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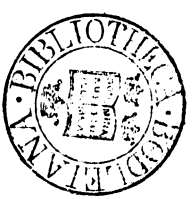
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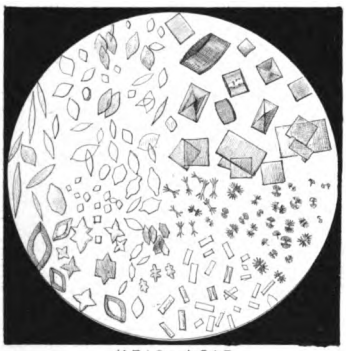
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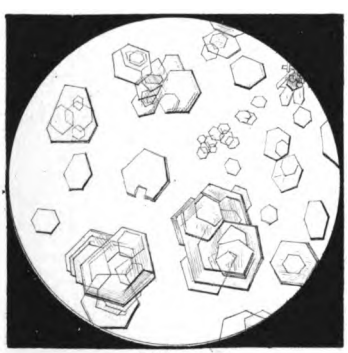
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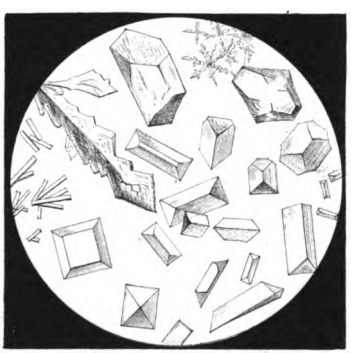
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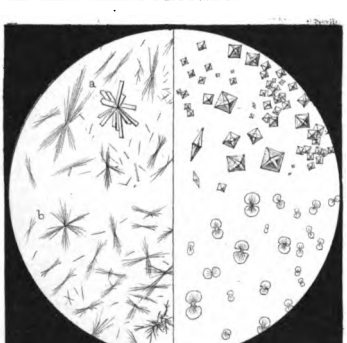
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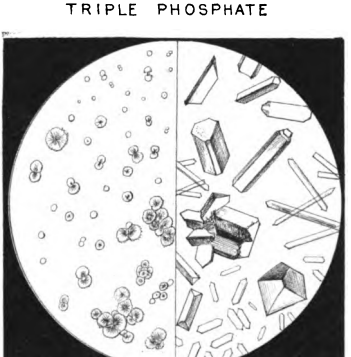
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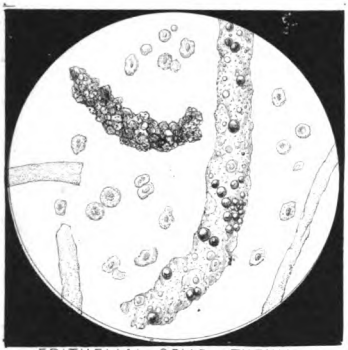
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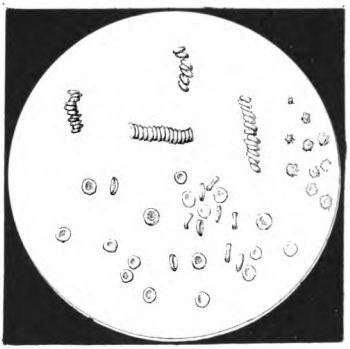
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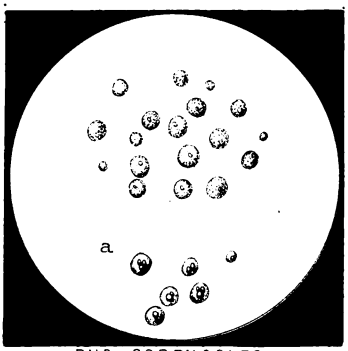
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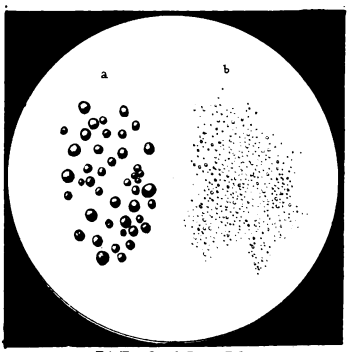
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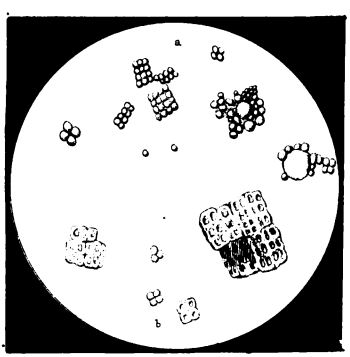
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AN

INTRODUCTION

TO

PHARMACEUTICAL CHEMISTRY.

BY

JOHN ATTFIELD, PH.D., F.C.S.,

PROFESSOR OF PRACTICAL CHEMISTRY TO THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN; FORMERLY DEMONSTRATOR OF CHEMISTRY AT ST. BARTHOLOMEW'S HOSPITAL.





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"But the greatest error of all is, mistaking the ultimate end of knowledge; for some men covet knowledge out of a natural curiosity and inquisitive temper; some to entertain the mind with variety and delight; some for ornament and reputation; some for victory and contention; many for lucre and a livelihood; and but few for employing the Divine gift of reason to the use and benefit of mankind. Thus some appear to seek in knowledge a couch for a searching spirit; others, a walk for a wandering mind; others, a tower of state; others, a fort, or commanding ground; and others, a shop for profit or sale, instead of a storehouse for the glory of the Creator and the endowment of human life."
—Lord Bacon.

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PREFACE.

This work is essentially a handbook of Practical Chemistry. It is intended as a laboratory guide for medical and pharmaceutical students, and as an aid to the study of pharmaceutical chemistry by the pupils of medical practitioners, and chemists and druggists.

The aim of the author has been threefold:—to give concise data for a complete course of qualitative and quantitative analysis; to associate with these data simple experiments in imitation of all the chemical processes of the British Pharmacopœia; and by means of short introductory, explanatory, and suggestive notes to direct attention to the principles and facts which the analytical and synthetical experiments are designed to illustrate. Practical toxicology and the chemical and microscopical characters of morbid urine, urinary deposits, and calculi are included, and questions on the whole work given in an Appendix.

Two leading features in the book will be found to be the separation of reactions having synthetical from those possessing analytical interest, and the addition of a large number of new reactions of the former class; the chemistry of the Pharmacopœia is thus brought prominently into view, while the art of analysis is made clear and concise. Only by such plans can any practical knowledge of chemistry be gained by medical students in the short period devoted to this subject during the summer session. Pharmaceutical students also will thus economize time, and, by viewing a chemical reaction from more than one point of view, be better able to acquire a philosophical conception respecting it

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than if performing experiments solely with an analytical or a synthetical object. Even those just entering on pharmacy will, by this mode of study, be able to attain a knowledge of chemistry without undue deduction of time from their other duties, or too lavish an expenditure in the purchase of apparatus.

The chemical notation of the work is in accordance with modern theories. Equations illustrative of pharmacopœial decompositions have a name attached to every formula; this has been done for the convenience of those who have been accustomed to the old method of notation. Chemical nomenclature has been modernized to the extent of defining the alkaline and earthy salts as those of potassium, sodium, ammonium, barium, calcium, magnesium, and aluminium, instead of potash, soda, ammonia, baryta, lime, magnesia, and alumina. The author confidently believes that this change, extensively adopted by scientific men, will be accepted and become popular with pharmaceutical chemists, as it is a step in the direction of consistency, simplicity, and truth. Hitherto the names of salts have included metals and metallic oxides, as sulphate of copper and sulphate of potash; henceforward they will include the names of metals only, thus—sulphate of copper and sulphate of potassium.

