, and finally yellow.

Alkaline and *earthy sulphates* are recognized in the dilute solution, acidulated with hydrochloric acid, by a white precipitate with barium chloride.

Magnesium and *calcium chlorides* are detected in the solution of sodium chloride by a white turbidity taking place upon the addition of a diluted solution of sodium carbonate. They may be distinguished and separated from each other by adding to a solution of the salt, ammonium chloride, ammonia-water, and solution of ammonium oxalate, when an ensuing white precipitate will indicate calcium; the liquid is then filtered, and to the filtrate a solution of ammonium or sodium phosphate is added, when the formation of a white, crystalline precipitate will reveal the presence of magnesium.

Metallic impurities may be detected by the occurrence of a dark coloration or precipitate, when the solution of the salt, acidulated with hydrochloric acid, is saturated with hydrogen sulphide, or, after filtration, if necessary, and neutralization with ammonia-water, by the subsequent addition of ammonium sulphide.

Estimation:

One gram of the powdered and dried salt yields, when completely precipitated by argentic nitrate, 2.450 grams of argentic chloride. Its purity, when free from other chlorides, may also be conveniently and accurately determined volumetrically, by dissolving 0.2 gram of the powdered and dried salt, in a beaker, in about 20 cubic centimeters of water, and, after the addition of a few drops of a solution of potassium chromate, allowing a decinormal solution of argentic nitrate (page 98) to flow into the liquid from a burette until, with constant stirring, the red coloration of argentic chromate remains permanent. The number of cubic centimeters of the silver solution required to produce this effect, when multiplied by the decimal 0.00584, will represent the amount of pure sodium chloride in the quantity under estimation. By the employment of exactly 0.292 gram of the salt, and proceeding as above, the number of cubic centimeters of the silver solution required to effect complete precipitation, when multiplied by 2, will indicate at once the percentage amount of pure sodium chloride.

SODII HYDRAS.

SODA. SODIUM SEU NATRIUM HYDRICUM. NATRIUM CAUSTICUM.

Caustic Soda. Soda. Sodium Hydrate.

Ger. Natriumhydroxyd, Aetznatron; Fr. Soude caustique; Sp. Sosa cáustica.

$NaOH$; 40.

Hard, white, fusible masses, in flat, tabular fragments or sticks, of a fibrous fracture, or a coarse, white powder; it is very deliquescent in moist air, but afterwards becomes dry in consequence of the absorption of carbonic acid gas, and the formation of sodium carbonate. It melts below a red heat to a clear, oily liquid, and at a strong red heat it is slowly volatilized unchanged. Heated upon the looped end of a platinum-wire, it imparts to the non-luminous flame an intense yellow color.

Sodium hydrate is soluble in 1.7 parts of water at 15° C. (59° F.), and in 0.8 part of boiling water, with the evolution of heat, and is also freely soluble in alcohol; when the concentrated aqueous solution is cooled to —8° C. (17.6° F.), the hydrate, $2NaOH + 7H_2O$, is deposited in large, transparent, monoclinic tables, which melt at 6° C. (42.8° F.). The solutions of sodium hydrate are highly alkaline and caustic, and act destructively upon animal tissues; when dropped into a diluted solution of plumbic acetate, it causes a white turbidity, which disappears again upon continued addition of the caustic solution, without leaving a black residue (evidence of the absence of sodium sulphide). When the concentrated aqueous solution is dropped into strong alcohol, no precipitate should take place, as its appearance would indicate the presence of sodium carbonate, sulphate, chloride, or other salts, less soluble in alcohol.

Sodium hydrate may readily be distinguished from potassium hydrate, by dropping concentrated solutions of the salts into solution of tartaric acid, care being taken that the acid reaction of the solution predominates; sodium hydrate will yield no precipitate unless containing potassium hydrate to a considerable extent, while potassium hydrate forms a white, granular precipitate.

Examination:

Sodium carbonate may be detected in the solution of the hydrate by effervescence, or by the formation of gas-bubbles, on the addition of a little acetic acid, and by the occurrence of a white turbidity upon the admixture of an equal volume of lime-water with the aqueous solution of the hydrate.

Chloride and *sulphate* are detected in the diluted solution, supersaturated with diluted nitric acid, by ensuing white precipitates when tested, in separate portions, with argentic nitrate for the former, and with barium nitrate for the latter.

Nitrate may be detected in the solution, supersaturated and strongly acidulated with sulphuric acid, by the addition of a drop of indigo solution, and gently heating; if nitrate be present, decoloration of the liquid will ensue.

Cyanide may be detected in the dilute solution of the salt, after the addition of a few drops of a solution of a ferrous and a ferric salt, and subsequent supersaturation with hydrochloric acid, by the formation of a precipitate of Prussian blue.

Silica and *aluminium salts* may be detected by supersaturating the dilute solution of sodium hydrate with an excess of nitric acid, and subsequently evaporating to dryness; the residue is treated with warm water, and should be wholly soluble; an insoluble residue would indicate silica; the solution is filtered, and the filtrate tested with ammonia-water, when the formation of a white, gelatinous precipitate would indicate aluminium salts.

Metallic impurities are detected by a dark coloration or turbidity of the solution, when saturated with hydrogen sulphide, and, in another portion of the solution, after previous supersaturation with hydrochloric acid.

Estimation:

2 grams of the dry sodium hydrate are dissolved in about 20 cubic centimeters of water, in a beaker, a few drops of litmus solution added, and a standard solution of oxalic or sulphuric acid (page 82) allowed to flow into the liquid from a burette until, with constant stirring, the blue tint of the liquid is just changed to a permanent pink. The number of cubic centimeters of normal acid solution thus required for the exact neutralization of the above amount of sodium hydrate, when multiplied by 2, will represent, without further calculation, its percentage purity. By the employment of other amounts of the hydrate, the calculation may readily be made, with the consideration that one cubic centimeter of the normal acid solution corresponds to 0.04 gram of pure sodium hydrate.

If the sodium hydrate contains carbonate, the above estimation will only be strictly correct when, in a weighed amount of the hydrate, the amount of carbonic acid contained therein is determined, as described on page 86; for 1 part of carbonic acid, 1.818 parts of sodium hydrate are deducted from the found amount of the latter, and the remainder then calculated as pure sodium hydrate.

The United States Pharmacopœia directs that to neutralize 2 grams of soda should require not less than 45 cubic centimeters of the volumetric solution of oxalic acid (corresponding to at least 90 per cent. of absolute sodium hydrate).

For the determination of the strength of aqueous solutions of sodium hydrate, as based upon the specific gravity of the latter, see *Liquor Sodæ*, page 413.

SODII HYPOPHOSPHIS.

SODIUM SEU NATRIUM HYPOPHOSPHOROSUM.

Hypophosphite of Sodium. Sodium Hypophosphite.

Ger. Unterphosphorigsaures Natrium; Fr. Hypophosphite de soude;
Sp. Hipofósfito de sosa.

$NaH_2PO_2 + H_2O$; 106.

Small, colorless, transparent, rectangular tables, of a pearly lustre, or a white, granular powder, containing one molecule (17 per cent.) of water of crystallization, and deliquescent on exposure to the air. When heated in a dry test-tube, the salt first loses its water of crystallization, and afterwards evolves spontaneously inflammable hydrogen phosphide, burning with a bright light; a residue of sodium pyrophosphate, containing traces of red amorphous phosphorus, is left behind, which imparts an intense yellow color to the non-luminous flame.

Sodium hypophosphite is soluble in 1 part of water, and in 30 parts of alcohol at 15° C. (59° F.), in 0.12 part of boiling water, and in 1 part of boiling alcohol (distinction from barium and calcium hypophosphites and sodium phosphate, which are insoluble in alcohol); it is insoluble in pure ether. Its aqueous solution has a sweetish, saline taste, a slightly alkaline reaction, and is gradually oxidized on exposure, especially when warm; it affords, when much diluted, a white precipitate with argentic nitrate, which quickly turns brown, and is converted into metallic silver; when acidulated with hydrochloric acid and added to an excess of solution of mercuric chloride, it first produces a white precipitate of mercurous chloride (calomel), and, on further addition, metallic mercury is separated.

Examination:

Carbonates may be detected in the aqueous solution of the salt by effervescence on the addition of an acid, and by the production of a white precipitate when added to lime-water.

Soluble phosphates and *phosphites* will be indicated in the aqueous solution by a white precipitate on the addition of a few drops of solution of calcium chloride; the presence of phosphates may also be recognized by adding to the solution a little test magnesium mixture, when a white, crystalline precipitate will be produced.

Sulphates and *chlorides* may be detected in the aqueous solution, acidulated with nitric acid, by testing it, in separate portions, with barium chloride for the former, and with argentic nitrate for the latter; a white precipitate in either instance will reveal the presence of such impurities.

Calcium and *Potassium Salts.*—The former will be indicated by a white precipitate on the addition of a few drops of solution of ammonium oxalate, and the latter by a white, crystalline precipitate on the addition of a concentrated solution of tartaric acid or sodium bitartrate.

Metallic impurities may be detected in the solution of the salt, acidulated with hydrochloric acid, by a dark coloration or a precipitate with hydrogen sulphide: or, after filtration, if necessary, and supersaturation with ammonia-water, by the addition of ammonium sulphide.

SODII HYPOSULPHIS.

SODIUM SEU NATRIUM HYPOSULFUROSUM SEU SUBSULFUROSUM SEU THIOSULFURICUM.

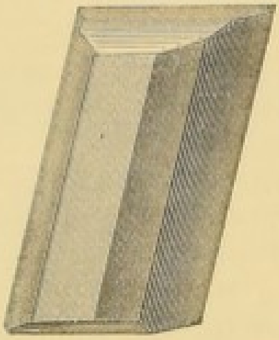
Hyposulphite of Sodium. Sodium Hyposulphite. Sodium Thiosulphate.[*]

Ger. Unterschwefligsaures Natrium, Thioschwefelsaures Natrium; Fr. Hyposulfite de soude; Sp. Hiposulfito de sosa.

$$Na_2S_2O_3 + 5H_2O = SO_2\Big\langle\begin{matrix}ONa\\SNa\end{matrix} + 5H_2O;\ 248.$$

Large, colorless, transparent, monoclinic prisms or tables (Fig. 164), having the specific gravity 1.736, and containing five molecules (36.3 per cent.) of water of crystallization; they are permanent at ordinary temperatures, but efflorescent in dry and warm air; when quickly heated to about 48° C. (118.4° F.), the salt melts in its water of crystallization, and, after becoming effloresced by exposure to a gentle heat, and subsequently heating to 100° C. (212° F.), the entire amount of water of crystallization is expelled; at a higher temperature it is decomposed, with the evolution of vapors of sulphurous acid and sulphur, which take fire, and burn away, leaving behind a reddish-yellow residue of neutral sodium sulphate, containing a little sulphide.

Fig. 164.



Sodium hyposulphite is soluble in 1.5 parts of water at 15° C. (59° F.), and in half its weight of boiling water, in the latter case attended by partial decomposition of the salt; it is also soluble in oil of turpentine, and causes the odor of the latter to disappear, but is insoluble in alcohol. The aqueous solution has a cooling and afterward a bitter taste, and a feebly alkaline reaction; on exposure to the air, it is gradually decomposed, the hyposulphite being converted into sulphur and sodium sulphite, which latter salt, on exposure of the solution to the air, is further decomposed into sulphur and sodium sulphate; when dropped into diluted hydrochloric, nitric, or sulphuric acid, solution of sodium hyposulphite gradually becomes turbid, sulphur being precipitated, and sulphurous acid disengaged.

With solution of barium chloride, a concentrated solution of sodium hyposulphite forms a white precipitate, which dissolves,

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[*] Since the discovery of the acid H_2SO_2, the appellation of sodium hyposulphite has been transferred to a salt of the composition $NaHSO_2$, while the acid entering into the composition of the above salt may be considered as sulphuric acid, in which an oxygen atom is replaced by sulphur, or, as thiosulphuric acid. The salt is therefore, scientifically, more correctly designated as sodium thiosulphate

however, upon sufficient dilution with water (evidence of the absence of sodium sulphate); when dropped into a dilute solution of argentic nitrate, a white precipitate is formed, which soon becomes yellow, and finally black; when, however, on the other hand, the argentic solution is dropped into the solution of sodium hyposulphite, the ensuing white precipitate of argentic hyposulphite is redissolved upon agitation, and the solution remains clear as long as sodium hyposulphite is in excess. With solution of ferric chloride, a transient violet coloration is produced, with the formation of sodium tetrathionate, while the ferric salt becomes reduced to the ferrous state:

$$Fe_2Cl_6 + 2Na_2S_2O_3 = 2FeCl_2 + Na_2S_4O_6 + 2NaCl.$$

When iodine, either alone or dissolved in alcohol, is added to solution of sodium hyposulphite, it is immediately decolorized, sodium iodide and tetrathionate being formed:

$$\underbrace{2Na_2S_2O_3.5H_2O}_{\substack{496\\(248)}} + \underbrace{I_2}_{\substack{253.2\\(126.6)}} = 2NaI + Na_2S_4O_6 + 10H_2O.$$

This reaction takes place in the proportion, approximately, of one part (126 6) of iodine to two parts (248) of crystallized sodium hyposulphite; a solution in these proportions dissolves iodine readily, with a brown color, but it is decolorized again upon the restoration of the above proportions by the addition of sodium hyposulphite.

Solution of sodium hyposulphite is a solvent for several otherwise insoluble compounds, as argentic oxide, argentic iodide, bromide, and chloride, plumbic iodide, plumbic and calcium sulphates, etc.

Examination:

Sodium sulphate is detected by the occurrence of a white precipitate, when a solution of 1 part of the salt in 80 parts of water is tested with barium nitrate.

Sodium carbonate is indicated by effervescence, when a concentrated solution of the salt is dropped into diluted acetic or hydrochloric acid.

Chloride may be detected by fusing the salt with twice its weight of pure potassium nitrate, dissolving the fused mass in water, and, after acidulating with nitric acid, testing with argentic nitrate; a white curdy precipitate will reveal the presence of chloride.

Sodium sulphide will be indicated in the aqueous solution of the salt by the formation of a white precipitate with zinc acetate, a black precipitate with an ammoniacal solution of argentic nitrate, and a violet-red coloration on the addition of sodium nitroprusside.

Sodium sulphite will be indicated by its more sparing solubility in water, and may be recognized in the aqueous solution by the production of a brown-red color with sodium nitro-prusside; if sodium sulphide is also present, the latter must first be removed by precipitation with zinc acetate before the application of the above test.

Calcium salts may be detected in the aqueous solution of the salt by the formation of a white precipitate when tested with ammonium oxalate.

Estimation:

The estimation of the salt may be readily and accurately accomplished volumetrically by the following process, which is based upon its property of combining with iodine, with the formation of sodium iodide and tetrathionate, as above described. 1 gram of crystallized sodium hyposulphite is dissolved, in a beaker, in 10 cubic centimeters of water, a little mucilage of starch is then added, and subsequently a decinormal solution of iodine (page 93) allowed to flow into the liquid from a burette until, with constant stirring, a permanent blue tint is produced. If the salt is perfectly pure, 40.32 cubic centimeters of the iodine solution will be thus required; if a smaller amount of the iodine solution effects a blue coloration of the liquid, the salt is impure, and the calculation may readily be made with the consideration that 1 cubic centimeter of the decinormal iodine solution corresponds to 0.0248 gram of pure crystallized sodium hyposulphite, $Na_2S_2O_3+5H_2O$. If the salt should have been found to contain sodium sulphide as an impurity, the latter must first be removed from the solution by precipitation with zinc acetate, and filtered, before being subjected to estimation with the solution of iodine.

The United States Pharmacopœia directs that a solution of 2 grams of the salt in 10 grams of water, agitated for a short time with 1 gram of iodine, should yield a colorless liquid, with at most only a faint, white opalescence (corresponding to about 98 per cent. of pure sodium hyposulphite).

SODII IODIDUM.

SODIUM SEU NATRIUM IODATUM.

Iodide of Sodium. Sodium Iodide.

Ger. Jodnatrium; Fr. Iodure de sodium; Sp. Ioduro de sodio.

NaI; 149.6.

A white, granular powder, or minute, colorless, cubical crystals, anhydrous when crystallized at temperatures above 40° C. (104° F.), or monoclinic prisms, containing two molecules (19.35

per cent.) of water of crystallization, when crystallized at ordinary temperatures. The salt is deliquescent on exposure to the air, and in a moist atmosphere becomes gradually decomposed, with the liberation of iodine and absorption of carbonic acid, acquiring thereby a reddish color; when exposed to heat, the salt fuses with the liberation of iodine and absorption of oxygen, and at a full red heat it is slowly volatilized. When a little of the salt is heated, in a test-tube, either in concentrated sulphuric acid, or with a little potassium bisulphate, violet-colored vapors of iodine are evolved; and when dissolved in a little water, a few drops of chlorine-water added, and the mixture subsequently shaken with a little chloroform or carbon bisulphide, a fine purple or violet color will be imparted to the latter. A fragment of the salt, when heated upon the looped end of a platinum-wire in the non-luminous flame, imparts to the latter an intense yellow color.

Sodium iodide is soluble in 0.6 part of water and in 1.8 parts of alcohol at 15° C. (59° F.), in 0.3 part of boiling water and in 1.4 parts of boiling alcohol, and is also freely soluble in glycerin. The aqueous solution possesses a saline, slightly bitter taste, and a neutral or feebly alkaline reaction; it gives no precipitate with tartaric acid, with sodium bitartrate, or with sodium carbonate, but forms a yellowish one with argentic nitrate, insoluble in diluted nitric acid or ammonia-water, and a vermilion-red one with mercuric chloride, soluble in an excess of either reagent.

Examination:

Impurities and admixtures, less soluble in alcohol, are indicated by a white turbidity or granular deposit, when a saturated aqueous solution of the salt is dropped into an excess of strong alcohol.

Potassium salts are indicated by a white, crystalline precipitate in the concentrated aqueous solution, when added to a strong solution of sodium bitartrate.

Chloride and *bromide* may be detected by dissolving 1 gram of the salt in 10 cubic centimeters of ammonia-water, and agitating the solution with a solution of 1.2 grams of argentic nitrate in 20 cubic centimeters of water; the mixture is then filtered, and the filtrate supersaturated with 7 cubic centimeters of concentrated nitric acid, when no immediate cloudiness of the liquid should be produced; a white turbidity or precipitate would indicate the presence of more than about 0.5 per cent. of chloride or bromide. If a precipitate is formed, it may be collected upon a filter, washed, and subsequently transferred to a test-tube, and agitated with chlorine-water; if argentic chloride, it remains unchanged; if bromide, the chlorine-water will assume a yellowish or reddish color, which, on agitation with chloroform, will be transferred to the latter.

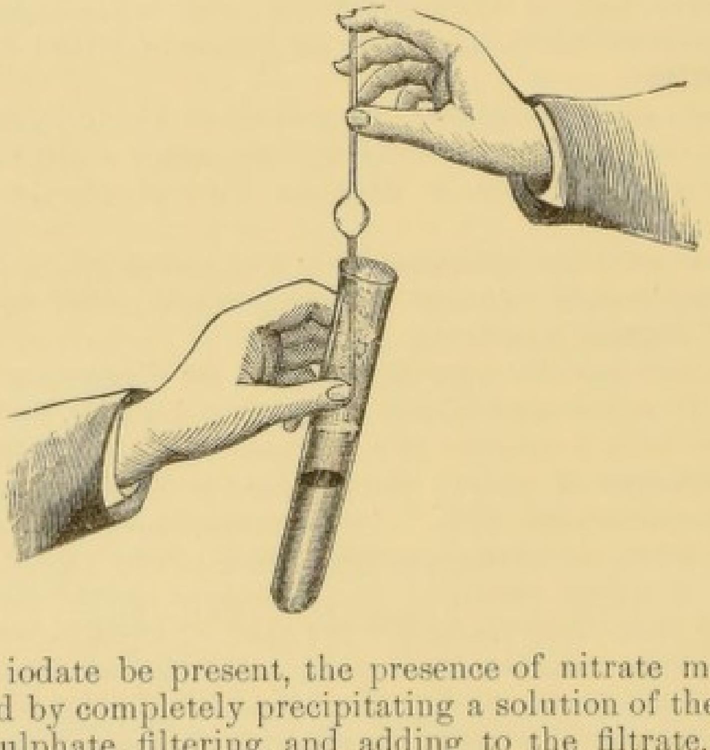
Carbonate may be detected, in the aqueous solution, by a white turbidity when mixed with twice or thrice its volume of lime-water, and will also be indicated by a strongly alkaline reaction, when a few fragments of the salt are placed upon moistened red litmus-paper.

Sulphate may be detected in the diluted solution of the iodide, previously acidulated with hydrochloric acid, by a white precipitate with barium chloride.

Iodate may be detected in the aqueous solution of the salt, by adding a few drops of mucilage of starch, and then a few drops of a concentrated solution of tartaric acid; if iodate be present, a violet or bluish coloration will ensue. Or, the aqueous solution, mixed with a few drops of a concentrated solution of tartaric acid, may be agitated with a little chloroform or carbon bisulphide, when the latter will assume a red or violet color if iodate be present.

Sodium nitrate may be detected in the aqueous solution, if the salt be free from iodate, by the addition of a few drops of mucilage of starch, and subsequently adding a little of this liquid to a mixture of zinc and diluted hydrochloric acid, in which the development of hydrogen is actively taking place; if any nitrate be present, the liquid will gradually assume a reddish-violet or blue color. If iodate be present, the presence of nitrate may also be determined by completely precipitating a solution of the salt with argentic sulphate, filtering, and adding to the filtrate, in a test-tube, a concentrated solution of ferrous sulphate, and afterwards concentrated sulphuric acid, so as to form two layers (Fig. 165); a dark-brown coloration at the line of contact of the two liquids will reveal the presence of nitrate.

Fig. 165.



Estimation:

A quantitative estimation of the purity of sodium iodide may be made by dissolving 1 gram of the salt in 10 grams of ammonia-water, and adding to the solution a solution of argentic nitrate until a precipitate ceases to be produced; the precipitate of argentic iodide is then collected upon a filter, well washed with water, and finally dried at 100° C. (212° F.) until of constant weight. If the sodium iodide is pure, 1.566 grams of argentic iodide should be obtained, or 100 parts of argentic iodide correspond to 63.83 parts of sodium iodide.

The estimation of the purity of sodium iodide may also be accomplished volumetrically by the following method. This is based upon the fact that mercuric chloride precipitates from a solution of sodium iodide, red mercuric iodide, which is soluble in an excess of a solution of sodium iodide with the formation of a soluble double salt, and the solution of the latter again yields upon the addition of mercuric chloride a precipitate of mercuric iodide:

$$\begin{aligned} 2\mathrm{NaI} + \mathrm{HgCl_2} &= \mathrm{HgI_2} + 2\mathrm{NaCl}, \\ \mathrm{HgI_2} + 2\mathrm{NaI} &= \mathrm{HgNa_2I_4}, \text{ or} \\ \underbrace{4\mathrm{NaI}}_{\substack{598.4 \\ (5)}} + \underbrace{\mathrm{HgCl_2}}_{\substack{271 \\ (2.26)}} &= \mathrm{HgNa_2I_4} + 2\mathrm{NaCl}. \end{aligned}$$

2.26 grams of mercuric chloride are dissolved in water to the measure of 100 cubic centimeters, and 5 grams of the sodium iodide under examination are likewise dissolved in water to the measure of 100 cubic centimeters.* 10 cubic centimeters of the sodium iodide solution are then brought into a beaker, which is placed upon a sheet of white paper, and to the solution is added, from a burette, the above solution of mercuric chloride until, with constant stirring, a permanent precipitate of mercuric iodide is just produced. The number of cubic centimeters of the mercuric chloride solution required to produce this reaction, when multiplied by 10, will represent the percentage amount of pure sodium iodide contained in the salt. The accuracy of the result of the estimation by the above method is not influenced by the presence of chloride or of considerable amounts of bromide.

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* The results attained by this method are rendered more accurate, when, instead of dissolving the mercuric chloride and sodium iodide in water, alcohol of 17.5 per cent. by volume is employed. From the formula $x = \frac{17.5 \cdot 100}{n}$, in which n represents the percentage strength of the alcohol to be diluted, the volume of alcohol may be calculated which must be added to the water in order to obtain 100 parts of alcohol of 17.5 per cent. by volume.

SODII NITRAS.

SODIUM SEU NATRIUM NITRICUM.

Nitrate of Sodium. Chili Saltpetre. Sodium Nitrate.

Ger. Salpetersaures Natrium ; Fr. Azotate de soude ; Sp. Nitrato de sosa.

$NaNO_3$; 85.

Anhydrous, colorless, transparent, obtuse-rhombohedral crystals of the hexagonal system (Fig. 166), having a specific gravity of 2.26; they are deliquescent in damp air, and generally of a moist appearance. The salt melts at 312° C. (594° F.) without decomposition, but, on further heating, becomes decomposed, with the evolution of oxygen, and leaves a residue which emits nitrous vapors on the addition of sulphuric acid; when thrown upon burning coals, the salt deflagrates, although not so violently as potassium nitrate, and imparts an intense yellow color to the non-luminous flame.

Fig. 166.

Sodium nitrate is soluble in 1.5 parts of water at 15° C. (59° F.), and in 0.6 part of boiling water; it is but sparingly soluble in cold alcohol, but soluble in 40 parts of boiling alcohol. The aqueous solution has a sharp, cooling, saline, and slightly bitter taste, and is neutral in its action upon litmus; when heated with potassium chloride or carbonate, it is decomposed, with the formation of potassium nitrate and sodium chloride or carbonate.

Its concentrated solution may readily be distinguished from that of potassium nitrate by not being acted upon by a solution of sodium bitartrate, which gives a white, granular precipitate with potassium nitrate.

Examination:

Chlorides and *sulphates* are detected in the diluted solution, after acidulation with diluted nitric acid, by white precipitates when tested, in separate portions, with argentic nitrate for chloride, and with barium nitrate for sulphate.

Sodium Iodide and Iodate.—To a solution of the salt a few drops of an aqueous solution of hydrogen sulphide are added, then a little mucilage of starch, and finally a few drops of chlorine-water allowed to flow upon the surface of the liquid; if either iodide or iodate is present, a blue zone will appear at the line of contact of the two liquids. If iodide and iodate are simultaneously present, the solution of the salt will also afford, on the simple addition of a few drops of diluted sulphuric acid, a yellow or brownish-yellow color, due to the elimination of free iodine, which, upon agitation with a little carbon bisulphide, will impart to the latter a violet-red color.

Iodate may be specially tested for, if desired, by dissolving a little of the salt in ten times its weight of water, acidulated with diluted sulphuric acid, adding to the solution a few drops of mucilage of starch, and subsequently a strip of pure metallic zinc; if iodate be present, a violet or bluish coloration of the liquid will be produced.

Calcium and *magnesium salts* are indicated in the warm solution of the salt by a white turbidity on the addition of a solution of sodium carbonate; they may be distinguished by adding a little ammonium chloride and ammonia-water to the dilute solution of the salt, and testing it with ammonium oxalate for calcium, and, after filtration, if necessary, by the addition of sodium phosphate for magnesium.

Metallic impurities will be indicated by a dark coloration or precipitate, when a solution of the salt, acidulated with hydrochloric acid, is saturated with hydrogen sulphide, or after filtration, if necessary, and neutralization with ammonia-water, by the subsequent addition of ammonium sulphide.

Estimation:

The proper amount of nitric acid contained in the salt may readily be determined by igniting it, at a red heat, in a small porcelain crucible, with an equal weight of concentrated sulphuric acid, until it ceases to lose weight. One gram of the salt, if perfectly pure, will thus afford a residue of sodium sulphate, weighing 0.835 gram. The determination of the proper amount of sodium in the salt, when free from potassium, may also readily be accomplished as follows. About 5 grams of the dry sodium nitrate, contained in a porcelain capsule, are repeatedly evaporated with a solution of about 8 grams of oxalic acid to dryness, until completely converted into sodium oxalate. The latter is then, by ignition, converted into sodium carbonate, which is dissolved in water, and, after the addition of a few drops of litmus solution, titrated with a standard solution of oxalic or sulphuric acid (page 82), as described under sodium carbonate, on page 545. The calculation may then be made with the consideration that one cubic centimeter of normal acid corresponds to 0.053 gram of sodium carbonate, or, as its equivalent, 0.085 gram of pure sodium nitrate.

SODII PHOSPHAS.

SODIUM SEU NATRIUM PHOSPHORICUM.

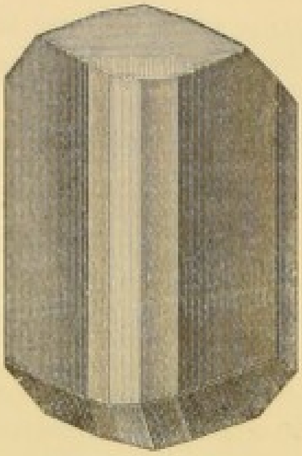
Phosphate of Sodium. Tribasic Sodium Phosphate. Di-sodium Hydrogen Orthophosphate.

Ger. Phosphorsaures Natrium; Fr. Phosphate de soude; Sp. Fosfato de sosa.

$Na_2HPO_4 + 12H_2O$; 358.

Large, colorless, transparent, monoclinic prisms (Fig. 167), containing 12 molecules (60.3 per cent.) of water of crystallization;

FIG. 167.



they readily effloresce and become opaque on exposure to the air, losing thereby, at common temperatures, 5 molecules (25.1 per cent.) of water, and become converted into a salt of the composition $Na_2HPO_4 + 7H_2O$, which may also be obtained from solutions of the ordinary salt, in a crystalline form, at temperatures above 33° C. (91.4° F.); on continued heating to 100° C. (212° F.), the salt loses the entire amount (60.3 per cent.) of water of crystallization. When heated to about 40° C. (104° F.), sodium phosphate first undergoes aqueous fusion, and afterward melts at a red heat into a limpid glass of sodium pyrophosphate, which becomes opaque on cooling.

Sodium phosphate is soluble in 6 parts of water at 15° C. (59° F.), and in 2 parts of boiling water, but is insoluble in alcohol. Its solution has a cooling, saline taste, a faintly alkaline reaction, affords no effervescence upon the addition of an acid, and gives with solution of argentic nitrate, a bright-yellow precipitate, soluble in both ammonia-water and nitric acid; the ammoniacal solution remains unchanged, when the test-tube, wherein it is contained, is immersed in boiling water (distinction from the similar argentic arsenite, whose ammoniacal solution deposits metallic silver upon the walls of the test-tube upon warming). With test magnesium mixture, sodium phosphate gives a white crystalline precipitate, insoluble in an excess of the salt as well as of the reagent.

Examination:

Sodium carbonate is detected by effervescence, upon the addition of hydrochloric acid to the concentrated solution of the salt.

Sulphates and *chlorides* are detected in the diluted solution, strongly acidulated with nitric acid, when tested in separate portions, with barium chloride for sulphate, and with argentic nitrate for chloride.

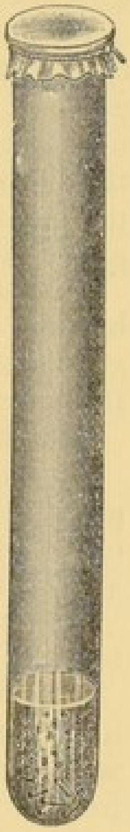
Calcium and *magnesium salts* will be indicated in the solution by a white precipitate on the addition of ammonia-water. They may be distinguished, by adding to the solution of the salt a few drops of a solution of ammonium oxalate, when a white precipitate will indicate calcium, and, after filtration, if necessary, and the addition of ammonia-water, an ensuing white, crystalline precipitate will reveal the presence of magnesium.

Metallic Impurities.—About 20 grams of the salt are dissolved in the requisite quantity of water, a few drops of hydrochloric acid added, and the solution, after being heated to boiling, is saturated with hydrogen sulphide; the flask is then corked and allowed to stand in a warm place for about twelve hours. A yellow precipitate would indicate arsenic, a dark one, the presence of other metallic impurities. The solution, after filtration, if necessary, may be neutralized with ammonia-water, and tested with ammonium sulphide, when an ensuing dark coloration or precipitate will likewise reveal the presence of metallic impurities.

As a confirmatory test, or if the presence of other metals requires a special test for arsenic, about 15 grams of the sodium phosphate are dissolved in a little more than an equal weight of pure, concentrated hydrochloric acid in a wide test tube, the solution being effected by dipping the tube into hot water and by agitation; a strip or roll of bright copper-foil is then completely immersed in the liquid, the tube again dipped into boiling water, and allowed to stand therein for half an hour. The copper must remain bright; a grayish or grayish-black coating of the copper would be evidence of the presence of *arsenic*.

Another simple test for arsenic consists in dissolving a little of the salt in dilute sulphuric acid, in a test-tube, adding thereto a few fragments of pure metallic zinc, and placing over the mouth of the tube a disk of white bibulous paper, previously moistened with a drop of solution of argentic nitrate (Fig. 168); if arsenic be present, a dark metallic stain will be produced upon the paper.

FIG. 168.



Estimation:

The purity of sodium phosphate may be quantitatively determined by dissolving 1 gram of the salt in about ten times its weight of water, and adding to the solution test magnesium mixture, until a precipitate ceases to be produced; the mixture is then allowed to stand for several hours, the precipitate collected upon a filter, washed with a mixture of one part of ammonia-water and three parts of water, and, after being allowed to dry, is brought into a weighed porcelain crucible, and strongly ignited at a red heat. If the salt be pure, the residue of magnesium pyrophosphate thus obtained will weigh 0.31 gram, or 100 parts of magnesium pyrophosphate correspond to 322.52 parts of crystallized sodium phosphate, $Na_2HPO_4 + 12H_2O$.

The purity of the salt, in the absence of other sodium salts, may also be determined by the estimation of the amount of contained sodium. 0.5 gram of the salt is dissolved in a little water, a solution of plumbic acetate added until a precipitate ceases to be produced, and subsequently filtered; the filtrate is then saturated with hydrogen sulphide, filtered from the precipitate of plumbic sulphide, and, after acidulation with hydrochloric acid, evaporated to dryness on the water-bath. The residue of sodium chloride is then brought into a weighed porcelain crucible, dried first at about 110° C. (230° F.), and finally gently ignited, and weighed. From the weight of the residue thus obtained the amount of phosphate may be calculated: 100 parts of sodium chloride corresponding to 305.98 parts of crystallized sodium phosphate, $Na_2HPO_4 + 12H_2O$.

SODII PYROPHOSPHAS.

SODIUM SEU NATRIUM PYROPHOSPHORICUM.

Pyrophosphate of Sodium. Sodium Pyro- or Tetraphosphate.

Ger. Pyrophosphorsaures Natrium; Fr. Pyrophosphate de soude;
Sp. Pirofosfato de sosa.

$Na_4P_2O_7 + 10H_2O$; 446.

Colorless, transparent, brilliant, monoclinic prisms, or a white granular powder, containing ten molecules (40.36 per cent.) of water of crystallization, and permanent in the air; when exposed to heat, the salt gives off its water of crystallization, without previously undergoing aqueous fusion (distinction from sodium phosphate), fuses at a higher temperature, and, on cooling, concretes to a crystalline semi-transparent mass.