It is hoped that the numerous etymological references scattered through the following pages will be found useful. Words in Greek have been rendered in English characters, letter for letter.

The author is indebted to his friends, Joseph Ince, F.L.S., for much assistance and many kind suggestions during the revision of the proof-sheets, and Henry B. Brady, F.L.S., for the excellent drawings from which the Plates have been engraved.

October 1867.

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PHARMACEUTICAL CHEMISTRY.

INTRODUCTION.

THIS book is intended as a guide to the student in acquiring a practical knowledge of chemistry, chiefly by means of personal experiment. He is recommended to read the first three pages, and then to commence work by preparing oxygen. The various paragraphs are printed in differently spaced type: those in the wider direct a student in his operations; those in the closer contain explanations of each operation, and are to be carefully read before proceeding to the experiments.

The numerous solid, liquid, and gaseous substances of which our earth and atmosphere, and, apparently, the sun, moon, and other celestial bodies are composed, may be resolved into sixty-three distinct forms of matter, appropriately termed Elements. Of these only a few occur naturally in the uncombined state, the greater number being disguised by a kind of union so close as to be concealed from ordinary methods of observation. Thus none of the common properties of water indicate that it is composed of two elements, both gases, but differing much from each other. Nor can the senses of sight, touch, and taste, or other

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common means of examination, detect in their concealment the three elements of which sugar is composed. The art by which these and all other compound substances are resolved into their elements, is termed Chemistry, derived, possibly, from the Arabic word *Kamai*, to conceal, whence *al kimiæ*, or alchemy, the earliest name for that art which at the time the name was given had but little more for its object than the transmutation of the baser metals into gold. The *art* of chemistry also includes the construction of compounds from elements, and the formation of substances of one character from those of another. The general principles or leading truths relating to the elements, to the manner in which they severally combine, and to the properties of the compound substances formed by their union, constitute the *science* of chemistry.

From these few words concerning the nature of the art and science of chemistry, it will be seen that in most of the occupations that engage the attention of man it plays an important part—in few more so than in Pharmacy*.

* Pharmacy (from φάρμακον, *pharmakon*, a drug) is the generic name for the operations of preparing or compounding medicines, whether performed by the Medical Practitioner or by the Chemist and Druggist. It is also sometimes applied, like the corresponding term Surgery, to the apartment in which the operations are conducted.

Persons who practise the art and science of Chemistry are known as chemists, though conventionally the latter name includes those who simply deal in chemicals. Hence has arisen the distinguishing appellations of Manufacturing, Analytical, and Pharmaceutical Chemists. The compounder of medicine is a chemist inasmuch as he is constantly engaged in operations with chemical substances used as remedial agents, his moral right to the title depending on the amount of chemical knowledge he possesses concerning those substances. If he keep an open shop, he is in Great Britain generally known as a Chemist and Druggist, his higher title being Pharmaceutical Chemist; indeed the latter is the one he legally assumes on passing certain Examinations, conducted by the Pharmaceutical Society of Great Britain. In most other countries of Europe duly qualified persons only are allowed to practise Pharmacy.

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All drugs and chemicals used in Pharmacy are composed of a few elements. An intimate knowledge of the properties of these, and of the various substances they form by combining with each other, a knowledge of the power or force (the chemical force or chemical affinity) by which the elements contained in those compounds are held together, and an application of such knowledge to the operations of Pharmacy must be the objects sought to be attained by the student for whom this work has been especially written. In other words, he must acquaint himself with facts, principles, and manipulation; when these are acquired, his labours in the educational laboratory may cease.

The Elements.—Only thirty-nine of the elements are of special interest to the student of Pharmacy; of these, about two-thirds are metals, and one-third non-metals*: the remainder are so seldom met with in nature as to have received no practical application either in medicine, art, or manufacture. Before intimately studying these elements, it is desirable to have some general notions concerning them: such a procedure will serve to introduce the student to his apparatus, and make him better acquainted with the various methods of manipulation†.

* Possibly some of these bodies may, hereafter, be proved to be compounds; but at present they cannot be resolved into simpler forms of matter.

† This allusion to apparatus need not discourage the youngest pupil in Pharmacy. He may, by studying the following pages, learn the chemical reactions which are constantly occurring in the course of making up medicines, may understand the processes by which the preparations he uses are manufactured, and may himself detect adulterations, impurities, or faults of manufacture, simply with the aid of a few phials, wine-glasses, or other similar vessels always at hand. Among the substances used in medicine, he will find nearly all the chemicals he will require; and if, in addition, he has a dozen test-tubes, and a few feet of glass tubing, he will be able to perform most of the experiments described.

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Metallic Elements.—With regard to the metallic elements, it may safely be assumed that the student has sufficient knowledge for present purposes; but little, therefore, need now be said respecting them. He has an idea of the appearance, relative weight, hardness, &c. of such metals as gold, silver, copper, lead, tin, zinc, and iron. If he has not a similar knowledge of mercury, antimony, arsenic, platinum, nickel, aluminium, magnesium, potassium, and sodium, he should commence his practical studies by seeing and handling specimens of each of these metals.

Non-metallic Elements.—With regard to the non-metallic elements, it is here supposed that the student has no general knowledge. He should commence his studies therefore by a series of operations as follows, on eight out of their number.

OXYGEN.

Preparation.—As oxygen is the most abundant element in nature, forming, though in a combined state, about one-half of the whole weight of our globe, it may safely be assumed that this element can readily be obtained in the free condition in a state of purity. In fact, the air itself contains about one-fifth of its bulk of oxygen, though that element cannot be separated sufficiently easily and readily for our present purpose. It is preferable to apply heat—that force which will often be noticed as antagonistic, so to speak, to chemical union,—heat generally separating particles of matter further from each other, while chemical attraction tends to bind them closer together: it is better to apply heat to certain compounds containing oxygen; the latter is then evolved in its normal, natural condition of gas. Several substances, when heated, yield oxygen; but, for convenience and economy, the crystalline body known as chlorate of potassium is best fitted for the experiment. The size and form of the vessel in which to heat it will of course depend on the quantity required; but for the purposes of the student the best is a *test-tube*, an instrument in constant requisition in studying practical chemistry. It is simply a thin tube of glass, a few inches in length, and half or three-quarters of an inch in diameter, closed by fusion at one

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end. It is made of thin glass, in order that it may be rapidly heated or cooled without risk of fracture.

Heat chlorate of potassium (say, as much as will lie on a shilling) in a test-tube, by means of a spirit- or gas-flame; gaseous oxygen is quickly evolved. Before applying heat, however, provision should be made for collecting the gas.

Collection of Gases.—Procure a piece of glass tubing about the thickness of a quill pen, and a foot or eighteen inches long, and fit it accurately to the test-tube by means of a cork. The tube is fixed in the cork through a round hole made by the aid of a rat-tail file. Setting aside the test-tube for a few minutes, proceed to bend the long piece of tubing to the most convenient shape for collecting the gas.

To bend Glass Tubes.—Hold the part of the tube required to be bent in any gas or spirit-flame (a fish-tail gas-jet answers very well), constantly rotating it, so that about an inch of the glass becomes heated. It will soon be felt to soften, and will now, yielding to the *gentle* pressure of the fingers, assume any required angle. In the present case, the tube should be heated at about four inches from one extremity, and bent to an angle of about 90 degrees.