Sodium pyrophosphate is soluble in 12 parts of water at 15° C. (59° F.), and in 1.1 parts of boiling water, but is insoluble in alcohol. Its aqueous solution possesses a saline taste and an alkaline reaction; it yields with a slight excess of a neutral solution of argentic nitrate a white precipitate of argentic pyrophosphate, and the filtrate therefrom is neutral in its action upon test-paper (additional distinction from sodium phosphate).

The solution of sodium pyrophosphate remains unchanged upon boiling, but if heated after the addition of a little nitric acid, it is gradually converted into the tribasic phosphate, and then affords the reactions of the latter, as described on page 562.

Examination:

Sodium phosphate will be indicated, when heated in a small glass tube, by the fusion of the salt previous to the elimination of the water; and also by the formation of a yellow precipitate with a neutral solution of argentic nitrate.

Carbonate is detected in the solution of the salt, by effervescence upon the addition of a little hydrochloric acid.

Sulphate and *chloride* may be detected in the diluted solution, after strongly acidulating with nitric acid, by white precipitates when tested in separate portions, with barium nitrate or chloride for the former, and with argentic nitrate for the latter.

Metallic impurities are detected in the warm aqueous solution, acidulated with hydrochloric acid, by saturation with hydrogen sulphide, and, after filtration, if necessary, and subsequent neutralization with ammonia-water, by a dark coloration or precipitate with ammonium sulphide.

SODII SALICYLAS.

SODIUM SEU NATRIUM SALICYLICUM.

Salicylate of Sodium. Sodium Salicylate.

Ger. Salicylsaures Natrium ; Fr. Salicylate de soude ; Sp. Salicilato de sosa.

$$2NaC_7H_5O_3 + H_2O = 2C_6H_4 \Big\langle \begin{array}{l} OH \\ CO{-}ONa \end{array} + H_2O;\ 338.$$

Small, white, crystalline plates, with a pearly lustre, or a crystalline powder, permanent in the air, and containing, for two molecules of the salt, one molecule (5.32 per cent.) of water of crystallization. When strongly heated, the salt becomes decomposed, with the evolution of inflammable vapors, and leaves a residue of sodium carbonate, amounting to between 30 and 31 per cent. of its original weight; this residue possesses a strongly alkaline reaction, effervesces with acids, and imparts an intense yellow color to the non-luminous flame.

Sodium salicylate is soluble in 1.5 parts of water and in 6 parts of alcohol at 15° C. (59° F.), and very soluble in boiling water and boiling alcohol; it is also freely soluble in glycerin, but very sparingly soluble in ether. The aqueous solution possesses a sweetish, saline, mildly alkaline taste, and a slight alkaline reaction, and affords a reddish-brown precipitate on the addition of a solution of ferric chloride. When the aqueous solution of the salt is supersaturated with hydrochloric or sulphuric acid, a voluminous white precipitate of salicylic acid is produced, which is readily soluble in boiling water, crystallizing out upon cooling; it is also freely soluble in ether, and assumes an intense violet color on the addition of a few drops of a solution of ferric chloride.

Examination:

The aqueous solution of sodium salicylate should be colorless and odorless, and its transparency should not be disturbed by the addition of an equal volume of alcohol.

Carbonates may be recognized in the solution of the salt by effervescence on the addition of dilute hydrochloric acid.

Chlorides and *sulphates* may be detected in a solution of 1 part of the salt in a mixture of 50 parts of alcohol and 25 parts of water, acidulated with nitric acid, and filtered, by testing it, in separate portions, with argentic nitrate for chlorides, and with barium chloride or nitrate for sulphates.

Organic impurities will be indicated by a brown or blackish coloration, when 1 part of the salt is agitated with about 15 parts of cold concentrated sulphuric acid.

SODII SANTONINAS.

SODIUM SEU NATRIUM SANTONINICUM.

Santoninate of Sodium. Sodium Santoninate.

Ger. Santoninsaures Natrium ; Fr. Santoninate de soude ; Sp. Santóninato de sosa.

$$2NaC_{15}H_{19}O_4+7H_2O;\ 698.$$

Colorless, transparent, tabular crystals, belonging to the rhombic system, which by exposure to sunlight slowly acquire a yellowish color; they contain, for 2 molecules of the salt, 7 molecules (18.05 per cent.) of water of crystallization, and effloresce slightly on the surface on exposure to dry air. When heated to 100° C. (212° F.), the salt loses its water of crystallization, and melts at 142° C. (287.6° F.), assuming thereby a fine red color, without, however, undergoing decomposition; at a higher temperature it chars, with the evolution of inflammable vapors, which burn with a very smoky flame, and finally leaves a strongly alkaline residue, which imparts an intense yellow color to the non-luminous flame.

Sodium santoninate is soluble in 3 parts of water and in 12 parts of alcohol at 15° C. (59° F.), in 0.5 part of boiling water and in 3.4 parts of boiling alcohol. The aqueous solution possesses a mildly saline, slightly bitter taste, and a feebly alkaline reaction; with diluted acids it yields a white, crystalline precipitate of santoninic acid, which, however, becomes rapidly converted into santonin, is readily dissolved by agitation with chloroform or ether, and yields, with an alcoholic solution of potassium hydrate, a scarlet-red liquid, which gradually becomes colorless.

Examination :

The cold aqueous solution of sodium santoninate should be colorless, should not effervesce on the addition of acids, and should afford no turbidity when mixed with an equal volume of alcohol.

Alkaline earths may be detected in a solution of 1 part of the salt in 20 parts of water, by a white turbidity or precipitate on the addition of a solution of sodium carbonate.

Sulphates and *chlorides* may be detected by dissolving a little of the salt in an equal weight of warm water, subsequently adding diluted nitric acid until a precipitate ceases to be produced, and, after filtration, testing the liquid, in separate portions, with barium chloride for sulphates, and with argentic nitrate for chlorides.

Alkaloids, which, by accident, have occasionally been found to occur in santonin, may be sought for in sodium santoninate by testing the acidulated aqueous solution of the salt with potassio-mercuric iodide, iodinized potassium iodide, picric or tannic acids; no turbidity or precipitate should be produced by either of these reagents.

SODII SULPHAS.

SODIUM SEU NATRIUM SULFURICUM.

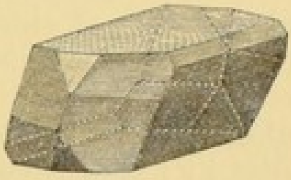
Sulphate of Sodium. Glauber's Salt. Sodium Sulphate.

Ger. Schwefelsaures Natrium, Glaubersalz; Fr. Sulfate de soude; Sp. Sulfato de sosa.

$Na_2SO_4 + 10H_2O$; 322.

Large, colorless, transparent, monoclinic prisms (Fig. 169), having the specific gravity of 1.481, and containing ten molecules (55.9 per cent.) of water of crystallization; they effloresce rapidly on exposure to the air, losing all the water of crystallization, and crumbling to a white powder. When heated to 33° C. (91.4° F.), the salt undergoes aqueous fusion, and at a higher temperature loses its water of crystallization, leaving an anhydrous residue, which melts at a red heat without decomposition. A fragment of the salt imparts an intense yellow color to the non-luminous flame.

FIG. 169.



Sodium sulphate is very soluble in water; 100 parts of water at 0° C. (32° F.) dissolve 12.17 parts, at 18° C. (64.4° F.) 48.28 parts, at 25° C. (77° F.) 99.48 parts, and at 33° C. (91.4° F.) 322.12 parts, of the crystallized salt; above that temperature the salt passes into the anhydrous state, in which it is less soluble, and the solution then separates the anhydrous salt in the form of small rhombic octohedrons. The solution saturated at 33° C. (91.4° F.) affords no crystals upon cooling to the ordinary temperature, but remains supersaturated; if, however, a fragment of the crystallized salt be added to the solution, it immediately solidifies, accompanied by a considerable rise of temperature. The supersaturated solution apparently contains a salt with 7 molecules of water of crystallization.

Sodium sulphate is also soluble in glycerin, but is insoluble in alcohol. The aqueous solution of the salt possesses a saline and feebly bitter taste, is neutral, remains unaltered with sodium carbonate as well as with sodium bitartrate, and gives a granular white precipitate with lime-water, and a copious white one with solutions of both barium and lead salts, which latter precipitates are insoluble in diluted acids.

If 1 gram of crystallized sodium sulphate be dissolved in a little water, the solution acidulated with hydrochloric acid, and completely precipitated by barium chloride, a precipitate of barium sulphate is produced, which, when collected upon a filter, washed, dried, and ignited, should weigh 0.723 gram.

Examination:

A solution of one part of the crystallized salt in four parts of water, tested with blue and with red litmus-paper, should not change the color of either.

Chloride may be detected in the diluted solution, acidulated with nitric acid, by a white turbidity or precipitate with argentic nitrate.

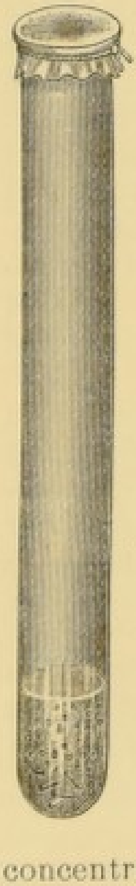
Carbonate may be detected in the solution of the salt by effervescence on the addition of an acid.

Ammonium sulphate may be recognized by the odor as well as by the rise of white vapors, when a little of the triturated salt is heated in a strong solution of potassium hydrate, and a glass rod, moistened with acetic acid, is held in the orifice of the test-tube.

Magnesium and *calcium salts* are detected in the solution by a white precipitate with sodium carbonate; a reddish or brownish appearance of the precipitate would indicate metallic impurities (iron and manganese); the presence of *manganese salts* may be confirmed by a brown precipitate upon the addition of a solution of chlorinated lime to the solution of the sodium sulphate, that of *iron* by a blue turbidity, when the solution of the salt is acidulated with hydrochloric acid and tested with potassium ferrocyanide.

Metals may further be detected in the diluted solution by adding a little ammonium sulphide, and allowing the mixture to stand for a few hours; a white turbidity would indicate *zinc*, and a brownish-black one, *copper;* a greenish-black one would confirm the presence of *iron*, and a pale-reddish one, that of *manganese*.

FIG. 170.



If a test for arsenic is required, about 2 grams of the crystallized sodium sulphate are dissolved in an equal weight of warm water in a wide test-tube; an amount of concentrated hydrochloric acid equal to about ten times the weight of the salt is then added, and a strip or roll of bright copper-foil completely immersed in the fluid; the tube is then dipped into boiling water and allowed to stand in the water for half an hour. The copper must remain bright; a grayish-black coating would indicate *arsenic*. The presence of arsenic may also readily be determined by adding to a solution of the salt, in a test-tube, a strong solution of potassium hydrate, subsequently a few fragments of pure metallic zinc, and placing over the mouth of the tube a cap of bibulous paper moistened with a drop of a solution of argentic nitrate (Fig. 170), and gently heating; if arsenic be present, a dark metallic stain will be produced on the paper.

Sulphite and *hyposulphite* may be detected in a solution of one part of the salt in three parts of water, by mixing it, in a test-tube, with one-third of its volume of concentrated hydrochloric acid, and heating it gently with a few fragments of granular zinc; the presence of either of the above salts will give rise to the formation of hydrogen sulphide, which may be recognized by placing a small bunch of cotton, moistened with solution of plumbic acetate, in the orifice of the tube, or by closing it with bibulous paper moistened with the plumbic solution (Fig. 170). A black coloration of the cotton or a dark stain upon the paper would indicate the presence of either or both of the above salts.

SODII SULPHIS.

SODIUM SEU NATRIUM SULFUROSUM.

Sulphite of Sodium. Sodium Sulphite.

Ger. Schwefligsaures Natrium; Fr. Sulfite de soude; Sp. Sulfito de sosa.

$Na_2SO_3 + 7H_2O$; 252.

Colorless, transparent, monoclinic prisms, containing seven molecules (50 per cent.) of water of crystallization; on exposure to the air, they effloresce somewhat, and the salt is gradually converted into sulphate, emitting a feeble odor of sulphur dioxide. This liability to decomposition is retarded, and the salt made more permanent, by exsiccating it at a gentle heat, when it undergoes aqueous fusion, loses its water of crystallization, and becomes white. It is this granular form in which sodium sulphite is now frequently met with. When this salt is exposed to a strong red heat, it fuses to a dirty yellowish mass, consisting of sodium sulphate and sulphide; these may be separated by extracting the cold residue with strong alcohol, which dissolves the sulphide, but not the sulphate.

Crystallized sodium sulphite is soluble in 4 parts of water at 15° C. (59° F.), and in 0.9 part of boiling water, but only sparingly in alcohol; its aqueous solution has a feeble alkaline reaction, and becomes turbid upon heating, but transparent again on cooling; on exposure of the solution to the air, the sulphite is gradually converted into sulphate with the separation of sulphur, as it is also by treatment with oxidizing agents, such as chlorine, hypochlorous acid, nitrous acid, etc. When acidulated, solution of sodium sulphite acts as a powerful reducing agent; it emits sulphur dioxide upon the addition of strong acids, slowly when cold, freely on warming, and, in the latter instance, with the separation of sulphur; when this test is performed with hydrochloric or sulphuric acid, and with the addition of a little zinc, hydrogen sulphide is evolved. With barium chloride or nitrate, solution of sodium sulphite forms white precipitates, soluble in diluted hydrochloric acid.

Examination:

Sodium sulphate may be detected in a solution of 1 part of the salt in 100 parts of water, strongly acidulated with hydrochloric acid, by a white precipitate on the addition of a few drops of solution of barium chloride.

Estimation:

About 0.5 gram of the salt is dissolved in a small portion of water, a little mucilage of starch added, and subsequently a decinormal solution of iodine (page 93) allowed to flow into the liquid from a burette until, with constant stirring, a permanent blue coloration of the liquid is just produced. The number of cubic centimeters of iodine solution, which are required to produce this reaction, when multiplied by the decimal 0.0126, will represent the amount of pure, crystallized sodium sulphite in the specimen under examination, and therefrom its percentage purity may readily be calculated.

The United States Pharmacopœia directs that if 0.63 gram of the salt be dissolved in 25 cubic centimeters of water, and a little gelatinized starch added, at least 45 cubic centimeters of the volumetric solution of iodine should be required, before a permanent blue tint appears after stirring (corresponding to at least 90 per cent. of pure sodium sulphite).

SODII SULPHOCARBOLAS.

SODIUM SEU NATRIUM SULFOCARBOLICUM SEU SULFOPHENOLICUM.

Sulphocarbolate of Sodium. Sodium Sulphocarbolate or Sulphophenolate.

Ger. Phenolsulfosaures Natrium; Fr. Sulfocarbolate de soude;
Sp. Sulfocarbólato de sosa.

$$NaC_6H_5.SO_4 + 2H_2O = C_6H_4\begin{cases} OH \\ SO_2\text{-}ONa \end{cases} + 2H_2O;\ 232.$$

Colorless, transparent, rhombic prisms, containing two molecules (15.51 per cent.) of water of crystallization, and permanent in the air. When heated to 100° C. (212° F.), the salt loses its water of crystallization, and becomes converted into a white powder; at a higher temperature it is decomposed, with the evolution of inflammable vapors, having the odor of phenol (carbolic acid), and leaving a white residue, amounting to 36 per cent. of the original weight; if this residue be dissolved in water, the solution filtered, acidulated with hydrochloric acid, and tested with a few drops of solution of barium chloride, a white precipitate of barium sulphate will be produced, insoluble in nitric or hydrochloric acid. A fragment of the salt, when heated in the non-luminous flame, imparts to the latter an intense yellow color.

Sodium sulphocarbolate is soluble in 5 parts of water and in 132 parts of alcohol at 15° C. (59° F.), in 0.7 part of boiling water and in 10 parts of boiling alcohol. The aqueous solution possesses a cooling, saline, slightly bitter taste, and is neutral in its action upon litmus; it yields, even when highly diluted, a deep violet color on the addition of a few drops of a solution of ferric chloride.

Examination:

Sulphate may be detected in a solution of 1 part of the salt in 100 parts of water by an immediate white turbidity or precipitate on the addition of a solution of barium chloride.

Barium and *calcium salts* may be detected in the aqueous solution, when tested in separate portions, with magnesium sulphate for the former, and with ammonium oxalate for the latter.

Metallic impurities will be indicated in the solution of the salt, either before or after acidulation with hydrochloric acid, by a turbidity or precipitate when saturated with hydrogen sulphide; the occurrence of a white precipitate with the latter reagent in the neutral solution of the salt would indicate the presence of *zinc*.

SPIRITUS ÆTHERIS NITROSI.

SPIRITUS NITROSO-ÆTHEREUS. SPIRITUS NITRI DULCIS.

Spirit of Nitrous Ether. Sweet Spirit of Nitre. Alcoholic Solution of Ethyl Nitrite.

Ger. Versüsster Salpetergeist; Fr. Ether azoteux alcoolisé;
Sp. Espíritu de nitro dulce.

A colorless or pale-yellow, volatile liquid, of a fragrant, ethereal odor, and sharp, aromatic, sweetish taste; its spec. grav. is 0.823 to 0.825 U. S. Pharm. (0.845 Brit. Pharm., and 0.840–0.850 Pharm. Germ.), and it should contain between 4 and 5 per cent. of ethyl nitrite. It is inflammable, reddens blue litmus-paper not at all or only faintly, and assumes a dark color upon the addition of a few drops of a solution of ferrous chloride or sulphate. When added to a dilute solution of potassium iodide, to which a few drops of dilute sulphuric acid and a little mucilage of starch have previously been added, a blue coloration will be produced.

Spirit of nitrous ether is miscible with water, alcohol, chloroform, ether, carbon bisulphide, benzol, and essential and fatty oils. A portion of the spirit, in a test-tube half filled with it, plunged into water heated to 63° C. (145.4° F.), and held there until it has acquired that temperature, will boil distinctly on the addition of a few small pieces of glass.

Examination:

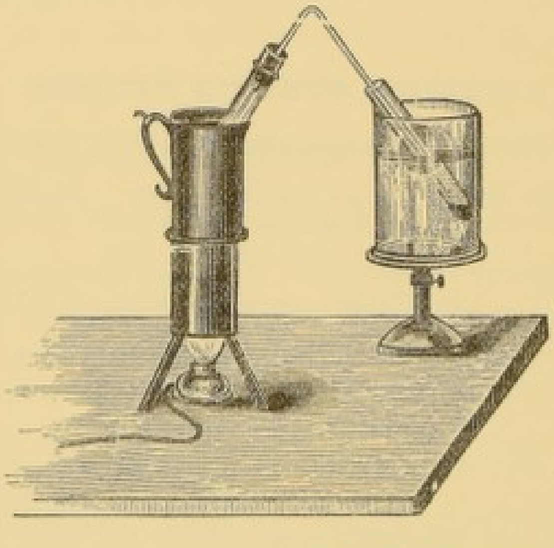
Aldehyde is indicated by a brown coloration of the spirit when agitated in a test-tube with a few fragments of fused potassium hydrate.

Acids.—Spirit of nitrous ether containing so much of free acid as to have a perceptible sour taste and an acid reaction upon blue litmus-paper, and to cause the rise of gas-bubbles from a few crystals of potassium bicarbonate when dropped into it, cannot be considered admissible for medicinal use.

Ethyl chloride may be detected by burning away a small quantity of the spirit upon a little water in a porcelain capsule, and by subsequently testing the water, after acidulation with a few drops of nitric acid, with a few drops of solution of argentic nitrate; the occurrence of a white turbidity would indicate the presence of ethyl chloride.

Methylic Alcohol.—About 30 cubic centimeters of the spirit are shaken with 2 to 3 grams of anhydrous (exsiccated) potassium carbonate; after subsiding, the supernatant spirit is decanted; about 15 cubic centimeters of this dehydrated spirit is introduced into a small flask, or a test-tube of a proper size (Fig. 171), 10 grams of anhydrous calcium chloride in powder are added, and, after thoroughly mixing, the flask is connected with a bent glass tube or a condenser, and is then placed in a water-bath for distillation; this distillation is continued until about 5 cubic centimeters of distillate have been obtained. The test-tube is then removed from the water-bath, and, when cool, 5 cubic centimeters of water are added, and the distillation once more resumed until a little more than 2 cubic centimeters of distillate are obtained. The latter distillate is mixed with 15 cubic centimeters of water, wherein 2 grams of potassium bichromate and 30 drops of concentrated sulphuric acid have been dissolved. After having allowed the mixture to stand for a quarter of an hour, it also is submitted to distillation, until 15 cubic centimeters of distillate are obtained; to this 2 grams of crystallized sodium carbonate are added, in a porcelain capsule, and the whole

FIG. 171.



evaporated to half its volume; it is then slightly supersaturated with acetic acid, filtered into a test-tube, and about 30 drops of solution of argentic nitrate added, and the whole gently boiled for about two minutes. If the spirit is free from methylic alcohol, the solution darkens, and often assumes transiently a purplish tinge, but continues quite transparent, and the test-tube, after being rinsed out and filled with water, appears clean. But, if the spirit contains even traces of methylic alcohol, the liquid becomes at first brown, then almost black and opaque, and a film of silver is deposited on the tube, which appears brown by transmitted light. When only 3 to 4 per cent. of methylic alcohol is present, the film is sufficiently thick to form a brilliant metallic mirror.

Estimation of the Quantity of Ethyl Nitrite:

Ten grams of the spirit of nitrous ether are digested in a strong glass-stoppered vial for about half an hour, on the water-bath, with about three times its volume of an alcoholic solution of pure potassium hydrate. The ethereal odor will then have disappeared, and the contents of the vial are transferred to a beaker, a little water added, and gently heated on the water-bath until the alcohol has evaporated. The remaining solution is then diluted to the measure of about 200 cubic centimeters, acidulated with dilute sulphuric acid, and a decinormal solution of potassium permanganate (page 89) allowed to flow into the liquid from a burette until, with constant stirring, the red color imparted to the liquid ceases to be discharged within a few minutes.

The exact strength of the potassium permanganate solution having been previously determined by means of metallic iron, as described on page 89, the amount of potassium permanganate, expressed in grams, contained in the volume of the solution employed, may readily be calculated; this number, when multiplied by 1.18, will represent the amount of pure ethyl nitrite in 10 grams of the spirit, and requires simply to be multiplied by 10 in order to express the percentage.

The reactions involved in the above operation may be represented by the following equations:

$$(\alpha)\ \underbrace{5C_2H_5\text{–}NO_2}_{375} + 5KOH = 5C_2H_5\text{–}OH + 5KNO_2$$

$$(\beta)\ 5KNO_2 + 3H_2SO_4 + \underbrace{K_2Mn_2O_8}_{316} = 5KNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

Therefore $\frac{375}{316} = 1.18$, and accordingly $xK_2Mn_2O_8 \times 1.18 = xC_2K_5\text{–}NO_2$

The United States Pharmacopœia directs that if 10 grams of spirit of nitrous ether be macerated with 1.5 grams of potassium hydrate for twelve hours, with occasional agitation, the mixture then diluted in a beaker with an equal volume of water, and set aside until the odor of alcohol has disappeared, then slightly acidulated with diluted sulphuric acid, and a solution of 0.335 gram of potassium permanganate gradually added, the color of the whole of this solution should be discharged (corresponding to the presence of at least 4 per cent. of pure ethyl nitrite).

STRYCHNINA.

STRYCHNINUM. STRYCHNIUM.

Strychnine. Strychnia.

Ger. Strychnin ; Fr. Strychnine ; Sp. Estricnina.

$C_{21}H_{22}N_2O_2$; 334.

Small, brilliant, octahedral crystals, or four-sided prisms of the rhombic system, colorless and transparent, or a white, crystalline powder, permanent in the air. When the crystals are very carefully heated, in small amount, they melt without decomposition, and may also to a slight extent be sublimed; when heated upon platinum-foil, they spread over the foil like melted resin and become decomposed, leaving a charred residue, which, at a stronger heat, is wholly dissipated (evidence of the absence of fixed admixtures).

Strychnine is soluble in 6700 parts of water and in 110 parts of alcohol at 15° C. (59° F.); in 2500 parts of boiling water and in 12 parts of boiling alcohol. It is also soluble in 6 parts of chloroform, 170 parts of benzol, 185 parts of amylic alcohol, 300 parts of glycerin, and 485 parts of carbon bisulphide, but is almost insoluble in ether, absolute alcohol, and petroleum benzin; dilute acids dissolve it freely and without color. The saturated alcoholic or aqueous solution possesses an alkaline reaction and an intensely bitter taste, which is still perceptible when diluted to such an extent that 700,000 parts of the solution contain but 1 part of the alkaloid.

FIG. 172.

When a few drops of cold concentrated nitric acid are added, by means of a glass rod or a small pipette (Fig. 172), to a little strychnine, or its salts, on a watch-glass or porcelain plate, it dissolves without any color, or with only a pale-greenish or yellow tint (distinction from brucine and morphine, and their salts, which give intensely red solutions). Strong sulphuric acid also dissolves strychnine and its salts without color (distinction from brucine, veratrine, and salicin, which yield red or purple colorations); but, when a minute fragment of a crystal or one drop of a solution of potassium bichromate or permanganate is added, the solution assumes at once a deep-violet or blue color, which successively changes from violet to red, and finally to green or yellow.*

When a cold, saturated alcoholic solution of strychnine is mixed with about an equal volume of an alcoholic solution of ammonium sulphide, and the mixture is allowed to stand for twelve hours, long, brilliant, orange-red needles are formed, having the composition $(C_{21}H_{22}N_2O_2)_2S_6H_2$, which are insoluble in water, alcohol, ether, and carbon bisulphide, and are decolorized and decomposed when treated with concentrated sulphuric acid, with the formation of strychnine sulphate, and of an oily compound of a penetrating odor, which, in contact with water, is resolved into sulphur and hydrogen sulphide. Strychnine only is known to produce this reaction.

When a little strychnine is agitated with a small amount of warm water, insufficient to dissolve it, it will dissolve readily upon the subsequent addition of a few drops of diluted sulphuric acid; this solution, when tested in separate portions, will yield precipitates with tannic acid, with potassio-mercuric iodide, and with iodinized potassium iodide; it will remain unaltered with potassium bicarbonate (distinction from the cinchona alkaloids), but it will yield a white precipitate with the alkaline hydrates, insoluble in an excess of the precipitant (further distinction from morphine), and also but sparingly soluble when agitated with ether, but readily soluble in chloroform.

Examination:

Incidental or fraudulent admixtures of other alkaloids are recognized by the above-described characteristics and reactions of strychnine.

Brucine and *salicin* are indicated by a red coloration with either concentrated nitric or sulphuric acid.

Brucine may also be recognized by its ready solubility in absolute alcohol (wherein strychnine is almost insoluble), and by the reaction of its solution in nitric acid with stannous chloride or ammonium sulphide (page 283). While pure strychnine affords a pale-green or yellowish solution with strong nitric acid, this will appear more or less red, if brucine be present, and will assume, after the addition of a little water and evaporation of the excess of acid, a deep violet color upon the subsequent addition of solu-

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* Only aniline and its salts are known to afford, with the same reagent, a similar reaction, which, however, is less of a violet and more of a blue tint throughout, and which does not appear immediately.

tion of stannous chloride, or ammonium sulphide; if the latter reagent has been employed, a white turbidity from the separation of sulphur may occur.

Santonin is recognized by its insolubility in dilute acids, and by its property of assuming a lemon-yellow color when the sample, covered with a sheet of thin white paper, is exposed to solar light for one or two days.

Cinchona alkaloids may be detected by a white precipitate, when a solution of the strychnine in dilute sulphuric acid is tested with solution of potassium bicarbonate.

Cinchonine may also be recognized by its insolubility in chloroform, remaining behind when a little powdered strychnine is exhausted with that solvent; its identity may then be ascertained by its properties, described on page 316.

For the separation of strychnine from other alkaloids with which it may be associated, or from complex organic mixtures, advantage may be taken of the sparing solubility of the crystalline chromate or picrate, as precipitated by a solution of potassium bichromate or picric acid, or the method described on page 108 may be employed. The chromate is specially adapted for obtaining its most characteristic reaction, which is produced by simple contact of the latter salt with a few drops of concentrated sulphuric acid. The picrate, although a yellow salt, forms a colorless solution with concentrated sulphuric acid, and is likewise admirably adapted for obtaining the reaction with potassium bichromate.

STRYCHNINÆ NITRAS.

STRYCHNINUM SEU STRYCHNIUM NITRICUM.

Nitrate of Strychnine or Strychnia. Strychnine Nitrate.

Ger. Salpetersaures Strychnin; Fr. Azotate de strychnine;
Sp. Nitrato de estricnina.

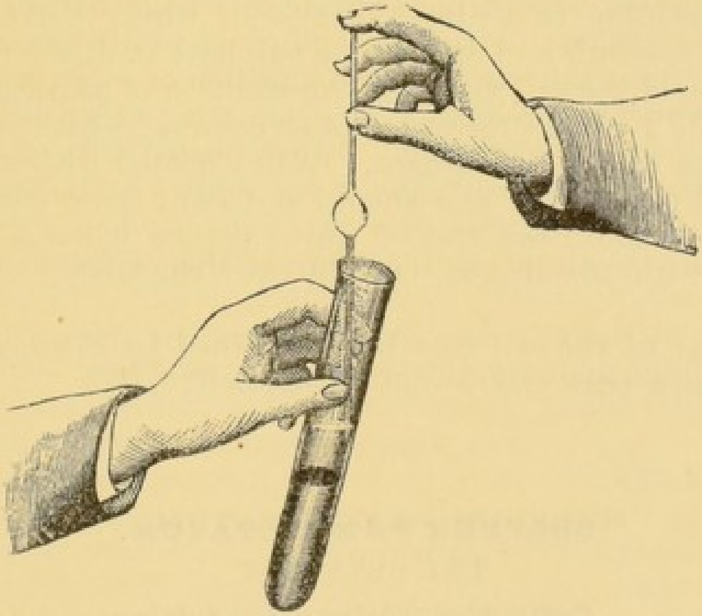
$C_{21}H_{22}N_2O_2.HNO_3$; 397.

Colorless, transparent, flexible needles, of a silky lustre, permanent in the air. When gently heated on platinum-foil they assume at first a yellowish color, and, at a higher temperature, deflagrate slightly, leaving a carbonaceous residue, which, at a red heat, is wholly dissipated (evidence of the absence of fixed admixtures).

Strychnine nitrate is soluble in 90 parts of water and in 70 parts of alcohol at 15° C. (59° F.), in 3 parts of boiling water and 5 parts of boiling alcohol, but insoluble in ether and carbon bisulphide. Its solutions are neutral, and have an intensely bitter taste. They yield, on the addition of solution of potassium hydrate, a white precipitate of strychnine, which is insoluble in an excess of the precipitant.

Strychnine nitrate answers to all the reactions of strychnine, and may be recognized by the characteristic coloration with strong sulphuric acid and potassium bichromate or permanganate, as described on page 575. In distinction from strychnine, it is furthermore specially characterized by heating a crystal of the salt, or a little of the solution with concentrated hydrochloric acid, to boiling, when a bright red color is produced. The evidence of being a nitrate is not readily obtained by the direct application of the ordinary tests, and in performing this reaction the strychnine should first be precipitated from the solution of the salt by the addition of a slight excess of potassium or sodium hydrate; the filtrate may then be tested by supersaturating it with hydrochloric acid, adding a drop of solution of indigo, and heating to boiling, when decoloration of the liquid will ensue; or, to the filtrate, concentrated sulphuric acid, in slight excess, may be added, and subsequently a saturated solution of ferrous sulphate allowed to flow upon the surface of the liquid by means of a pipette, so as to form two layers (Fig. 173); a dark-brown coloration will take place at the junction of the two liquids.

Fig. 173.



The methods for testing the purity of strychnine nitrate are the same as described with strychnine on pages 575, 576. It needs only to be added that the salt should not emit ammoniacal odors, when heated with a strong solution of potassium hydrate, nor, upon heating with the latter, should it cause the rise of white vapors, when a glass rod, moistened with acetic acid, is held over the orifice of the test-tube.

STRYCHNINÆ SULPHAS.

STRYCHNINUM SEU STRYCHNIUM SULFURICUM.

Sulphate of Strychnine or Strychnia. Strychnine Sulphate.

Ger. Schwefelsaures Strychnin; Fr. Sulfate de strychnine; Sp. Sulfato de estricnina.

$(C_{21}H_{22}N_2O_2)_2.H_2SO_4+6H_2O$; 874.

Fine, colorless, and transparent prismatic crystals, containing six molecules (12.24 per cent.) of water of crystallization, and slightly efflorescent on exposure to dry air. When heated to about 185° C. (365° F.) they lose the water of crystallization, without previously fusing; at a higher temperature they become charred and decomposed, and, at a red heat, they burn away without residue (evidence of the absence of fixed admixtures).

Strychnine sulphate is soluble in 42 parts of water and in 60 parts of alcohol at 15° C. (59° F.), in 2 parts of boiling water and in 2 parts of boiling alcohol. It is also soluble in 26 parts of glycerin, but is insoluble in ether. Its solutions are intensely bitter; their deportment with reagents answers to that of strychnine, and they also afford the characteristic reaction with sulphuric acid and potassium bichromate or permanganate; the evidence of being a sulphate may be obtained by the white precipitate, insoluble in hydrochloric acid, which barium nitrate yields with a solution of strychnine sulphate in dilute nitric acid. The solution of the salt yields on the addition of solution of potassium hydrate a white precipitate of strychnine, which is insoluble in an excess of the precipitant. When heated with solution of potassium hydrate, the salt should not emit ammoniacal odors, nor should it cause the rise of white vapors when a glass rod, moistened with acetic acid, is held over the orifice of the test-tube.

The purity of the salt may be ascertained by the same tests as described with pure strychnine, on pages 575, 576.

SULPHUR PRÆCIPITATUM.

LAC SULFURIS.

Precipitated Sulphur. Lac Sulphur.

Ger. Gefällter Schwefel, Schwefelmilch; Fr. Soufre précipité; Sp. Azufre precipitado.

S; 32.

A fine, slightly coherent powder, of a pale yellowish or grayish color, without taste or smell, and free from grittiness, consisting, when seen under the microscope, of minute, opaque globules, without any admixture of crystalline matter. When thrown upon burning coal, or heated in an open vessel, precipitated sulphur first emits a little hydrogen sulphide, then fuses, and burns wholly away at a stronger heat.

Precipitated sulphur is insoluble in the common solvents, but is readily and wholly soluble in carbon bisulphide, and in strong, boiling solutions of potassium and sodium hydrates, and also more or less in benzol, in hot oil of turpentine, and other essential and fatty oils.

Examination:

Fixed admixtures are indicated by a white ash or a non-volatile residue when a small portion of the sulphur is strongly heated in an open porcelain crucible.