Source of heat.—The source of heat for the test-tube may be the flame of an ordinary spirit-lamp, or, still better where coal-gas is procurable, a mixture of the latter with air. The simple flame of a common argand gas-burner is preferred by some operators, especially when the usual glass chimney is replaced by a metal one about four or five inches long. If a piece, or cap, of wire gauze be fixed on to the top of the metal chimney, then the unlit gas which issues from the jets of the argand-burner becomes mixed with air inside the chimney, and the mixture when lit on the outer side of the gauze, burns with a flame as smokeless and as little coloured as that of a spirit-lamp. Gas-lamps especially constructed to burn a mixture of coal-gas and air are sold by chemical-apparatus manufacturers.

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Fit the cork and bent tube into the test-tube; the apparatus will then be ready for delivering gas at a convenient distance from the heated portion of the arrangement. To collect it, have ready three or four test-tubes filled with water, and inverted in a basin, or other similar vessel, also containing water, taking care to keep the mouths of the tubes a little below the surface. Now apply heat to the chlorate contained in the test-tube, and so arrange the open end of the bent tube under the water that the gas which presently issues may bubble into and gradually fill the inverted test-tubes. The first tubeful may be rejected, as it probably consists of little more than the air originally in the apparatus, and which has been displaced by the oxygen. That which comes afterwards will be pure oxygen.

On the large scale, oxygen may be made in the same way, larger vessels being employed. Less heat also will be necessary if the chlorate of potassium be previously mixed with very fine sand, or, still better, with about a fourth of its weight of common black oxide of manganese.

Note.—It may be as well to state that nearly all gases, whether for experimental or practical purposes, are collected and stored in a similar manner. Even coal-gas is generated at gas-works in iron retorts very much the shape of test-tubes, only they are as many feet long as a test-tube is inches; and the well-known gigantic gas-holders may be viewed as inverted iron test-tubes of great diameter.

Properties.—One characteristic of this non-metallic element is invisibility. Again, it obviously is not very soluble in water, or it could not be collected by the aid of that liquid.

The student should know, however, that it is soluble to a certain extent, or fishes could not breathe.

The next noticeable feature is its want of taste and smell. Removing one of the tubes from the water by placing the thumb over its mouth, apply for a second a lighted wood match to the

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orifice; the gas will be found to be incombustible. Extinguish the flame of the match, and then quickly introduce the still incandescent carbonaceous extremity of the wood halfway down the test-tube, the wood will at once burst into flame, owing to the extreme violence with which oxygen supports combustion. These tests of the presence of oxygen may of course also be applied at the extremity of the delivery-tube whilst the gas is being evolved. (It is desirable to retain two tubes of the gas for use in subsequent experiments.)

Memorandum.—At present it is not advisable that the student should trouble himself with the consideration of the chemical action which occurs either in the elimination of oxygen from its compounds, or in the separation of any of the following non-metallic elements from their combinations. It is to the properties of the elements themselves that he should restrict his attention. Working thus from simple to more complex facts, he will in due time find that the comprehension of such actions as occur in the preparation of these few elements will be easier than if he attempted their study now.

HYDROGEN.

Preparation and Collection.—The element Hydrogen is also a gas, and is made from its commonest compound, water, by the agency of zinc or iron and sulphuric acid. The apparatus used for making oxygen may be employed for this experiment; but no lamp is required. Place several pieces of thin zinc* in the generating-tube, and cover them with water. The collecting-tubes being ready, add about half a teaspoonful of strong sulphuric acid (oil of vitriol) to the zinc and water, and fit on the

* The best form is *granulated zinc* (*Zincum Granulatum*, B. P.), made by heating scraps of common sheet zinc in a ladle over a fire, and as soon as melted pouring, in a slow stream, into a pail of water from a height of 8 or 10 feet. Each drop of zinc thus yields a thin little bell, which, for its weight, presents a large surface to the action of the acid water. If the zinc is allowed to become hotter than necessary, the little bells will not be formed.

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delivery-tube; the hydrogen is at once evolved. Having rejected the first portions, collect four or five tubes of the gas in the manner described under Oxygen.

This process is similar to that of the 'British Pharmacopœia' (see p. 141 of that work). In making larger quantities, bottles may be used instead of test-tubes.

Properties.—Like oxygen, hydrogen is invisible, inodorous, and tasteless. If made with iron it has a strong odour, but this is due to impurities contained in the metal. Apply a flame to the mouth of the delivery-tube; ignition of the hydrogen ensues, showing that, unlike oxygen, it is combustible. Immerse a lighted match into a tube containing hydrogen; the gas is ignited, but the match becomes extinguished. This shows that hydrogen is not a supporter of combustion. Hydrogen in burning unites with the oxygen of the air and forms water, which may be condensed on a cool glass or other surface. Prove this by holding a glass vessel a few inches above a hydrogen-flame. In burning the hydrogen contained in one of the tubes, the flame is best seen when the tube is held mouth upwards, and water poured in so as to force out the gas gradually. If, instead of this gradual combination of the two elements oxygen and hydrogen, they be mixed together in the right proportions and then ignited, explosion results. Prepare a mixture of this kind by filling up with hydrogen a test-tube from which one-third of the water has been expelled by oxygen. Remove the tube from the water, placing a finger over over the mouth, and, having a lighted match ready, apply the flame; a slight explosion will result, owing to the instantaneous combination of the two elements, and the expansive force of the steam produced.

The noise of such explosions is caused by concussion between the particles of the gaseous body and those of air.

The force of the explosion, or, in other words, the expansive

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force of the steam produced, is exceedingly slight, certainly very far below that necessary to break the test-tube. Some force, however, is exerted, and hence the necessity of the precaution previously suggested of allowing all the air which may be in a hydrogen-apparatus to escape before proceeding with the experiments. If a flame be applied to the delivery-tube before all the hydrogen is expelled, the probable result will be ignition of the mixture of hydrogen and oxygen (of the air) and consequent explosion. But even in this case the generating-vessel is not often fractured unless it be large and of thin glass, the ordinary effect being that the cork is blown out, and the delivery-tube broken on falling to the ground.

Hydrogen is a prominent constituent of all the substances used for producing artificial light, such as tallow, oil, and coal-gas. The explosive force of large quantities, such as a roomful, of coal-gas and air, though vastly below that of an equal weight of gunpowder, is well known to be sufficient at least to blow out that side of the room which offers least resistance.

Hydrogen is the lightest substance known. It was formerly used for filling balloons, but was soon superseded by coal-gas. Coal-gas is not so light as hydrogen, but is cheaper and more easily obtained. The lightness of hydrogen may be rendered evident by the following experiment:—Fill two test-tubes with the gas, and hold one with its mouth downwards and the other with its mouth upwards. The hydrogen will have escaped from the latter in a few seconds, whereas the former will still contain the gas after the lapse of some minutes. This may be proved by applying a lighted match to the mouths of the respective tubes.

Mem.—The relative weight or specific gravity of oxygen is sixteen times that of hydrogen. A tube holding one grain of hydrogen will hold sixteen grains of oxygen.

It is desirable to retain two tubes of hydrogen for use in subsequent experiments.

PHOSPHORUS.

Phosphorus (*Phosphorus*, B. P.) is a solid element, in appear-

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ance and consistence resembling white wax; but it gradually becomes yellow by exposure to light. It takes fire very readily, and should therefore be kept under water. When wanted for use it must be cut under water.