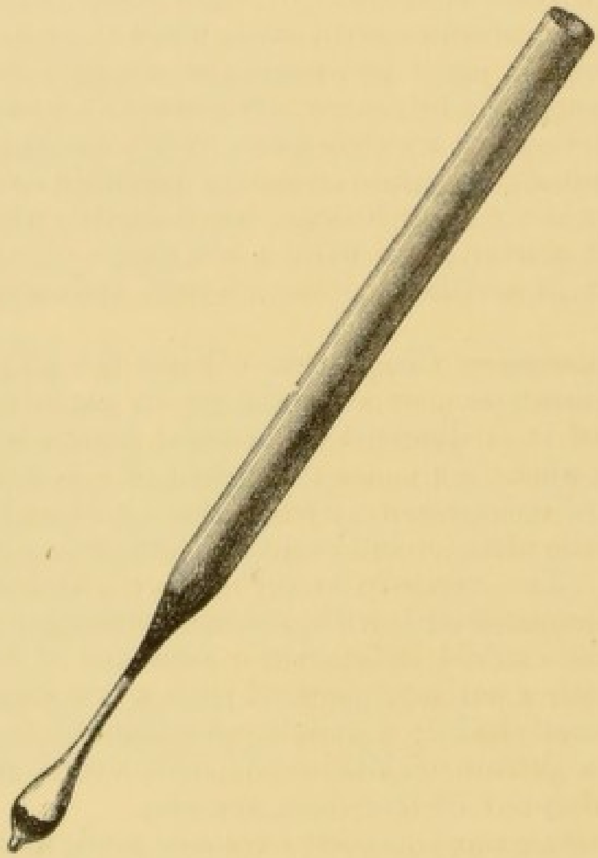
Calcium Sulphate.—A small portion of the sulphur is triturated with about ten times its weight of tepid water, and the mixture agitated for a few minutes until cold, when it is filtered; the filtrate must not act upon test-paper, as an acid reaction would indicate long exposure to the air; nor must it leave any residue upon evaporation upon a watch-glass, which would indicate either insufficient washing, or an admixture of a soluble fixed compound; a white precipitate of the filtrate, when tested with ammonium oxalate in one portion, and with a few drops of nitric acid and barium nitrate in another portion, would indicate calcium sulphate.

Earthy Carbonates or Phosphates.— When the sulphur leaves a residue on incineration, or on solution in carbon bisulphide, a small portion of it is digested for several hours, with occasional agitation, with about ten times its weight of a mixture consisting of equal parts of concentrated hydrochloric acid and water; effervescence upon the addition of the acid would indicate the presence of carbonates. The mixture is then filtered, and one portion of the filtrate supersaturated with sodium carbonate; an ensuing white precipitate would indicate the presence of the above admixtures; the other portion is heated with a few drops of solution of ammonium molybdate; a yellow coloration of the liquid, and, after a while, a yellow crystalline deposit, would indicate phosphates (if the sulphur be free from arsenic).

Any admixture, except *powdered resin* or *pitch*, which are recognized by a sooty flame when ignited, and by their solubility in strong alcohol or ether, may be quantitatively determined by remaining undissolved upon digesting a known quantity of the sulphur with carbon bisulphide, or, when calcium sulphate is the only admixture, by complete incineration of a weighed quantity of the sulphur in a tared porcelain crucible; the weight of the remaining anhydrous calcium sulphate, with one-fourth thereof added to compensate for the loss of the water of crystallization, gives the amount of crystalline calcium sulphate present in the quantity of sulphur under examination.

Arsenic may be detected by triturating a portion of the sulphur with about ten times its weight of ammonia-water or a saturated solution of ammonium carbonate, and subsequently digesting the mixture in a corked test-tube, for about one hour, with occasional agitation; the liquid is then filtered, and a portion of the filtrate supersaturated with hydrochloric acid; the formation of a yellow precipitate, either at once or upon subsequent saturation of the liquid with hydrogen sulphide, would indicate arsenic; the rest of the filtrate is evaporated to dryness in a small porcelain capsule; if a residue remains, it is detached by triturating it with a little powdered magnesite, or pumice-stone, a little potassium cyanide is then added, and the mixture, after being introduced into a reduction-tube (Fig. 174), is first gently heated in order to expel moisture, which may be removed by means of a strip of bibulous paper, and the contents of the tube subsequently strongly heated; whereupon, the formation of a metallic mirror and the evolution of a garlic-like odor would further indicate arsenic.

FIG. 174.



An admixture of *starch* may be recognized by examination of the precipitated sulphur under the microscope, or by boiling a small portion of it with about ten times its weight of water, and testing the cooled liquid with one drop of solution of iodinized potassium iodide. The occurrence of a blue coloration would show such an adulteration.

SULPHUR SUBLIMATUM.

FLORES SULFURIS.

Sublimed Sulphur. Flowers of Sulphur.

Ger. Sublimirter Schwefel, Schwefelblumen; Fr. Soufre sublimé; Sp. Azufre sublimado.

S; 32.

A gritty, yellow, tasteless, and odorless powder, consisting, when seen under the microscope, of a mixture of minute, smooth globules, and of rhombic-octahedral crystals. When heated in a dry tube, sulphur fuses at 115° C. (239° F.), forming an amber-colored fluid, which, when heated to from 220 to 250° C. (428 to 482° F.), becomes more and more thick and tenacious, and assumes a deep brownish-red color; at a temperature approaching the boiling-point, 448° C. (818° F.), it becomes thin and liquid again, and volatilizes in colorless vapors, which condense on cooling; when heated with free access of air, sulphur takes fire at about 270° C. (518° F.), and slowly burns away with a pale-blue flame, forming sulphurous-acid gas.

Sublimed sulphur is insoluble in water, and almost insoluble in alcohol and in ether; it dissolves to some extent in chloroform, and for the most part in carbon bisulphide,* in benzol, and in warm or boiling essential and fatty oils; it is wholly soluble in a hot concentrated solution of potassium or sodium hydrate.

Commercial sublimed sulphur has generally an acid reaction upon moist test-paper, and contains traces of oxygen acids of sulphur, occasionally also of selenium, and frequently of sulphides of arsenic, all which impurities have to be eliminated from such sulphur as is intended for medicinal use (SULPHUR LOTUM, SULPHUR DEPURATUM); this is effected by digesting the crude sublimed sulphur for a few days with very dilute ammonia-water, or with a solution of ammonium carbonate, and by subsequent thorough washing with water, and drying.

Examination:

Washed sulphur should not redden moist blue litmus-paper, nor affect the color of water which has been slightly blued with litmus-tincture, when agitated with a little of the sulphur. Warm

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* Both the *amorphous* (spec. grav. 1.95) and the *monoclinic* (spec. grav. 1.96, fusing-point 120° C., 248° F.) modifications of sulphur are almost insoluble in carbon bisulphide, while the *rhombic* form (spec. grav. 2.05, fusing-point 115° C., 239° F.) is readily soluble therein. Both the former varieties pass into the rhombic form, slowly at ordinary temperatures, and more rapidly at higher ones. Therefore, the older sublimed sulphur is, the more soluble it is in carbon bisulphide.

There are, however, minor varieties of both the amorphous and the crystalline modifications of sulphur, which appear to differ in their deportment with solvents, and thereby also to alter the solubility of sublimed sulphur in carbon bisulphide.

water, when rubbed with the sulphur in a mortar, should yield a filtrate which leaves no residue upon evaporation on platinum-foil or on a watch-glass.

Mineral and *fixed admixtures* are recognized by a non-volatile residue, either upon complete dissipation of the sulphur in a porcelain crucible, or upon dissolving a small portion of the sulphur in a strong boiling solution of potassium or sodium hydrate.

Arsenic may be detected by digesting the sublimed sulphur for several hours, with about four times its weight of a concentrated solution of ammonium carbonate. This dissolves only the arsenic sulphides or arsenious acid; the former may be recognized by a yellow precipitate, either at once or after a while, when a portion of the filtrate is supersaturated with hydrochloric acid, and by a yellow residue upon evaporation of the filtrate on a water-bath, as also by the formation of a metallic mirror when this residue is heated in a dry reduction-tube with potassium cyanide (Fig. 174, page 580); the arsenic present in the form of arsenious acid may be detected in a portion of the above obtained acid filtrate by the formation of a yellow precipitate upon saturation with hydrogen sulphide.

Selenium may be detected by heating to boiling a mixture consisting of about two parts of the sulphur, and a solution of one part of potassium cyanide in twenty parts of water; when cool, this mixture is filtered, and the filtrate supersaturated with concentrated hydrochloric acid—taking care not to inhale the vapors of the evolved hydrocyanic acid; the solution is allowed to stand in a corked vial for about twenty-four hours. A *reddish* turbidity or deposit would indicate selenium. If the sulphur contains arsenic sulphides, they will give rise to the simultaneous formation of a yellow precipitate, which, however, will appear more or less reddish in hue when selenium is contained in the sulphur.

Another method consists in digesting the sulphur with a neutral, saturated solution of potassium sulphite; the liquid is then filtered, and subsequently supersaturated with hydrochloric acid, when, if selenium be present, a flocculent precipitate of a reddish color will be produced. The precipitate, after drying, may be further tested for its identity, if required, by the development of the characteristic and exceedingly unpleasant odor upon heating.

SULPHURIS IODIDUM.

SULFUR IODIDUM. SULFUR IODATUM.

Iodide of Sulphur. Sulphur Iodide.

Ger. Jodschwefel; Fr. Iodure de soufre; Sp. Ioduro de azufre.

A grayish-black solid, usually occurring in pieces of a radiated crystalline appearance externally, and having the characteristic odor of iodine, a slightly acid taste, and a faintly acid reaction.

Sulphur iodide is an unstable compound, and is readily decomposed; on exposure to the air it gradually loses iodine; it is also decomposed by boiling water with the volatilization of the iodine, and, when heated in the air, the iodine passes off in vapor, and is wholly expelled, leaving a residue of sulphur, which burns away at a strong heat with a pale blue flame.

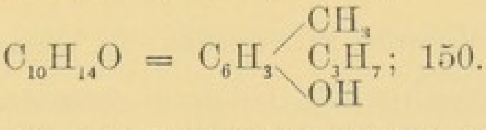
Sulphur iodide is insoluble in water, but this takes up a trace of iodine; it is soluble in carbon bisulphide and also in about 60 parts of glycerin; alcohol and ether, as well as strong solutions of potassium iodide, or of potassium hydrate, deprive it completely of the iodine, leaving the sulphur behind; in this way, sulphur iodide may be examined, by exhausting 50 parts of it with alcohol, when only 10 parts of sulphur should remain behind; and, when this is divided into two portions, one of them should burn away at a strong heat, with the odor of sulphurous acid, and the other must be completely soluble in carbon bisulphide.

THYMOL.

THYMOLUM.

Thymol. Methyl-propyl-phenol.

Ger. Thymol; Fr. Thymol; Sp. Timol.



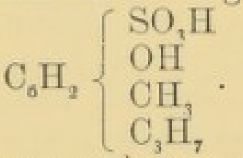
$$C_{10}H_{14}O = C_6H_3\begin{cases}CH_3\\C_3H_7\\OH\end{cases};\ 150.$$

Large, transparent, colorless crystals, belonging to the hexagonal system, having an aromatic thyme-like odor, a pungent, aromatic taste, and neutral in their action upon litmus. In the crystalline condition thymol has the specific gravity of 1.028, but, when liquefied, it is lighter than water and swims upon the surface; it melts at from 50 to 52° C. (122 to 125.6° F.), remaining liquid at lower temperatures, and boils at from 228 to 230° C. (442.4 to 446° F.); at the temperature of the water-bath, or when heated on platinum-foil, it is rapidly volatilized, leaving no residue.

Thymol is soluble in about 1200 parts of water at 15° C. (59° F.), and in 900 parts of boiling water; in 1.5 parts of alcohol, in 120 parts of glycerin, and very freely soluble in ether, chloroform, carbon bisulphide, benzol, benzin, glacial acetic acid, the fixed and volatile oils, and solutions of potassium and sodium hydrate, especially upon warming; it forms a colorless, syrupy liquid when triturated with an equal weight of camphor. The aqueous and alcoholic solutions are neutral in their action upon litmus, and afford no coloration on the addition of a few drops of solution of ferric chloride (distinction from and absence of carbolic acid).

If thymol be dissolved in about half its weight of glacial acetic acid, an equal volume of sulphuric acid subsequently added, and the mixture gently warmed, a beautiful reddish-violet color is produced, which is very permanent, and is not destroyed by an excess of acid or by boiling.

When fused thymol is gradually mixed with an equal volume of concentrated sulphuric acid, and the mixture maintained at a temperature of 60° C. (140° F.) for about one hour, it solidifies on cooling to a crystalline mass of thymol-sulphonic acid,



$$C_6H_2\left\{\begin{array}{l}SO_3H\\OH\\CH_3\\C_3H_7\end{array}\right.$$

. If this be dissolved in water, and the solution subsequently poured into ten times its volume of water, and digested with an excess of lead or barium carbonate, and filtered, the filtrate will assume, on the addition of a trace of ferric chloride, a beautiful violet-blue color.

VERATRINA.

VERATRINUM. VERATRIUM.

Veratrine. Veratria.

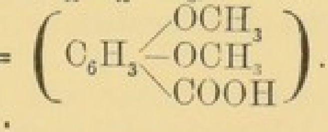
Ger. Veratrin; Fr. Vératrine; Sp. Veratrina.

A white or grayish-white, coherent powder, or, more rarely, minute, efflorescent, prismatic crystals, without smell, but exciting violent sneezing when admitted into the nostrils. Heated upon platinum-foil, veratrine fuses into a yellow liquid, which, on cooling, solidifies to a transparent yellow mass; at a stronger heat, it is charred, and burns wholly away.

Veratrine is soluble in 3 parts of alcohol at 15° C. (59° F.), and more freely in boiling alcohol; also soluble in 6 parts of ether, 2 parts of chloroform, 96 parts of glycerin, and 56 parts of olive oil; it is almost insoluble in cold, and very sparingly soluble in boiling, water, requiring of the latter 1560 parts for solution, but imparts to it an acrid taste and a feebly alkaline reaction; dilute acids dissolve it freely with the formation of mostly uncrystallizable, gum-like salts. The solution in diluted acids has a persistent acrid, though not bitter, taste, causing a sensation of tingling, with numbness of the tongue. It gives a white precipitate with tannic acid and with potassio-mercuric iodide, a brown one with iodinized solution of potassium iodide, and a white one with the alkaline hydrates, soluble in a large excess of the precipitant, and more readily in alcohol, ether, and chloroform.

Concentrated sulphuric acid dissolves veratrine with a yellow color, which successively becomes orange, purple, and deep red or violet; gentle heat accelerates this reaction, and, if to the freshly prepared acid solution a few drops of bromine-water be added, the liquid assumes at once a purple-red color. On triturating veratrine with sulphuric acid in a glass mortar, the yellow or yellowish-red solution exhibits, in reflected light, a fine greenish-yellow fluorescence, which becomes more intense on adding more sulphuric acid. If a little cane-sugar be strewn upon the surface of the solution of veratrine in concentrated sulphuric acid, or if the alkaloid, previously triturated with about five times its weight of cane-sugar, be brought into concentrated sulphuric acid, the mixture assumes successively a yellowish, then a green, and finally a beautiful blue color, afterwards slowly changing to red and gray. Concentrated hydrochloric acid dissolves veratrine in the cold without coloration, but, upon gently heating, the solution assumes a permanent dark red color. Concentrated nitric acid does not effect any coloration with veratrine; nor does concentrated sulphuric acid, when diluted with one-third its bulk of water, produce any coloration, unless heated.

When heated with caustic alkalies, veratrine is resolved into a new base, *verine*, $C_{28}H_{45}NO_8$, and *dimethyl-protocatechuic* or *veratric acid*, $C_9H_{10}O_4$ =



$$\left(C_6H_3\begin{cases}OCH_3\\OCH_3\\COOH\end{cases}\right).$$

Examination:

Mineral or other *insoluble admixtures* may readily be detected by their insolubility in chloroform and in alcohol, or by leaving a non-volatile residue when heated upon platinum-foil.

Foreign alkaloids may in many instances be detected by their greater solubility in hot water, and may subsequently be recognized in the solution by means of the appropriate reagents.

Brucine remains undissolved when digested with ether;* it may also be confirmed or recognized by dissolving a little of the veratrine in concentrated nitric acid, diluted with an equal part of water; veratrine yields a colorless solution, which, however, will

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* The solubility of commercial veratrine in ether varies, some kinds being less readily soluble, and the crystalline more so than the amorphous.

appear red when brucine is present; the red solution changes to yellow upon heating, and, by the subsequent addition of a few drops of a solution of stannous chloride or ammonium sulphide, a violet color will be produced. None of these color reactions will take place with pure veratrine.

For the separation of veratrine from other alkaloids, or from complex organic mixtures with which it may be associated, see page 108.

ZINCI ACETAS.

ZINCUM ACETICUM.

Acetate of Zinc. Zinc Acetate.

Ger. Essigsaures Zinkoxyd; Fr. Acétate de zinc; Sp. Acetato de zinc.

$Zn(C_2H_3O_2)_2 + 3H_2O$; 236.9.

Colorless, translucent, six-sided tablets or scales, belonging to the monoclinic system, of a pearly, unctuous lustre, flexible, and with a faint odor of acetic acid, which is freely evolved when the crystals are treated with sulphuric acid; they contain three molecules (22.88 per cent.) of water of crystallization, and are ordinarily permanent in the air, but efflorescent in air that is dry and warm. When heated upon charcoal, before the blow-pipe, zinc acetate undergoes aqueous fusion, solidifies again, after the evaporation of the water of crystallization, and emits vapors of acetic acid, and the products of decomposition of the latter; finally zinc oxide is left behind, which is yellow while hot, and white when cold. When this residue is moistened with one drop of solution of cobaltous nitrate, and heated to redness, it will appear green, after cooling.

Zinc acetate is soluble in 3 parts of water and in 30 parts of alcohol at 15° C. (59° F.); in 1.5 parts of boiling water and in 3 parts of boiling alcohol. The aqueous solution has an astringent, metallic taste, and a slightly acid reaction; it gives a white precipitate of zinc sulphide with hydrogen sulphide or ammonium sulphide, and a white precipitate of zinc ferrocyanide with potassium ferrocyanide; it also forms white precipitates with the alkaline hydrates and carbonates, of which those with the hydrates, and with ammonium carbonate, are redissolved by an excess of the precipitant, but these solutions are precipitated again, by boiling, if not too concentrated.

Solution of zinc acetate acquires a red color, upon the addition of a few drops of a dilute solution of a ferric salt.

Examination:

If a solution of one part of the salt in ten parts of water be completely precipitated by hydrogen sulphide, and filtered, the filtrate should leave no residue upon evaporation.

Metallic impurities will be indicated by a dark coloration or a precipitate, when a solution of the salt, acidulated with hydrochloric acid, is saturated with hydrogen sulphide.

Iron, *aluminium*, and *alkaline earths* will be indicated in the solution of the salt by a brownish coloration or an insoluble precipitate upon the addition of an excess of solution of ammonium carbonate; if to the clear filtrate a white precipitate be produced upon the subsequent addition of a few drops of solution of sodium phosphate, *magnesium* salts will be indicated.

Alkaline salts may be recognized by a strongly alkaline reaction, when a small portion of the salt is completely reduced upon charcoal, before the blow-pipe, and the residue tested with moist blue litmus-paper; or, a solution of the salt is completely precipitated by ammonium sulphide and filtered; the filtrate evaporated to dryness, and subsequently ignited; a fixed residue, having a strongly alkaline reaction, will indicate the above-mentioned impurity.

ZINCI BROMIDUM.

ZINCUM BROMATUM.

Bromide of Zinc. Zinc Bromide.

Ger. Bromzink; Fr. Bromure de zinc; Sp. Bromuro de zinc.

$ZnBr_2$; 224.5.

A white, or nearly white, granular powder, very deliquescent, having a sharp saline and metallic taste, and neutral in its action upon litmus. When strongly heated, it fuses, and, at a higher temperature, may be sublimed in the form of white, prismatic needles.

Zinc bromide is very freely soluble in water and in alcohol. Its aqueous solution yields white precipitates with potassium ferrocyanide and ammonium sulphide, and a yellowish-white one with argentic nitrate, soluble in a large excess of ammonia-water; it also forms white precipitates with the alkaline hydrates and carbonates, of which those with the hydrates, and with ammonium carbonate, are redissolved by an excess of the precipitant, but these solutions are precipitated again, by boiling, if not too concentrated. If to the solution a few drops of carbon bisulphide be added, and subsequently chlorine-water, drop by drop, and the mixture agitated, the carbon bisulphide will assume a yellowish or brownish-red color.

One gram of the dry salt, when completely precipitated by argentic nitrate, yields a precipitate of argentic bromide, which, when washed and dried, should weigh 1.67 grams.

Examination:

Metallic impurities will be indicated in the solution of the salt, acidulated with hydrochloric acid, by a dark coloration or a precipitate upon saturation with hydrogen sulphide.

Iron, *aluminium*, and *alkaline earths* will be indicated in the solution of the salt by a brownish coloration or an insoluble precipitate upon the addition of solution of ammonium carbonate in excess; if to the clear filtrate a white precipitate be produced upon the subsequent addition of a few drops of solution of sodium phosphate, *magnesium* salts will be indicated.

Alkalies and *alkaline earths* may be recognized by completely precipitating a solution of the salt with ammonium sulphide, filtering, evaporating the filtrate to dryness, and subsequently igniting; a fixed residue, having a strongly alkaline reaction to test-paper, will reveal the above-mentioned impurities.

ZINCI CARBONAS PRÆCIPITATUS.

ZINCUM CARBONICUM PRÆCIPITATUM.

Precipitated Carbonate of Zinc. Precipitated Zinc Carbonate.

Ger. Basisch kohlensaures Zinkoxyd; Fr. Carbonate de zinc; Sp. Carbonato de zinc.

$$2(ZnCO_3) + 3Zn(OH)_2; \quad 546.5.$$

An impalpable white powder, permanent in the air, and without odor or taste. When strongly heated in a small porcelain crucible, or when heated on charcoal before the blow-pipe, it loses water and carbonic acid gas, and leaves a residue of zinc oxide, which is yellow while hot and white when cold.

Precipitated zinc carbonate is insoluble in both water and alcohol, but dissolves readily in acetic and the dilute mineral acids, with the liberation of carbonic acid gas. When the salt, in slight excess, is digested with dilute hydrochloric acid, and the solution subsequently filtered, the filtrate should afford the reactions and correspond to the tests of purity described under zinc chloride, on pages 589, 590; when digested with a small amount of water, and filtered, the filtrate should leave no residue on evaporation, indicating the absence of soluble salts.

ZINCI CHLORIDUM.

ZINCUM CHLORATUM. ZINCUM MURIATICUM.

Chloride of Zinc. Zinc Chloride.

Ger. Chlorzink ; Fr. Chlorure de zinc ; Sp. Cloruro de zinc.

$ZnCl_2$; 135.7.

A colorless, coherent, granular powder, or colorless, opaque rods or fragments, very deliquescent and caustic. When heated to about 115° C. (239° F.), zinc chloride fuses to a clear liquid, which, on cooling, congeals to a white or grayish-white mass; at a higher temperature it volatilizes with partial decomposition, emitting dense white vapors, which condense on cooling in the form of needle-shaped crystals, and leaving behind a slight residue, which is yellow while hot and white when cold.

Zinc chloride is soluble in water, glycerin, alcohol, and ether, giving more or less turbid, and slightly acid, solutions, which, however, become clear upon the addition of hydrochloric acid; the aqueous solution yields white precipitates with potassium ferrocyanide, ammonium sulphide, and with the alkaline hydrates and carbonates, of which those with the alkaline hydrates and ammonium carbonate are readily soluble in an excess of the precipitant; the latter solutions may be again precipitated either by hydrogen sulphide or by boiling. The solution of zinc chloride, acidulated with nitric acid, yields, when diluted with water, a curdy white precipitate with argentic nitrate, soluble in ammonia-water, and it occasions white precipitates with liquids containing albumen or gluten.

One gram of the dried salt, when completely precipitated with argentic nitrate, yields a precipitate of argentic chloride, which, when washed and dried, should weigh 2.11 grams.

Examination:

Metallic impurities (arsenic, cadmium, copper, lead) may be detected in the solution of the salt, acidulated with hydrochloric acid, by a dark coloration or a precipitate upon saturation with hydrogen sulphide. If a black precipitate is produced, it may indicate either lead or copper; these may be distinguished by the addition of ammonia-water in excess to a little of the original solution, when a blue coloration of the liquid will reveal the presence of *copper*. If a yellow precipitate is produced in the acidulated solution by hydrogen sulphide, it will indicate either *arsenic* or *cadmium;* these may be distinguished or separated from each other by digesting the precipitate with ammonium sulphide, in which arsenious sulphide is soluble; or, a small portion of the zinc chloride, dissolved in concentrated hydrochloric acid, is heated to boiling with a few drops of solution of stannous chloride or a fragment of pure tin-foil, when an ensuing brown precipitate will reveal the presence of arsenic. The presence of cadmium will likewise be further indicated in a solution of the salt by the addition of potassium or sodium hydrate in excess, in which the precipitated cadmium hydrate is insoluble.

Calcium and *Magnesium Chlorides, Alkalies and their Salts.*—A solution of the salt is completely precipitated by ammonium sulphide, filtered, and the filtrate tested with ammonium oxalate; a white precipitate will reveal the presence of *calcium;* the filtrate from the latter, if present, is subsequently tested with ammonium phosphate, when an ensuing white crystalline precipitate will indicate magnesium. The final filtrate from the preceding test, when evaporated to dryness, and ignited at a gentle heat, should leave no residue, otherwise an admixture of *alkalies* or their salts will be indicated.

Ammonium chloride (ammonio-zinc chloride) may be detected by an ammoniacal odor, and by white vapors when a glass rod, moistened with acetic acid, is held in the orifice of the test-tube, wherein a small portion of the salt is heated with a strong solution of potassium hydrate.

Sulphate may be recognized in the diluted solution, acidulated with hydrochloric acid, by an ensuing white precipitate on testing with barium chloride.

ZINCI IODIDUM.

ZINCUM IODATUM.

Iodide of Zinc. Zinc Iodide.

Ger. Jodzink; Fr. Iodure de zinc; Sp. Ioduro de zinc.

ZnI_2; 318.1.

A white, or nearly white, granular powder, which, when exposed to the air, first absorbs water and deliquesces, and afterwards takes up oxygen with the liberation of iodine. When strongly heated, it readily fuses to a colorless liquid, and, at a higher temperature, sublimes in the form of quadratic prisms or needles.

Zinc iodide is very freely soluble in both water and alcohol, yielding solutions which possess a sharp saline and metallic taste and an acid reaction. The aqueous solution yields white precipitates with potassium ferrocyanide, ammonium sulphide, and the alkaline hydrates and carbonates, of which those with the alkaline hydrates and ammonium carbonate are readily soluble in an excess of the precipitant; the latter solutions may again be precipitated by hydrogen sulphide or by boiling. The aqueous solution also yields a yellow precipitate with solution of plumbic acetate, and a red one with mercuric chloride; the latter precipitate being soluble in an excess of the precipitant. If to a solution of the salt a little chlorine-water be added, and the mixture subsequently agitated with a few drops of chloroform or carbon bisulphide, the latter will acquire a reddish or violet color.

One gram of the dried salt, when completely precipitated by argentic nitrate, yields a precipitate of argentic iodide, which, when washed and dried at 100° C. (212° F.), should weigh 1.47 grams.

Examination:

Zinc or ammonium chlorides (ammonio-zinc chloride) may be detected by completely precipitating a solution of the salt with argentic nitrate, collecting the precipitate on a filter, and, after washing with water, digesting it with ammonia-water; the mixture is then filtered, and the filtrate supersaturated with nitric acid, when an ensuing white precipitate will reveal the presence of chloride.

Metallic and *other impurities* may be detected by the same tests and method of examination, as described under zinc chloride, on pages 589, 590.

ZINCI OXIDUM.

ZINCUM OXYDATUM. FLORES ZINCI.

Oxide of Zinc. Zinc Oxide.

Ger. Zinkoxyd, Zinkweiss; Fr. Oxyde de zinc; Sp. Oxido de zinc.

ZnO; 80.9.

A soft, white powder, having occasionally a pale yellowish tint, inodorous and tasteless, and not becoming discolored in contact with hydrogen sulphide. When heated in a dry tube or a porcelain crucible, it neither fuses nor volatilizes, but assumes a lemon-yellow color, which disappears again on cooling; when the oxide is subsequently heated with a mixture of equal parts of acetic acid and water, it dissolves wholly and without effervescence. When moistened with one drop of solution of cobaltous nitrate, and heated in the flame of the blow-pipe, zinc oxide assumes a green color.

Zinc oxide is insoluble in water, glycerin, and alcohol, but soluble in diluted acids, forming colorless solutions, which, with the exception of the solution in acetic acid, are not affected by hydrogen sulphide, and the latter solution should afford with this reagent a purely white precipitate; the neutral solutions, with the exception of the acetate, are only incompletely precipitated by hydrogen sulphide, but completely by ammonium sulphide; when alkaline, they are wholly precipitated by both reagents. The solutions of zinc oxide form white precipitates with the alkaline hydrates and carbonates, of which those with the former, and with ammonium carbonate, are soluble in an excess of the precipitant, but they are reprecipitated from these solutions, if not too concentrated, by boiling. Zinc oxide is, therefore, soluble in concentrated solutions of the alkaline hydrates (when free from carbonates), and of ammonium carbonate.

Zinc oxide absorbs carbonic acid slowly from the atmosphere.

Examination:

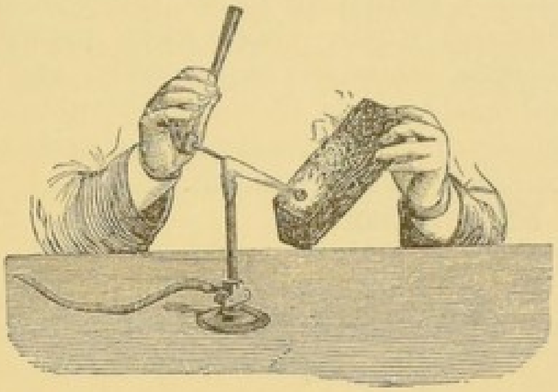
Sulphates and *Chlorides.*—A small portion of the zinc oxide is agitated for a few minutes with about ten times its weight of boiling water, and subsequently filtered; a few drops of the filtrate, evaporated upon platinum-foil, should leave no residue; nor should the filtrate, after the addition of a few drops of nitric acid, give any reaction with barium nitrate or with argentic nitrate.

Carbonate, Sulphates and Phosphates of the Alkaline-Earths, and *Alumina.*—The oxide left on the filter in the preceding test is dissolved, with the aid of heat, in a small amount of acetic acid diluted with an equal volume of water; effervescence would indicate *carbonates*, and an insoluble residue, *calcium* or *barium sulphates* (zinc oxide prepared in the dry way generally leaves a small gray residue, consisting of minute particles of metallic zinc, readily soluble in hydrochloric or nitric acid); the solution is filtered, if necessary, and is then supersaturated with ammonia-water; the ensuing white turbidity must disappear upon the addition of an excess of the reagent; a permanent turbidity would indicate *earthy phosphates* or *alumina.*

Metallic Impurities (copper, lead, arsenic, and cadmium).—A portion of the zinc oxide is dissolved in dilute hydrochloric acid, the solution diluted with a little water, and subsequently saturated with hydrogen sulphide; an ensuing black precipitate would indicate either *copper* or *lead.* The former will have been indicated in the preceding test by a blue coloration of the liquid upon supersaturating the acid solution of the oxide with ammonia-water; it may also be detected in the dilute acid solution by a brown coloration on the addition of a few drops of solution of potassium ferrocyanide. Lead may be specially tested for, if required, by dissolving a small portion of the zinc oxide in 10 times its weight of warm diluted acetic acid, and to the clear solution subsequently adding a few drops of solution of potassium iodide; an ensuing yellow coloration or precipitate would reveal the presence of lead.

If a yellow precipitate has been produced in the acid solution by hydrogen sulphide, it will indicate either *arsenic* or *cadmium.* These may be distinguished as follows: The precipitate is collected on a filter, washed with water, and digested with a concentrated solution of ammonium carbonate; arsenious sulphide is thereby dissolved, and may be confirmed by the application of Fleitmann's test, as described on pages 36, 37, or, if the solution be not too dilute, it may be reprecipitated by subsequent supersaturation with hydrochloric acid. Cadmium sulphide is insoluble in ammonium carbonate, and may be recognized by a red-brown coating of the coal, when heated with a little exsiccated sodium carbonate upon charcoal before the blow-pipe (Fig. 175).

FIG. 175.



As a confirmatory test for arsenic, or to detect a minute quantity of it, a small portion of the oxide may be dissolved in about ten times its weight of concentrated hydrochloric acid, and, after the addition of a few drops of concentrated solution of stannous chloride or a fragment of pure tin-foil, heated to boiling; a brown turbidity would confirm the presence of arsenic.

Iron, *Calcium*, and *Magnesium*.—The acid solution, after saturation with hydrogen sulphide, as described in the preceding test, is neutralized with ammonia-water, and completely precipitated by ammonium sulphide; a purely white precipitate should ensue; a black coloration would indicate *iron*. The filtrate from the latter precipitate is heated to boiling, filtered, and the filtrate tested with ammonium oxalate, when a white precipitate will reveal the presence of *calcium;* the filtrate from the latter precipitate is subsequently tested with ammonium phosphate, when a white, crystalline precipitate will indicate *magnesium*.

ZINCI PHOSPHIDUM.

ZINCUM PHOSPHORATUM.

Phosphide of Zinc. Zinc Phosphide.

Ger. Phosphorzink; Fr. Phosphure de zinc; Sp. Fosfido de zinc.

Zn_3P_2; 256.7.

A grayish powder, or minutely crystalline, friable fragments, having a bright, metallic, bismuth-like lustre. It possesses a faint odor, and the taste of phosphorus, and is permanent in the air. When strongly heated, with exclusion of air, zinc phosphide fuses and is completely volatilized; if heated with access of air it is principally converted into zinc phosphate.

Zinc phosphide is insoluble in water or alcohol, but is readily and completely soluble in dilute hydrochloric and sulphuric acids, with the evolution of spontaneously inflammable hydrogen phosphide. When dissolved in dilute hydrochloric acid, with the employment of a slight excess of the salt, filtered, and subsequently heated to expel the hydrogen phosphide, a solution is obtained which yields white precipitates with potassium ferrocyanide, ammonium sulphide, and with the alkaline hydrates and carbonates; of these, the precipitates produced by the alkaline hydrates and ammonium carbonate are readily soluble in an excess of the precipitant.

Examination:

Zinc phosphate, traces of which are usually contained in the phosphide, may be extracted by digestion with a cold solution of ammonium chloride, and may subsequently be recognized by an ensuing white crystalline precipitate on the addition of ammonia-water and solution of magnesium sulphate.

Metallic and other impurities may be detected in the solution of zinc phosphide in diluted hydrochloric acid by the same tests and methods of examination as described under Zinc Chloride, on pages 589, 590.

ZINCI SULPHAS.

ZINCUM SULFURICUM.

Sulphate of Zinc. White Vitriol. Zinc Sulphate.

Ger. Schwefelsaures Zinkoxyd, Weisser Vitriol; Fr. Sulfate de zinc; Sp. Sulfato de zinc.