Phosphorus is a characteristic constituent of bones, and is always prepared from that source by a process which will be described subsequently.

Properties.—Dry a piece about one-fourth the size of a pea by quickly and carefully pressing it between the folds of porous paper; place it on a plate, and ignite by touching it with a piece of warm wire or wood. Observe that the product of combustion is a dense white smoke, which must be confined at once by placing an inverted tumbler, test-glass, or other similar vessel over the phosphorus. The fumes rapidly aggregate, and fall in white flakes on the plate. When this has taken place, and the phosphorus is no longer burning, moisten the powder with a few drops of water, and observe that some of the water is converted into steam, an effect due to the intense affinity with which the two combine, and the liberation of some of the heat previously existing in the substances.

The powder produced by the combustion of phosphorus is phosphoric anhydride; the combination of the latter with the elements of water is termed phosphoric acid, which dissolves in the water, forming a dilute solution of phosphoric acid. The Diluted Phosphoric Acid of the 'British Pharmacopœia' is such a solution, made, however, in a different way, and, of course, of a definite strength.

NITROGEN.

The chief source of this gaseous element is the atmosphere, nearly four-fifths of which consists of nitrogen (the remaining fifth is almost entirely oxygen).

Preparation.—Burn a piece of dried phosphorus, the size of a

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pea, in a confined portion of air. The oxygen is thus removed, and nitrogen alone remains. The readiest mode of performing this experiment is to fix a piece of earthenware (the lid of a small porcelain crucible answers very well) on a piece of cork, so that it may float in a dish of water. Place the phosphorus on the lid, ignite by a warm rod, and then invert a tumbler, or any glass vessel of about a half-pint capacity, over the burning phosphorus, so that the mouth of the glass may dip into the water. Let the arrangement rest for a short time, and then decant the gas into test-tubes in the manner already indicated.

Larger quantities are made in the same way. Other combustibles, such as sulphur or a candle, might be used to burn out the oxygen from a given quantity of air, but none answer so quickly and completely as phosphorus; added to which, the product of their combustion would not always be dissolved by water, but would remain with and contaminate the nitrogen.

The student may notice that the statement concerning the composition of the air is roughly confirmed in preparing nitrogen, about one-fifth of the volume of the air originally in the glass vessel having disappeared, its place being occupied by water from the dish.

Properties.—Like oxygen and hydrogen, nitrogen is invisible, tasteless, and inodorous. It is only slightly soluble in water. It is distinguished from all other gases by the absence of any characteristic or positive properties. Apply a flame to some contained in a tube; it will be found to be incombustible. Immerse a lighted match in the gas; the flame is extinguished, showing that nitrogen is a non-supporter of combustion.

The chief office of nitrogen in the air is to dilute the energetic oxygen.

Nitrogen is fourteen times as heavy as hydrogen.

The air is nearly fourteen and a half (14·4) times as heavy as hydrogen.

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CHLORINE.

This element is a gas. Its chief source is common salt, more than half of which is chlorine.

Preparation.—About a quarter of an ounce of salt and the same amount of black oxide of manganese are placed in a test-tube with sufficient water to cover them; on adding a small quantity of sulphuric acid, the evolution of chlorine commences.

As the action of the sulphuric acid on the salt in the above process is mainly to give hydrochloric acid, the latter acid and the black oxide of manganese may be used in making the gas, instead of salt, sulphuric acid, and black oxide of manganese. This is the process of the 'British Pharmacopœia' (see p. 185 of that work).

Collection and Properties.—Chlorine is a most suffocating gas. Great care must, consequently, be observed in experimenting with this element. As soon as its penetrating odour indicates that it is escaping from the test-tube, the cork and delivery-tube should be fitted on, and the gas allowed to pass to the bottom of another test-tube half filled with water. When thirty or forty small bubbles have passed, their evolution being assisted by slightly heating the generating-tube, the latter should be removed to the cupboard usually provided in laboratories for performing operations with noxious gases, or dismounted, and the contents washed away. The water in the collecting-tube will now be found to smell of the gas, chlorine being, in fact, soluble in about half its bulk of water. Chlorine-water is officinal in the 'British Pharmacopœia' (*Liquor Chlori*).

The *Vapor Chlori*, B. P., or Inhalation of Chlorine, is simply moist chlorinated lime so placed that some of the chlorine given off may be inhaled.

During these manipulations the operator will have observed that chlorine is of a light green colour. The tint is readily ob-

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served when the gas is collected in large vessels. As it is soluble in water, it cannot be economically collected over that liquid. Being, however, nearly twice as heavy as air, it may be collected by simply allowing the delivery-tube to pass to the bottom of the test-tube or dry bottle.

The distinctive property of chlorine is its bleaching-power. Prepare some coloured liquid by placing a few chips of logwood or other dyeing-material in a test-tube half full of hot water. Pour off some of this red decoction into another tube, add a few drops of the chlorine-water, and note how rapidly the colour is destroyed.

Chlorine readily decomposes noxious gases, and hence is a most powerful *disinfectant*.

If the student has the opportunity of generating the gas in a closed chamber or in the open air, a test-tube of the same size as one of those in which hydrogen has been retained from a previous operation, is filled with the gas. The hydrogen-tube is then inverted over that containing the chlorine, the mouths being kept together by encircling them with a finger. After the gases have mixed, the mouths of the tubes are quickly in succession brought near a flame, when explosion occurs, and fumes of hydrochloric acid gas are formed.

The hydrochloric acid of pharmacy is a solution of this gas (made in a more economical way) in water.

Chlorine is thirty-five and a half times as heavy as hydrogen.

SULPHUR, CARBON, IODINE.

The physical properties of these elements are probably familiar to the student. Their leading chemical characters will also be understood when he recalls a few facts concerning each.

Sulphur.—Burn a small piece of sulphur; a penetrating odour

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is produced, due to the formation of a colourless gas, the same as that formed on igniting a common sulphur-tipped lucifer match.

This product is a perfectly definite chemical compound of the oxygen of the air with the sulphur. It is termed sulphurous acid gas.

CARBON is familiar in the forms of soot, coke, charcoal, graphite (plumbago, wrongly termed blacklead), and diamond. The presence of carbon in wood, and in other vegetable and animal matter, is at once rendered evident by heat. Place a little tartaric acid on the end of a knife in a flame; the blackening that occurs is due to the separation of carbon. The black matter at the extremity of a piece of half-burned wood is also carbon.

Carbon, like hydrogen, phosphorus, and sulphur, has a great affinity for oxygen at high temperatures. A striking evidence of that affinity is the evolution of sufficient heat to make the materials concerned red- or even white-hot. When ignited in the dilute oxygen of the air, carbon simply burns with a moderate glow, as seen in an ordinary coke or charcoal fire, but when ignited in pure oxygen, the intensity of its combination is greatly exalted. The product of the combination of the two elements is an invisible gas termed carbonic acid.

IODINE.—The main chemical characteristic of iodine is its great affinity for metals. Place a piece of iodine, about the size of a pea, in a test-tube with a small quantity of water, and add a few iron-filings or small nails. On gently warming, or even shaking if longer time be allowed, the colour and odour of the iodine disappears; it has combined with the iron. If the solution be filtered, a clear aqueous solution of the compound of the two elements is obtained.

This compound is called iodide of iron. Its solution, made as above, and mixed with sugar, forms, when of a certain strength,

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the ordinary syrup of iodide of iron of pharmacy (*Syrupus Ferri Iodidi*, B. P.). A strong solution mixed with sugar and liquorice root constitutes the corresponding pill (*Pilula Ferri Iodidi*, B. P.).