$ZnSO_4 + 7H_2O$; 286.9.

Colorless, transparent rhombic prisms (Figs. 176 and 177) or acicular needles, containing 7 molecules (43.89 per cent.) of water of crystallization, and efflorescing slowly on exposure to the air. When heated at 100° C. (212° F.) they lose 6 molecules (37.6 per cent.) of water, the remaining molecule of water being eliminated

FIG. 176.

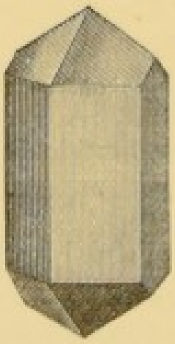
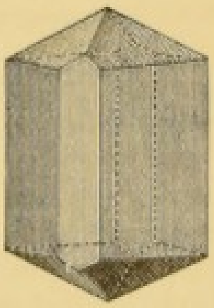


FIG. 177.



only at a temperature of from 230 to 240° C. (446 to 464° F.); at a stronger heat, the salt is decomposed, sulphur dioxide and oxygen being evolved, while a basic salt remains behind; at a white heat, it is completely decomposed, leaving a residue of zinc oxide, which, when moistened with one drop of solution of cobaltous nitrate, and heated again to redness, assumes a green color (magnesium sulphate, when similarly treated, gives a reddish coloration, alum a blue one).

Zinc sulphate is readily soluble in water, 100 parts of which dissolve at 10° C. (50° F.) 138 parts, at 20° C. (68° F.) 161.5 parts, and at 100° C. (212° F.) 653.5 parts, of the crystallized salt; it is soluble in about 3 parts of glycerin, and in an excess of the solutions of the alkaline hydrates, but it is little soluble in strong, and not at all in absolute, alcohol; the aqueous solution reddens blue litmus-paper and has a metallic styptic taste, remains colorless with solution of tannic acid, and gives a copious white precipitate with highly diluted solution of barium chloride. Its deportment with reagents is the same as described under Zinc Oxide, on pages 591, 592.

Examination:

Metallic Impurities.—A concentrated solution of zinc sulphate is slightly acidulated with a few drops of diluted hydrochloric acid, and subsequently saturated with hydrogen sulphide; no turbidity or coloration should ensue; a dark or yellowish coloration or precipitate would indicate *copper*, *lead*, *cadmium*, or *arsenic*. The filtered liquid, upon subsequent supersaturation with ammonia-water, should yield a perfectly white precipitate; a dark coloration would indicate the presence of *iron*.

The same test may serve to distinguish at once magnesium sulphate from zinc sulphate; these substances, being isomorphous and of a similar appearance, are liable to be taken one for the other; solution of magnesium sulphate is not acted upon by hydrogen sulphide, ammonium sulphide, or potassium ferrocyanide, and the precipitate produced by solutions of potassium or sodium hydrate are insoluble in an excess of the precipitant.

Magnesium and *aluminium sulphates* are further indicated by the following tests: To a solution of the zinc sulphate a little ammonium chloride is added, and subsequently ammonia-water in considerable excess; the precipitate first formed should become completely dissolved; an insoluble flocculent precipitate would indicate *aluminium*. The filtered liquid is subsequently tested with ammonium phosphate, when the immediate or gradual formation of a white, crystalline precipitate will indicate *magnesium*.

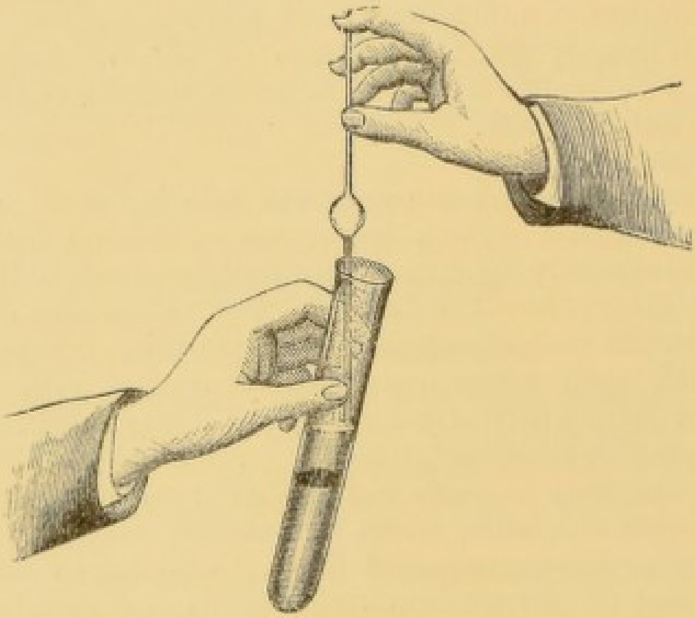
Potassium and *sodium sulphates* may be detected by adding to a solution of the zinc sulphate a solution of plumbic acetate until a precipitate ceases to be produced, filtering, and subsequently completely precipitating the zinc and excess of lead by hydrogen sulphide; the filtered liquid upon evaporation to dryness should leave no residue; a non-volatile residue, imparting a brown color to moistened turmeric paper, would indicate the above-mentioned impurities.

Ammonium salts may be recognized by the odor of ammonia, and by the development of white fumes, when a glass rod, moistened with acetic acid, is held over the orifice of the test tube in which a little zinc sulphate has been heated with a strong solution of potassium hydrate.

Chlorides may be detected in a dilute solution of the salt, acidulated with nitric acid, by a white precipitate on the addition of solution of argentic nitrate.

Nitrates may be detected by ensuing decoloration of the liquid, when a solution of the salt, tinted with a drop of indigo solution, is gently heated with a few drops of concentrated sulphuric acid; or, a crystal of ferrous sulphate is dissolved in a solution of the salt, and the liquid carefully poured upon a little concentrated sulphuric acid, in a test-tube, so as to form two layers (Fig. 178); a violet or brown coloration at the line of contact of the two liquids will reveal the presence of nitrates.

FIG. 178.



ZINCI SULPHOCARBOLAS.

ZINCUM SULFOCARBOLICUM. ZINCUM SULFOPHENYLICUM.

Sulphocarbolate or Sulphophenylate of Zinc. Zinc Sulphocarbolate.

Ger. Phenolsulfosaures Zinkoxyd ; Fr. Sulfocarbolate de zinc ;
Sp. Sulfocarbolato de zinc.

$Zn(C_6H_4.OH.SO_3)_2+8H_2O$; 554.9.

Colorless, transparent, rhombic prisms or plates, or a white, crystalline powder, odorless, or possessing but a slight odor of phenol, and readily efflorescing on exposure to dry air. The salt contains 8 molecules (26 per cent.) of water of crystallization, which are expelled at a temperature of 130° C. (266° F.); when more strongly heated, the salt is decomposed, with the liberation of sulphur dioxide and phenol, and leaving a residue of carbon and zinc sulphate, which, at a strong red heat, is completely converted into zinc oxide.

Zinc sulphocarbolate is soluble in 2 parts of water and 5 parts of alcohol at 15° C. (59° F.), yielding slightly acid solutions, which, when diluted, afford a deep violet color on the addition of a few drops of solution of ferric chloride, and a white precipitate upon saturation with hydrogen sulphide; it also yields white precipitates with potassium ferrocyanide, ammonium sulphide, and with the alkaline hydrates and carbonates, of which those with the alkaline hydrates and ammonium carbonate are readily soluble in an excess of the precipitant.

One hundred parts of the salt, when strongly ignited at a red heat, leave a residue of zinc oxide, weighing 14.58 parts.

Examination:

Zinc sulphate may be detected by the incomplete solubility of the salt in alcohol, or by the occurrence of a turbidity or precipitate when a concentrated aqueous solution of the salt is dropped into alcohol, as also by the formation of a white precipitate when the dilute aqueous solution of the salt is tested with barium chloride.

Metallic impurities may be detected by a dark coloration or a precipitate when the aqueous solution of the salt, acidulated with hydrochloric acid, is saturated with hydrogen sulphide.

Salts of the Alkalies and Alkaline-Earths.—A portion of the salt is dissolved in ten times its weight of water, and to the solution ammonia-water in slight excess is added, until the precipitate at first produced is redissolved; an incomplete solution would indicate the presence of *aluminium* and *magnesium.* The clear liquid is subsequently saturated with hydrogen sulphide until the zinc has become completely precipitated, filtered, and the filtrate tested with ammonium carbonate; a white precipitate would indicate *barium* or *calcium;* the filtrate from the latter precipitate, should such have been produced, is evaporated to dryness, and subsequently ignited in a small porcelain crucible, when a non-volatile residue will indicate *salts of the alkalies.*

ZINCI VALERIANAS.

ZINCUM VALERIANICUM.

Valerianate of Zinc. Zinc Valerianate.

Ger. Baldriansaures Zinkoxyd; Fr. Valérianate de zinc; Sp. Valerianato de zinc.

$Zn(C_5H_9O_2)_2+H_2O$; 284.9.

White, pearly, lamellar crystals, or a white, scaly, crystalline powder, permanent in the air, somewhat unctuous to the touch, and with a feeble odor of valerianic acid. It contains 1 molecule (6.3 per cent.) of water of crystallization, which is eliminated at a temperature of 100° C. (212° F.), and is not again absorbed by subsequent exposure to the air; at a higher temperature (about 146° C. = 284° F.) the salt fuses, with partial decomposition, to a clear, thick liquid, and solidifies again upon cooling in a crystalline form; when strongly heated, it evolves white, inflammable vapors, leaving a residue of zinc oxide, which, when moistened with a drop of a solution of cobaltous nitrate, and reheated to redness, becomes green.

Zinc valerianate is soluble in 100 parts of water and in 40 parts of alcohol at 15° C. (59° F.), and is also soluble in glycerin, and in an excess of ammonia-water, but only sparingly in ether or chloroform. Its solutions redden blue litmus-paper, and become turbid upon gently warming, but clear again on cooling; by prolonged boiling, an insoluble basic salt is deposited, having the composition $Zn(C_5H_9O_2)_2+2Zn(OH)_2$. The salt is also readily soluble in diluted acids, but with decomposition, and consequent turbidity from the elimination of the valerianic acid, which gradually collects as an oily stratum upon the surface of the aqueous solution; an addition of ammonia-water at first increases the turbidity, but, when added in excess, forms a clear solution, which yields a white precipitate with ammonium sulphide.

The deportment of solutions of zinc valerianate with reagents, after the elimination of the acid by hydrochloric or sulphuric acid, is the same as described under Zinc Oxide, on pages 591, 592.

One gram of the salt, when moistened with nitric acid, evaporated to dryness, and ignited at a red heat, should leave a residue of zinc oxide weighing 0.283 gram; or, when the anhydrous salt has been employed, the residue should weigh 0.303 gram.

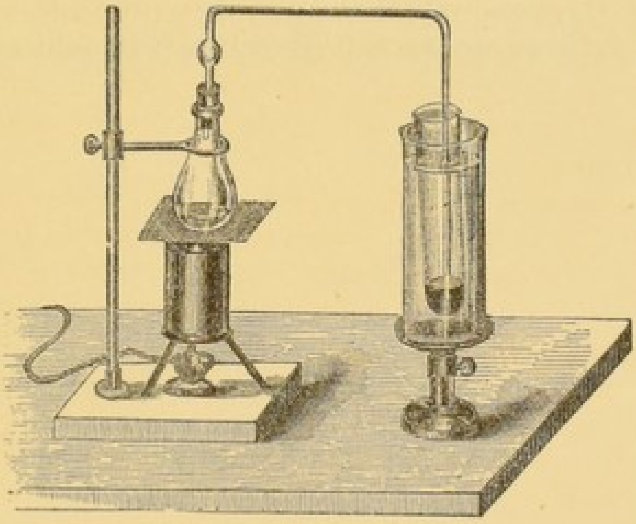
Examination:

Zinc acetate may be detected by agitating a little of the triturated zinc valerianate, in a test-tube, with about four times its weight of cold water, and adding to the filtrate one or two drops of ferric chloride; the liquid, if necessary, is filtered again, and must appear almost colorless; a reddish tint would indicate acetic acid.

Tartaric and Oxalic Acids.—The undissolved valerianate of the preceding test is rinsed through the broken filter into a test-tube, and is agitated with a sufficient quantity of ammonia-water; a complete solution must take place, which should retain its transparency on the addition of a few drops of solution of calcium chloride; a white turbidity or precipitate would indicate the above-mentioned acids or their respective salts.

Zinc butyrate may be detected by the occurrence of a turbidity or precipitate when a cold, concentrated solution of the salt is mixed with a concentrated solution of cupric acetate; or, about 5 grams of the salt are triturated, and added, in a small flask, to a mixture consisting of 10 grams of concentrated sulphuric acid and 10 grams of water; the mixture is submitted to distillation at a gentle heat (Fig. 179), until about 2 grams of distillate are obtained; this is agitated with a little concentrated solution of cupric acetate, which should not immediately affect the transparency of the liquid, but it forms, after a while, oily drops of anhydrous cupric valerianate, which, after from 5 to 20 minutes, pass into a greenish-blue crystalline deposit of hydrated cupric valerianate. If, however, the salt consists mainly or wholly of butyrate, the transparency of the liquid would at once be impaired by the formation of a crystalline precipitate.

FIG. 179.



The presence of butyrate, if the amount be not too small, will likewise be indicated by dissolving the salt in the smallest possible amount of warm, absolute alcohol, saturating with hydrogen sulphide, and, after filtration, allowing the filtrate to evaporate spontaneously; if the residual acid consists of ordinary butyric acid, it will be miscible in all proportions with water, whereas valerianic acid requires 25 parts of water for solution.

Boric acid may be detected by triturating a little of the salt with a few drops of alcohol, and by igniting and burning the mixture, with stirring; a green coloration of the flame, especially toward the termination of the ignition, would indicate boric acid.

Sulphates and *chlorides* may be detected in the aqueous solution of the salt by acidulating with nitric acid, heating, in order to expel the liberated valerianic acid, and subsequently testing the filtered liquid, in separate portions, with barium chloride for sulphates, and with argentic nitrate for chlorides; a white precipitate in either instance would reveal the presence of such impurities.

Salts of the Alkalies and Alkaline Earths.—A portion of the salt is agitated with a sufficient quantity of ammonia-water to form a complete solution; an insoluble residue would indicate *aluminium* or *magnesium.* The ammoniacal liquid is subsequently completely precipitated by hydrogen sulphide or ammonium sulphide, filtered, and the filtrate tested with ammonium carbonate; an ensuing white precipitate would indicate *barium* or *calcium;* the filtrate from the latter precipitate, if such has been produced, is evaporated to dryness, and subsequently ignited in a small porcelain crucible, when a non-volatile residue will indicate *salts of the alkalies.*

TABLES AND INDEX.

TABLES.

TABLE OF ELEMENTARY BODIES, WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminium	Al	27	Molybdenum	Mo	95.5
Antimony	Sb	120	Nickel	Ni	58
Arsenic	As	74.9	Niobium	Nb	94
Barium	Ba	136.8	Nitrogen	N	14
Beryllium (Glucinum)	Be	9	Osmium	Os	198.5
Bismuth	Bi	210	Oxygen	O	16
Boron	B	11	Palladium	Pd	105.7
Bromine	Br	79.8	Phosphorus	P	31
Cadmium	Cd	111.8	Platinum	Pt	194.4
Caesium	Cs	132.6	Potassium	K	39
Calcium	Ca	40	Rhodium	Rh	104.1
Carbon	C	12	Rubidium	Rb	85.3
Cerium	Ce	141	Ruthenium	Ru	104.2
Chlorine	Cl	35.4	Scandium	Sc	44
Chromium	Cr	52.4	Selenium	Se	78.8
Cobalt	Co	58.9	Silicon	Si	28
Copper	Cu	63.2	Silver	Ag	107.7
Didymium	Di	144.6	Sodium	Na	23
Erbium	E	165.9	Strontium	Sr	87.4
Fluorine	Fl	19	Sulphur	S	32
Gallium	G	68.8	Tantalum	Ta	182
Gold	Au	196.2	Tellurium	Te	128
Hydrogen	H	1	Thallium	Tl	203.7
Indium	In	113.4	Thorium	Th	233
Iodine	I	126.6	Tin	Sn	117.7
Iridium	Ir	192.7	Titanium	Ti	48
Iron	Fe	55.9	Tungsten	W	183.6
Lanthanum	La	138.5	Uranium	U	238.5
Lead	Pb	206.5	Vanadium	V	51.3
Lithium	Li	7	Ytterbium	Yb	172.7
Magnesium	Mg	24	Yttrium	Y	89.8
Manganese	Mn	54	Zinc	Zn	64.9
Mercury	Hg	199.7	Zirconium	Zr	90

TABLE OF THERMOMETRIC EQUIVALENTS

According to the Centigrade and Fahrenheit Scales.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
—40°	—40°.0	+16°	+60°.8	+72°	+161°.6	+128°	+262°.4
39	38.2	17	62.6	73	163.4	129	264.2
38	36.4	18	64.4	74	165.2	130	266.0
37	34.6	19	66.2	75	167.0	131	267.8
36	32.8	20	68.0	76	168.8	132	269.6
35	31.0	21	69.8	77	170.6	133	271.4
34	29.2	22	71.6	78	172.4	134	273.2
33	27.4	23	73.4	79	174.2	135	275.0
32	25.6	24	75.2	80	176.0	136	276.8
31	23.8	25	77.0	81	177.8	137	278.6
30	22.0	26	78.8	82	179.6	138	280.4
29	20.2	27	80.6	83	181.4	139	282.2
28	18.4	28	82.4	84	183.2	140	284.0
27	16.6	29	84.2	85	185.0	141	285.8
26	14.8	30	86.0	86	186.8	142	287.6
25	13.0	31	87.8	87	188.6	143	289.4
24	11.2	32	89.6	88	190.4	144	291.2
23	9.4	33	91.4	89	192.2	145	293.0
22	7.6	34	93.2	90	194.0	146	294.8
21	5.8	35	95.0	91	195.8	147	296.6
20	4.0	36	96.8	92	197.6	148	298.4
19	2.2	37	98.6	93	199.4	149	300.2
18	0.4	38	100.4	94	201.2	150	302.0
17	+ 1.4	39	102.2	95	203.0	151	303.8
16	3.2	40	104.0	96	204.8	152	305.6
15	5.0	41	105.8	97	206.6	153	307.4
14	6.8	42	107.6	98	208.4	154	309.2
13	8.6	43	109.4	99	210.2	155	311.0
12	10·4	44	111.2	100	212.0	156	312.8
11	12.2	45	113.0	101	213.8	157	314.6
10	14.0	46	114.8	102	215.6	158	316.4
9	15.8	47	116.6	103	217.4	159	318.2
8	17.6	48	118.4	104	219.2	160	320.0
7	19.4	49	120.2	105	221.0	161	321.8
6	21.2	50	122.0	106	222.8	162	323.6
5	23.0	51	123.8	107	224.6	163	325.4
4	24.8	52	125.6	108	226.4	164	327.2
3	26.6	53	127.4	109	228.2	165	329.0
2	28.4	54	129.2	110	230.0	166	330.8
1	30.2	55	131.0	111	231.8	167	332.6
0	32.0	56	132.8	112	233.6	168	334.4
+1	33.8	57	134.6	113	235.4	169	336.2
2	35.6	58	136.4	114	237.2	170	338.0
3	37.4	59	138·2	115	239.0	171	339.8
4	39.2	60	140·0	116	240.8	172	341.6
5	41·0	61	141.8	117	242.6	173	343.4
6	42.8	62	143.6	118	244.4	174	345.2
7	44.6	63	145.4	119	246.2	175	347.0
8	46.4	64	147.2	120	248.0	176	348.8
9	48.2	65	149.0	121	249.8	177	350.6
10	50.0	66	150.8	122	251.6	178	352.4
11	51.8	67	152.6	123	253.4	179	354.2
12	53.6	68	154.4	124	255.2	180	356.0
13	55.4	69	156.2	125	257.0	181	357.8
14	57.2	70	158.0	126	258.8	182	359.6
15	59.0	71	159.8	127	260.6	183	361.4

TABLE OF THERMOMETRIC EQUIVALENTS.—*Continued.*

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
+184°	+363.2°	+221°	+429.8°	+258°	+496.4°	+295°	+563.0°
185	365.0	222	431.6	259	498.2	296	564.8
186	366.8	223	433.4	260	500.0	297	566.6
187	368.6	224	435.2	261	501.8	298	568.4
188	370.4	225	437.0	262	503.6	299	570.2
189	372.2	226	438.8	263	505.4	300	572.0
190	374.0	227	440.6	264	507.2	301	573.8
191	375.8	228	442.4	265	509.0	302	575.6
192	377.6	229	444.2	266	510.8	303	577.4
193	379.4	230	446.0	267	512.6	304	579.2
194	381.2	231	447.8	268	514.4	305	581.0
195	383.0	232	449.6	269	516.2	306	582.8
196	384.8	233	451.4	270	518.0	307	584.6
197	386.6	234	453.2	271	519.8	308	586.4
198	388.4	235	455.0	272	521.6	309	588.2
199	390.2	236	456.8	273	523.4	310	590.0
200	392.0	237	458.6	274	525.2	311	591.8
201	393.8	238	460.4	275	527.0	312	593.6
202	395.6	239	462.2	276	528.8	313	595.4
203	397.4	240	464.0	277	530.6	314	597.2
204	399.2	241	465.8	278	532.4	315	599.0
205	401.0	242	467.6	279	534.2	316	600.8
206	402.8	243	469.4	280	536.0	317	602.6
207	404.6	244	471.2	281	537.8	318	604.4
208	406.4	245	473.0	282	539.6	319	606.2
209	408.2	246	474.8	283	541.4	320	608.0
210	410.0	247	476.6	284	543.2	330	626.0
211	411.8	248	478.4	285	545.0	340	644.0
212	413.6	249	480.2	286	546.8	350	662.0
213	415.4	250	482.0	287	548.6	360	680.0
214	417.2	251	483.8	288	550.4	370	698.0
215	419.0	252	485.6	289	552.2	380	716.0
216	420.8	253	487.4	290	554.0	390	734.0
217	422.6	254	489.2	291	555.8	400	752.0
218	424.4	255	491.0	292	557.6	410	770.0
219	426.2	256	492.8	293	559.4	420	788.0
220	428.0	257	494.6	294	561.2	430	806.0

Formulæ for converting degrees of the Centigrade scale into those of Fahrenheit (D representing the degree to be converted).

If above the freezing point of water, 32° F. (0° C.) $\frac{D}{5} \times 9 + 32.$

If below freezing, but above ° F. (—17.77° C.) $32 - \left(\frac{D}{5} \times 9\right).$

If below 0° F. (—17.77° C.) $-\left(\frac{D}{5} \times 9\right) - 32.$

Formulæ for converting degrees of the Fahrenheit scale into those of Centigrade.

If above the freezing point of water, 32° F. (0° C.) $\frac{(D - 32)}{9} \times 5.$

If below freezing, but above 0° F. (—17.77° C.) $-\frac{(32 - D)}{9} \times 5.$

If below 0° F. (— 17.77° C.) $-\frac{(D + 32)}{9} \times 5.$

TABLE FOR CONVERTING METRIC MEASURES OF CAPACITY INTO UNITED STATES FLUID MEASURES.

Cubic centimeters.	Minims.	Cubic centimeters.	Fluid ounces.	Fluid dr'hms.	Minims.	Cubic centimeters.	Fluid ounces.	Fluid dr'hms.	Minims
0·01	0.16	0.65	..	..	10.55	46	1	4	26.40
0.02	0.32	0.70	..	..	11.36	47	1	4	42.60
0.03	0.49	0.75	..	..	12.17	48	1	4	58.80
0.04	0.65	0.80	..	..	12.98	49	1	5	15.00
0.05	0.81	0.85	..	..	13.80	50	1	5	31.80
0.06	0.97	0.90	..	..	14.61	60	2	..	14.40
0.07	1.14	0.95	..	..	15.42	70	2	2	56.40
0.08	1.30	1	..	..	16.23	80	2	5	36.60
0.09	1.46	2	..	..	32·46	90	3	..	21.00
0.10	1.62	3	..	..	48·69	100	3	3	3 60
0.11	1.79	4	..	1	4.80	110	3	5	46.20
0.12	1.95	5	..	1	21.00	120	4	..	28.20
0·13	2.11	6	..	1	37.20	130	4	3	8.40
0.14	2.27	7	..	1	53.40	140	4	5	52.80
0.15	2.43	8	..	2	9.60	150	5	..	35.40
0·16	2.60	9	..	2	25.80	160	5	3	18.00
0·17	2.76	10	..	2	42.60	170	5	6	
0.18	2.92	11	..	2	58.83	180	6	..	40.20
0.19	3.08	12	..	3	15.06	190	6	3	24.60
0.20	3.25	13	..	3	31·29	200	6	6	7.20
0.21	3.41	14	..	3	57·40	225	7	4	52.85
0.22	3.57	15	..	4	13.60	250	8	3	39.00
0.23	3.74	16	..	4	19.80	275	9	2	24.65
0.24	3.90	17	..	4	36.00	300	10	1	10.80
0.25	4.06	18	..	4	52.20	325	10	7	56.40
0.26	4.22	19	..	5	8.40	350	11	6	42.60
0.27	4.39	20	..	5	24.60	375	12	5	28.20
0.28	4.55	21	..	5	40.83	400	13	4	14·40
0.29	4.71	22	..	5	57.06	425	14	3	
0.30	4.87	23	..	6	13.29	450	15	1	46.20
0.31	5.03	24	..	6	29.40	475	16	..	31.80
0.32	5.19	25	..	6	45.60	500	16	7	18.00
0.33	5.36	26	..	7	1.80	525	17	6	3.60
0.34	5.52	27	..	7	18.00	550	18	4	49.80
0.35	5.68	28	..	7	34.20	575	19	3	35.40
0.36	5.84	29	..	7	50.40	600	20	2	21.60
0.37	6.01	30	1	..	4.80	625	21	1	17.20
0.38	6.17	31	1	..	21.03	650	21	7	53.40
0.39	6.33	32	1	..	37.26	675	22	6	49.00
0.40	6.49	33	1	..	53.49	700	23	5	25.20
0.41	6.65	34	1	1	9.60	725	24	4	10.80
0.42	6.81	35	1	1	25.80	750	25	2	57.00
0.43	6.98	36	1	1	42.00	775	26	1	42.60
0.44	7.14	37	1	1	58.20	800	27	0	28.80
0.45	7.30	38	1	2	14.40	825	27	7	14.40
0.46	7.46	39	1	2	30.60	850	28	6	0.60
0.47	7.63	40	1	2	49.20	875	29	4	46.20
0.48	7.79	41	1	3	5.43	900	30	3	32.40
0.49	7.95	42	1	3	21.66	925	31	2	18.00
0.50	8.12	43	1	3	37.89	950	32	1	4.20
0.55	8.93	44	1	3	54.00	975	32	7	49.80
0.60	9.74	45	1	4	10.20	1000	33	6	36.00

TABLE FOR CONVERTING UNITED STATES FLUID MEASURES INTO METRIC MEASURES OF CAPACITY.

Minims.	Cubic centimeters.	Minims.	Fluid drachms.	Cubic centimeters.	Fluid ounces.	Cubic centimeters.
1	0.06	43	..	2.64	3	88.67
2	0.12	44	..	2.71	4	118.24
3	0.18	45	..	2.77	5	147.81
4	0.25	46	..	2.83	6	177.39
5	0.31	47	..	2.89	7	206.96
6	0.37	48	..	2.95	8	236.53
7	0.43	49	..	3.01	9	266.10
8	0.49	50	..	3.08	10	295.68
9	0.55	55	..	3.39	11	325.25
10	0.62	60	..	3.70	12	354.82
11	0.68	65	..	4.01	13	384.40
12	0.74	70	..	4.31	14	413.97
13	0.80	75	..	4.62	15	443.54
14	0.86	80	..	4.93	16	473.11
15	0.92	85	..	5.24	17	502.69
16	0.99	90	..	5.54	18	532.26
17	1.05	95	..	5.85	19	561.93
18	1.11	100	..	6.16	20	591.50
19	1.17	110	..	6.78	21	621.08
20	1.23	120	..	7.39	22	650.65
21	1.29	..	3	11.09	23	680.22
22	1.36	..	4	14.79	24	709.80
23	1.42	..	5	18.48	25	739.37
24	1.48	..	6	22.18	26	768.94
25	1.54	..	7	25.88	27	798.51
26	1.60	..	8	29.57	28	828.09
27	1.66	..	9	33.27	29	857.66
28	1.73	..	10	36.97	30	887.23
29	1.79	..	11	40.66	31	916.80
30	1.85	..	12	44.36	32	946.38
31	1.91	..	13	48.06	40	1183.00
32	1.97	..	14	51.75	45	1330.81
33	2.03	..	15	55.45	48	1419.53
34	2.10	..	16	59.10	50	1478.74
35	2.16	..	17	62.85	55	1626.55
36	2.22	..	18	66.54	60	1774.46
37	2.28	..	19	70.24	64	1892.75
38	2.34	..	20	73.94	80	2366.00
39	2.40	..	21	77.63	96	2839.11
40	2.46	..	22	81.33	112	3312.22
41	2.52	..	23	85.03	128	3785.51
42	2.58				256	7571.02

TABLE FOR CONVERTING METRIC WEIGHTS INTO TROY WEIGHTS.

Grams.	Exact equivalents in grains.	Approximate equivalents in Troy weights.				Grams.	Exact equivalents in grains.	Approximate equivalents in Troy weights.			
		Ounce.	Drachms.	Scruples.	Grains.			Ounces.	Drachms.	Scruples.	Grains.
0.01	0.1543	..	..	..	$\frac{1}{6}$	12.0	185.188	..	3	..	$5\frac{1}{5}$
0.02	0.3086	..	..	..	$\frac{1}{3}$	13.0	200.621	..	3	1	$\frac{3}{5}$
0.03	0.4630	..	..	..	$\frac{6}{13}$	14.0	216.053	..	3	1	16
0.04	0.6173	..	..	..	$\frac{7}{11}$	15.0	231.485	..	3	2	$11\frac{1}{2}$
0.05	0.7717	..	..	..	$\frac{3}{4}$	16.0	246.918	..	4	..	$6\frac{9}{10}$
0.06	0.9260	..	..	..	$\frac{9}{10}$	17.0	262.350	..	4	1	$2\frac{1}{3}$
0.07	1.0803	..	..	..	1	18.0	277.782	..	4	1	$17\frac{4}{5}$
0.08	1.2347	..	..	..	$1\frac{1}{4}$	19.0	293.215	..	4	2	$13\frac{1}{5}$
0.09	1.3890	..	..	..	$1\frac{1}{3}$	20.0	308.647	..	5	..	$8\frac{3}{5}$
0.1	1.543	..	..	..	$1\frac{1}{2}$	21.0	324.079	..	5	1	$4\frac{1}{10}$
0.2	3.086	..	..	..	3	22.0	339.512	..	5	1	$19\frac{1}{2}$
0.3	4.630	..	..	..	$4\frac{3}{5}$	23.0	354.944	..	5	2	15
0.4	6.173	..	..	..	$6\frac{1}{8}$	24.0	370.376	..	6	..	$10\frac{2}{5}$
0.5	7.716	..	..	..	$7\frac{3}{4}$	25.0	385.809	..	6	1	$5\frac{4}{5}$
0.6	9.259	..	..	..	$9\frac{1}{4}$	26.0	401.241	..	6	2	$1\frac{1}{4}$
0.7	10.803	..	..	..	$10\frac{3}{4}$	27.0	416.673	..	6	2	$16\frac{3}{4}$
0.8	12.346	..	..	..	$12\frac{1}{3}$	28.0	432.106	..	7	..	$12\frac{1}{10}$
0.9	13.889	..	..	..	14	29.0	447.538	..	7	1	$7\frac{1}{2}$
1.0	15.432	..	..	..	$15\frac{1}{2}$	30.0	462.970	..	7	2	3
2.0	30.865	..	..	1	$10\frac{4}{5}$	31.0	478.403	..	7	2	$18\frac{2}{5}$
3.0	46.297	..	..	2	$6\frac{1}{4}$	32.0	493.835	1	..	..	$13\frac{4}{5}$
4.0	61.729	..	1	..	$1\frac{3}{4}$	40.0	617.294	1	2	..	$17\frac{3}{10}$
5.0	77.162	..	1	..	$17\frac{1}{6}$	45.0	694.456	1	3	1	$10\frac{1}{2}$
6.0	92.594	..	1	1	$12\frac{3}{5}$	50.0	771.617	1	4	2	$11\frac{3}{5}$
7.0	108.026	..	1	2	8	60.0	925.941	1	7	1	6
8.0	123.459	..	2	..	$3\frac{1}{2}$	70.0	1080.264	2	2	..	$\frac{1}{4}$
9.0	138.891	..	2	..	$18\frac{9}{10}$	80.0	1234.588	2	4	1	$14\frac{3}{5}$
10.0	154.323	..	2	1	$14\frac{1}{3}$	90.0	1388.911	2	7	..	9
11.0	169.756	..	2	2	$9\frac{3}{4}$	100.0	1543.235	3	1	2	$3\frac{1}{4}$

TABLE FOR CONVERTING TROY WEIGHTS INTO METRIC WEIGHTS.

Grains.	Grams.	Grains.	Grams.	Grains.	Grams.	Grains.	Grams.
1	0.0648	30	1.944	59	3.823	88	5.702
2	0.1296	31	2.009	60	3.888	89	5.766
3	0.1944	32	2.073	61	3.952	90	5.831
4	0.2592	33	2.138	62	4·017	91	5.896
5	0.3240	34	2.203	63	4.082	92	5.961
6	0.3888	35	2.268	64	4.147	93	6.026
7	0.4536	36	2.332	65	4.211	94	6.090
8	0.5184	37	2.397	66	4.276	95	6.155
9	0.5832	38	2.462	67	4.341	96	6.220
10	0.6480	39	2.527	68	4.406	97	6.285
11	0.7130	40	2.592	69	4.471	98	6.350
12	0.7776	41	2.656	70	4.535	99	6.414
13	0.8424	42	2.721	71	4.600	100	6.479
14	0.9072	43	2.786	72	4.665	120	7.776
15	0.972	44	2.851	73	4.730	150	9.719
16	1.037	45	2.916	74	4.795	180	11.664
17	1.102	46	2.980	75	4.859	200	12.958
18	1.166	47	3.045	76	4.924	240	15.552
19	1.231	48	3.110	77	4.989	300	19.440
20	1.296	49	3.175	78	5.054	360	23.328
21	1.361	50	3.234	79	5.118	400	25.920
22	1.426	51	3.304	80	5.183	480	31.103
23	1.490	52	3.369	81	5.248	500	32.396
24	1.555	53	3.434	82	5.313	600	38.875
25	1.620	54	3.499	83	5.378	700	45.354
26	1.685	55	3.564	84	5.442	800	51·833
27	1.749	56	3 628	85	5.507	900	58.313
28	1.814	57	3.693	86	5.572	960	62.207
29	1.869	58	3.758	87	5.637	1000	64.792

INDEX.

(The Latin names are in *Italics.*)

THE END.