THE ELEMENTS, THEIR SYMBOLS, Etc.

The student has now obtained a general idea of the nature of several of the more frequently occurring elements. Some additional facts concerning them may be gathered from the following Table, which gives the name in full, the symbol (or short-hand character*) of the name, and its origin.

For the purposes of study the elements may be divided into three classes, viz., those frequently used in pharmacy, those seldom, and those never used.

Name.	Symbol.	Derivation of Name.
Oxygen	O	From ὀξὺς (oxūs) *acid*, and γένεσις (genesis) *generation*, i. e. generator of acids. It was supposed to enter into the composition of all acids when first discovered.
Hydrogen	H	From ὕδωρ (udōr) *water*, and γένεσις (genesis) *generation*, in allusion to the product of its combustion in air.
Nitrogen	N	From νίτρον (nitron), and γένεσις (genesis), *generator of nitre*.
Carbon	C	From *carbo*, *coal*, which is chiefly carbon.
Chlorine.....	Cl	From χλωρὸς (chlōros) *green*, the colour of this element.
Iodine	I	From ἴον (ion) *a violet*, and εἶδος (eidos) *likeness*, in reference to the colour of its vapour.
Sulphur	S	From *sal* a *salt*, and πῦρ (pūr) *fire*, indicating its combustible qualities. Its common name, *brimstone*, has the same meaning, being the slightly altered Saxon word *brynstone*, i.e. burnstone.
Phosphorus ..	P	Φῶς (phōs) *light*, and φέρειν (pherein) *to bear*. The light it emits may be seen on exposing it in a dark room.
Potassium .... (Kalium.)	K	Kalium, from *kali*, Arabic for *ashes*. Manufactories in which certain compounds of

* The symbol is also much more than the short-hand character, as will presently be apparent.

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Name.	Symbol.	Derivation of Name.
		potassium and allied sodium-salts are made are called alkali-works to this day. Potassium, from *pot-ash*; so called because obtained by evaporating the lixivium of wood-ashes in pots. From such ashes the element was first obtained, hence the name.
Sodium ..... (Natrium.)	Na	Natrium, from *natron*, the old name for certain natural deposits of carbonate of sodium. Sodium, from *soda-ash* or *sod-ash*, the residue of the combustion of masses or *sods* of marine plants. These were the sources of the metal.
Ammonium ..	Am (NH_4)	This body is not an element, but its components exist in all ammoniacal salts, and apparently play the part of such elements as potassium and sodium. Sal ammoniac (chloride of ammonium) was first obtained from near the temple of Jupiter Ammon in Libya; hence the name.
Barium	Ba	From *βαρὺς* (barūs) *heavy*, in allusion to the high specific gravity of "heavy spar," the most common of the barium minerals.
Calcium.....	Ca	*Calx*, *lime*, the oxide of calcium.
Magnesium ..	Mg	From *Magnesia*, the name of the town (in Asia Minor) near which the substance now called "native carbonate of magnesia" was first discovered.
Iron ..... (Ferrum.)	Fe	The spelling is from the Saxon *iren*, the pronunciation probably from the kindred Gothic "*iarn*;" the derivation is unknown to the author.
Aluminium ..	Al	The metallic basis of alum was at first confounded with sulphate of iron, which was the alum of the Romans, and was so called in allusion to its tonic properties, from *als*, *to nourish*.
Zinc	Zn	The derivation of this word is unknown to the author.
Arsenicum....	As	Ἀρσενικὸν (arsenikon), the Greek name for orpiment, a sulphide of arsenicum. Common white arsenic is an oxide of arsenicum.
Antimony .... (Stibium.)	Sb	Στίβι (stibi), or στίμμι (stimmi) was the Greek name for the native sulphide of antimony. The word antimony is said to be derived from ἀντὶ (anti) *against*, and *moine*, French for *monk*, from the fact that certain monks were poisoned by it.

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Name.	Symbol.	Derivation of Name.
Copper ..... (Cuprum.)	Cu	From *Cyprus*, the name of the Mediterranean island where this metal was first worked.
Lead ..... (Plumbum.)	Pb	The Latin word is expressive of "something heavy," and the Saxon *læd* has a similar signification.
Mercury..... (Hydrargyrum.)	Hg	Hydrargyrum, from ὕδωρ (udōr) *water*, and ἄργυρος (arguros) *silver*, in allusion to its liquid and lustrous characters. Mercury, after the messenger of the gods, on account of its susceptibility of motion. The old name *quicksilver* also indicates its ready mobility and argentine appearance.
Silver..... (Argentum.)	Ag	Ἄργυρος (arguros) *silver*, from ἀργὸς (argos) *white*. Words resembling the term *silver* occur in several languages, and indicate a white appearance.

The following are names of some of the less frequently occurring elements, compounds of which, however, are alluded to in the British Pharmacopœia or are met with in pharmacy.

Name.	Symbol.	Derivation of Name.
Bromine.....	Br	From βρῶμος (brōmos), a *stink*. It has an intolerable odour.
Fluorine.....	Fl	Fluo *to flow*. Its source (fluoride of calcium) is commonly used as a flux in metallurgic operations.
Boron.....	Bo	From *borak* or *baurak*, the Arabic name of *borax*, the substance from which the element was first obtained.
Silicon	Si	From *silex*, Latin for *flint*, which is nearly all silica (an oxide of silicon).
Lithium.....	L	From λίθειος (litheios) *stony*, in allusion to its supposed existence in the mineral kingdom only.
Strontium	Sr	This name is commemorative of *Strontian*, a mining-village in Argyleshire, Scotland, in the neighbourhood of which the mineral known as *strontianite* or carbonate of strontium was first found.
Cerium	Ce	Discovered in 1803, and named after the

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Name.	Symbol.	Derivation of Name.
		planet *Ceres*, which was discovered on Jan. 1, 1801. The oxalate, CeC_2O_4, $3H_2O$, is officinal, but seldom used.
Chromium ..	Cr	From χρῶμα (chrōma) *colour*, in allusion to the characteristic appearance of its salts.
Manganese....	Mn	Probably a mere transposition and repetition of most of the letters of the word magnesia, with whose compounds those of manganese were confounded till the year 1740.
Cobalt	Co	*Cobalus* or *Kobold* was the name of a demon supposed to inhabit the mines of Germany. The ores of cobalt were formerly troublesome to the German miners, and hence received the name their metallic radical now bears.
Nickel	Ni	*Nickel*, from *nil*, is a popular German term for *worthless*. The mineral now known as nickel ore was formerly called by the Germans *Kupfernickel*, *false copper*, on account of its resemblance to copper (*Kupfer*) ore. When a new metallic element was found in the ore, the name nickel was retained.
Tin (Stannum).	Sn	Both words are possibly corruptions of the old British word *staen*, or the Saxon word *stan*, a stone. Tin was first discovered in Cornwall, and the ore (an oxide) is called *tinstone* to the present day.
Gold (Aurum).	Au	*Aurum* (Latin) from a Hebrew word signifying the colour of fire. Gold, an old Saxon word expressive of *yellow*, the colour of this metal.
Platinum ...	Pt	Or *platina* (Spanish), the diminutive of *plata*, *silver*, in allusion to its inferiority in lustre, but otherwise general resemblance to silver.
Bismuth.....	Bi	Slightly altered from the German *Wismuth*, derived from *Wiesematte* "a beautiful meadow," a name given to it originally by the old miners in allusion to the prettily variegated tints presented by the freshly exposed surface of this crystalline metal.
Cadmium	Ca	Καδμεία (Kadmeia) was the ancient name of calamine (carbonate of zinc), with which carbonate of cadmium was long confounded, the two often occurring together.

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Gold, Platinum, Tin, and Silicon are here classed with the less important elements, because their compounds are seldom used in pharmacy.

The student will notice that the symbol of an element is simply the first letter of its Latin name, which is generally the same as in English. Where two names begin with the same letter, the less important has an additional letter added.

The student may now proceed to study the manner in which substances react chemically with each other.

That this tendency to act, when the bodies are brought into contact under favourable circumstances, exists, is obvious from the preceding experiments, and indeed from the operations of every-day life. In a common fire, coal needs only to have its temperature slightly raised to afford it an opportunity of showing the liking or affinity which it and the oxygen of the air have for each other. The evolution of heat in this instance is only one of the incidents of the action. The presence of chimneys and the means of ventilation are adjuncts to a fire, which should at once suggest that there are still more deeply hidden incidents of the mutual action of coal and air. Such a formation of complex bodies from simple ones, and the resolution of complex into simple bodies, has probably been noticed by the student in his observations of nature. From the air and the earth vegetables construct complex matters, which are resolved into their original simple forms after having served as food for animals. To discover and remember the laws which govern these transformations, the general student of Chemistry educes elements from compounds, and builds up compounds from elements,—the student of Pharmaceutical Chemistry restricting his attention to those with which he is more immediately concerned.

This tendency to combination being a prominent feature in everything material, the mind naturally assumes the existence of some sort of power or energy in matter by which its particles are bound together, a sort of force or affinity which only needs opportunity to manifest itself. In order to distinguish this force from those of gravitation, heat, light, electricity, and magnetism, it is called chemical force or chemical affinity.

Chemical Force.

Having thus acquired a knowledge of certain facts concerning each element, the experiments already performed may be reviewed

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and a few others conducted in order to obtain a clear idea of the manner in which chemical substances act on each other, and to learn how memoranda concerning those actions are best recorded on paper and in the mind.

The student must look upon every particle of matter, solid, liquid, or gaseous, as being the seat of a certain amount of a peculiar attractive energy or force, commonly termed chemical affinity. The exertion of chemical affinity is of course only possible when the substances in question are in close contact. Thus it was necessary to bring the oxygen, hydrogen, phosphorus, chlorine, sulphur, carbon, iodine, and iron into intimate contact before reaction occurred. The exact nature of these actions, as indeed of all in which substances act chemically (*i. e.* with obvious alteration of properties in the product), would seem to be an interchange, most generally a mutual one, of the particles of which the bodies consist.

Take, for example, the experiment in which two volumes of hydrogen and one volume of oxygen were caused to combine. The production of flame and noise were evidences that chemical action of some kind had taken place; had the experiment been performed in dry vessels, evidence of the precise action would have been found in the bedewment or moisture produced by the condensation of the water on the sides of the tube. Similar evidence was afforded on holding a cool glass surface over the hydrogen-flame. The action is expressed in the following way:—

$$H_2 + O = H_2O,$$

or more correctly, for a reason that will be given immediately,

$$2H_2 + O_2 = 2H_2O.$$

Here the symbols H and O standing alone indicate the state of things prior to the experiment. Standing in juxtaposition thus, H_2O, they indicate the result of the experiment.

Small figures multiply symbols, large figures multiply formulæ. H is a symbol, H_2O is a formula.

The sign *plus* (+) between the symbols H_2 and O indicates that the one element is simply mixed with or added to the other.

The sign =, or *equal*, has the usual signification given to it in arithmetic.

The foregoing aggregation of symbols or short-hand characters, viz. H_2O, is a convenient picture of the facts that have already come before us, viz., that water is formed of the elements hydrogen, H, and oxygen, O, and, moreover, that it was formed of two

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measures or volumes of hydrogen, H_2, to one of oxygen, O. These symbols so arranged have a deeper signification still, as will soon be apparent.

Another experiment already performed, illustrating the character of the manifestations of chemical force, was that in which the red-hot carbon of wood was plunged into oxygen. The evidence of chemical action in that case was the sudden inflammation of the carbonaceous extremity of the wood. The particles of carbon and oxygen having intense attraction or affinity for each other at that temperature, rushed together so impetuously as suddenly to emit a large quantity of the heat naturally existing in them, an amount sufficient to raise the particles to a white heat. Here it may be again remarked that this attraction, distinguished from all others by the term chemical, is the only form of attraction by which the properties of the product are rendered totally different from those of its constituents. The action between carbon and oxygen is expressed on paper in the following way:—

$$C_2 + 2O_2 = 2CO_2.$$

CO_2 is the composition of the well-known gas commonly termed carbonic acid.

The student should here draw for himself similar equations, showing the formation of the other bodies he produced—namely, hydrochloric acid (H Cl), phosphoric anhydride (P_2O_5), sulphurous acid gas (SO_2), and iodide of iron (FeI_2), submitting the same to a tutor or other authority to assure himself of their correctness.

Note.—In the foregoing experiments illustrations occur of the formation of compounds having the gaseous, liquid, and solid conditions, in one of which three forms all the matter in the universe exists.

The student will notice that in the above equations an element existing in the free state is symbolized by its initial letter and the figure $_2$. This is because there are good grounds for believing that these elements and most others never exist in single particles, but that if the particle of an element has not the opportunity of combining with a particle of another element, it will combine with another particle of like nature to itself.

The grounds for this statement are shortly as follows:—Equal volumes of elementary or compound gases, under similar pressure, expand equally when heated, and contract equally when cooled; equal volumes must, therefore, be similarly constituted, must

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contain an equal number of molecules (the diminutive of mole or mass—literally, little masses), all of the same size. For example, in a previous experiment a test-tubeful of chlorine and a test-tubeful of hydrogen gave on mixture and explosion two test-tubefuls of hydrochloric acid gas. Now it could be easily demonstrated that these three gases expand equally on the addition of heat, and contract equally on its abstraction. Hence the inference that the number and size of the molecules of each volume are similar. We of course have no conception of the actual number of molecules of a gas a test-tube, or any other vessel, is capable of containing; but whatever it be, that number is constant for all. Imagine that it is 1000; then 1000 of hydrogen and 1000 of chlorine have given 2000 of hydrochloric acid. But each molecule of hydrochloric acid contains a particle of hydrogen and a particle of chlorine. Therefore the 1000 *molecules* of hydrogen must have contained 2000 *particles*, and the 1000 molecules of chlorine, 2000 particles of chlorine. In other words, every molecule of an elementary gas consists of two particles or, dropping the indefinite word particle, two atoms, (*ἄτομος*, indivisible, from the privative *α*, *a*, and *τέμνω*, *temno*, to cut). (See also Hofmann's 'Modern Chemistry,' pp. 136–162).

A particle, or rather an *atom*, is the smallest portion of matter which can exist in a state of combination; a molecule, the smallest portion of matter which can exist in the free state. *The symbol* of an element is intended to indicate one atom of that element, thus H and Cl respectively indicate one atom of hydrogen and one atom of chlorine. A symbol also indicates one volume of the element in the state of gas, supposing it to be capable of existing in that form. Two symbolical letters indicate two atoms or volumes—that is, one molecule of the element—thus OO, or rather O_2. The formula of a compound always indicates the molecule or two volumes of the compound in the gaseous state, and also the number of atoms or gaseous volumes concerned in the formation of the compound. Thus H Cl is the *formula* of the molecule of a compound containing one atom each of the elements hydrogen and chlorine. Further, like the formulæ of all molecules, it is the picture of two volumes of hydrochloric acid, one volume being chlorine, and the other hydrogen. It shows, therefore, that the volume of chlorine and the volume of hydrogen suffered no condensation on combining to form a molecule compounded of both. Similarly H_2O indicates the existence of a body containing hydrogen and oxygen, two volumes of which in the gaseous state (*i. e.* steam) were formed from two volumes of

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hydrogen and one volume of oxygen, which three volumes must have suffered condensation to two-thirds their bulk—the molecule containing two atoms of H to one of O. This body is water.

There is a third body equal in importance to hydrochloric acid and water, with which the student should become acquainted at this stage of study. It is ammonia. Ammonia cannot, like hydrochloric acid and water, be prepared directly from its elements. The process that may here be adopted by the student is the same as that by which it is prepared on a very large scale in manufactories; for present purposes it will be sufficient to use test-tubes. Heat a few grains of sal-ammoniac with about an equal weight of slaked lime and a little water in a test-tube; ammonia gas is given off, and may be recognized by its well-known odour. It is very soluble in water. Pass a delivery-tube, fitted as described for the preparation of oxygen and hydrogen, into a second test-tube, at the bottom of which is a little water; solution of ammonia (*Liquor Ammoniæ*, B. P.) will thus be formed. Ammonia gas is composed of one atom of nitrogen with three atoms of hydrogen; its formula is NH_3; two volumes of it contain one volume of nitrogen combined with three atoms or volumes of hydrogen. Its constituents have therefore suffered condensation to one-half their normal bulk.

Atomic Weights.

If there be such things as atoms (and the mind necessarily assumes their existence), they must have weight. What are these weights? The weights of the atoms, or the atomic weights of the gaseous elements already studied, must differ from each other to the extent that equal volumes of those elements differ in weight. For equal volumes contain an equal number of molecules, of course of equal size, and each molecule is composed of two atoms; so that equal volumes contain an equal number of atoms. Now, bulk for bulk, chlorine is thirty-five and a half (35·5) times as heavy as hydrogen; so that the molecule of chlorine must be 35·5 times the weight of the mole-

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cule of hydrogen; for molecules are equal in bulk. And as the molecules of chlorine and hydrogen contain two atoms each, the atom of chlorine must be 35·5 times as heavy as that of hydrogen=1. By parity of reasoning the atomic weight of oxygen is 16; for oxygen is found, by experiment, to be 16 times as heavy as hydrogen. Similarly the atomic weight of nitrogen is found to be 14. The atomic weight of carbon is 12,—not because its vapour has been proved to be 12 times as heavy as hydrogen, for it has never yet been converted into the gaseous state, but because no gaseous compound of carbon, which has been analyzed, has been found to contain in 2 volumes (1 of which, if hydrogen, would weigh 1 part) less than 12 parts of carbon.

By thus weighing equal volumes of gaseous elements, or equal volumes of gaseous compounds of non-volatile elements, and ascertaining by analysis the proportion of the non-volatile element, whose atomic weight is being sought, to the volatile element, whose atomic weight is known, the atomic weights of a large number of the elements have been determined. Some of the elements, however, do not form volatile compounds of any kind; the stated atomic weights of these elements, therefore, are at present simply the proportions by weight in which they combine with elements whose atomic weights have been determined, the proportions being in most cases checked by the relation of the element to other forces, especially heat.

Though the symbols of the common elements should be committed to memory, their atomic weight need be sought out only as occasion may arise. A complete Table will be found at the end of the volume.

The composition of hydrochloric acid, water, ammonia, carbonic acid, or any other compound, as well as the weight of an element that may be concerned in its formation, cannot be ascertained by actual experiment until the student is far advanced in practical chemistry; at present, therefore, he must derive such knowledge from books or tutors.

The student must never regard the atomic weight of an element as its equivalent. The word equivalent means "equal in value" (from *æquus* equal, and *valens* being worth). The amounts of oxygen, nitrogen, and carbon which are equal in value to 1 part by weight of hydrogen, which will, in other words, do the work of 1 of hydrogen, combine with or displace 1 of hydrogen, are 8, 4·66, and 3 respectively. For water contains 1 part by weight of hydrogen to 8 parts of oxygen; ammonia gas contains 1 part, by weight, of hydrogen to 4·66 parts of nitrogen; and carbonic

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acid gas contains, by weight, 3 parts of carbon to 8 of oxygen. 1, 8, 4·66, and 3 are the equivalents of hydrogen, oxygen, nitrogen, and carbon. To consider the elements from an equivalent point of view is to regard them in an aspect of uninteresting uniformity. Oxygen in its relations to hydrogen, instead of being equal in value, equivalent, is essentially bivalent (of double worth, from *bis*, twice, and *valens*); an atom of it will displace two atoms of hydrogen, or combine with the same number; nitrogen is trivalent (from *tres*, three, and *valens*); and carbon quadrivalent (from *quatuor*, four, or *quater*, four times, and *valens*). Chlorine, iodine, and bromine, as well as potassium, sodium, and silver among the metals, are, like hydrogen, univalent. Barium, strontium, calcium, magnesium, zinc, cadmium, mercury, and copper, like oxygen, are bivalent. Phosphorus, arsenic, antimony, and bismuth, like nitrogen, usually exhibit trivalent properties; but the composition of certain compounds of these elements shows that the several atoms are really quinquivalent (*quinquies*, five times, and *valens*), though in most of their salts two-fifths of the chemical power of the atom is latent (two-fifths of their affinities remain in a state of mutual saturation). Gold and boron are really, as well as apparently, trivalent. Silicon (the characteristic element of flint and sand), tin, aluminium, platinum, and lead resemble carbon in being quadrivalent. Sulphur, chromium, manganese, iron, cobalt, and nickel are sexivalent (from *sex*, six, or *sexies*, six times, and *valens*). This *quantivalence* (from *quantitas*, quantity, and *valens*), also termed *atomicity* and *dynamicity* of the elements, may be ascertained at any time on referring to the Table of the names of the elements, where, as recommended by Odling, dashes, $'$ $''$ $'''$ $''''$ $'''''$ $''''''$, or Roman numerals, ^{I}, ^{II}, ^{III}, ^{IV}, ^{V}, ^{VI}, are attached to the symbols of each element to indicate their uni-, bi-, tri-, quadri-, quinqui-, or sexivalence. The quantivalence of elements, as they one after another come under the notice of the student, should be carefully committed to memory; for the composition of compounds can often be thereby predicated with accuracy, and remembered with ease. For instance, the hydrogen compounds of chlorine, Cl', oxygen, O'', nitrogen, N''', and carbon, C'''', will be respectively $H'Cl'$, H'_2O'', H'_3N''', and H'_4C'''',—one univalent atom, H', balancing or saturating one univalent atom, Cl'; two univalent atoms, H'_2, and one bivalent atom, O'', saturating each other; three univalent atoms, H'_3, and one trivalent atom, N''', saturating each other; and four univalent atoms, H_4, and one quadrivalent atom, C'''', saturating each other. Car-

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bonic acid gas, $C^{IV}O^{II}_2$, again, is a saturated molecule containing one quadrivalent and two bivalent atoms.

The student will find, as he proceeds, that what has been stated regarding the real and apparent quantivalence of nitrogen applies to several other elements, so that the available power of an atom is not always indicated by its absolute power, its total quantivalence—just as the available power of a steam-tug to draw a ship is not its total power, but only the excess over and above that expended on its own propulsion.

THE ELEMENTS AND THEIR COMPOUNDS.

Having thus obtained a general idea of the nature of such elements as have especial interest for the medical and pharmaceutical student, and which include indeed all with which any student of chemistry should at present occupy his attention, we may pass on to consider in detail the relations of the elements to each other. The elements themselves, in the free condition, are seldom used in medicine, being nearly always associated, bound together by the chemical force; in this combined condition, therefore, they must be studied. Each combination of elements or chemical compound will, in the following pages, be regarded as containing two parts or roots, two radicals:—the one usually metallic, or, to speak more generally, basylous; the other often a non-metallic, simple or complex, acidulous radical. The basylous radicals, or metals, will be considered first, the acidulous radicals afterwards. Each radical will be studied from two points of view, the synthetical and the analytical: that is to say, the properties of an element on which the preparation of its compounds depends will be illustrated by operations performed in test-tubes or small dishes, and thus the chemistry of the Pharmacopœia be systematically learnt; then the reactions by which the element is detected, though combined with other substances, will be performed, and so the student be instructed in qualitative analysis. Synthetical and analytical reactions are, in truth, frequently identical, the object with which they are performed giving them synthetical interest on the one hand, or analytical interest on the other. Thus iodide of potassium may be added to corrosive sublimate with the view of preparing red iodide of mercury, or with the view of detecting mercury in corrosive sublimate.

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A good knowledge of chemistry may be acquired synthetically by manufacturing on a small scale specimens of the salts of the different metals, or analytically by going through a course of pure qualitative analysis. But the former demands a larger expenditure of time than most students have to spare, while under the latter system they generally lose sight of the synthetical interest which attaches to analytical reactions.

POTASSIUM.

Symbol K. Atomic weight 39.

Memoranda.—The chief sources of the potassium salts are the nitrate, found in soils, especially in warm countries, and the compounds of potassium existing in plants. The latter, vegetable salts of potassium, are chiefly converted into carbonate when the wood is burned. Large quantities of carbonate are thus produced in North America and Russia; and it is from this salt, purified (*Potassæ Carbonas*, B. P.), that nearly all other compounds of potassium are made. An exception occurs in cream of tartar* (*Potassæ Tartras Acida*, B. P.), which is simply the purified natural potassium salt of the grape-vine.

Potassium itself is isolated with some difficulty by distilling a mixture of its carbonate and charcoal. It rapidly oxidizes in the air, and hence is always kept below the surface of mineral naphtha, a liquid containing no oxygen. The atom of potassium is univalent.

Reactions having (*a*) Synthetical and (*b*) Analytical Interest.

(*a*) *Synthetical Reactions.*

These are actions utilized in manufacturing preparations of potassium. The word *synthesis* is from *σύνθεσις* (*sūnthĕsis*), a

* "It is called *tartar*," says Paracelsus, "because it produces oil, water, tincture, and salt, which burn the patient as tartarus does." *Tartarus* is Latin (Τάρταρος, Tartaros, Greek) for *hell*. The products of its destructive distillation are certainly somewhat irritating in taste and smell; the properties of the "salt" (carbonate of potassium) that is left are well known. A boiling solution of tartar yields a crust of minute crystals on cooling; hence the term *cream of tartar*.

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putting together, as opposed to analysis, from ἀναλύω (*analuo*), I resolve.

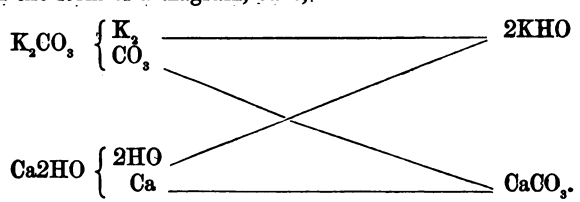
First Synthetical Reaction.—Boil together, for a few minutes, in a test-tube, five or six grains of carbonate of potassium (K_2CO_3) and a like quantity of slaked lime (Ca2HO) with a small quantity of water. Set the mixture aside in the test-tube rack to cool.

This liquid is a solution of caustic potash, or hydrate of potassium (KHO). Made of a prescribed strength, it forms the *Liquor Potassæ*, B. P.

In this reaction the metals of the two salts change places; from K_2CO_3 and Ca2HO there are produced $CaCO_3$ and 2KHO, from carbonate of potassium and hydrate of calcium there result carbonate of calcium and hydrate of potassium. The student should express this fact in his note-book as an equation, thus,—

$$K_2CO_3 + Ca2HO = 2KHO + CaCO_3,$$

or in the form of a diagram, thus,—



With regard to the group of atoms represented by the symbols CO_3 and HO, only a few words need be said here. CO_3 is the grouping found in all carbonates; it is as characteristic of carbonates as K is of potassium salts. HO is characteristic of all hydrates. CO_3 is a bivalent grouping or root, HO univalent; hence CO_3 is found united with two univalent atoms, as in carbonate of potassium, K_2CO_3, or with one bivalent atom, as in carbonate of calcium, $CaCO_3$; and HO is found united in single proportion with univalent atoms as in hydrate of potassium, KHO, or in double proportion with bivalent atoms as in hydrate of calcium, Ca2HO. The student has only to learn the quantivalence of a metal, and he at once knows the formula of its carbonate and hydrate, though he may never have seen the formula of either. And the formulæ of all other metallic salts are constructed on the same principle. But beyond ascertaining the formulæ

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and quantivalence of the various groupings characteristic of carbonates, hydrates, nitrates, sulphates, acetates, &c., he should not now devote special attention to the subject of the constitution of salts, but at present restrict his observation to what may be called the metallic or basylous side of salts.

Solution of potash generally contains a trace of alumina dissolved from the lime, but not enough to interfere with the use of the liquid in medicine. If the solution is required for analytical purposes, it may be obtained free from alumina in the manner suggested by Redwood. Half a gallon is made by mixing half a pound of slaked lime with about three pints of water, placing the mixture in a half-gallon bottle (Winchester quart), and adding to it, in small quantities at a time, a solution of half a pound of carbonate of potassium dissolved in the other pint of water, shaking the mixture well for some minutes after each addition. The whole is now set on one side till clear, and then if a small quantity poured into a test-tube does not effervesce on the addition of hydrochloric acid, the solution is fit for use. If carbonic gas is evolved on adding the acid, the mixture must be again well shaken.

Solution of potash evaporated to dryness and the residue fused and poured into moulds constitutes *Potassa Caustica*, B. P. It often contains chlorides and sulphates, detected by nitrate of silver and a barium salt, as described subsequently in connexion with hydrochloric and sulphuric acids.

Second Synthetical Reaction.—Into a test-tube put a few grains of carbonate of potassium previously mixed with about half its weight of sulphur. Heat the mixture gradually until it ceases to effervesce. The resulting fused mass is the *Potassa Sulphurata*, Sulphurated Potash, of the British Pharmacopœia.

This salt is not a definite chemical compound, but a mixture of several substances, among which are sulphate of potassium, (K_2SO_4) and one or more of the sulphides of potassium. In short, the chemical character of this compound is well indicated by its vague name. It is of the colour of liver when freshly prepared (whence the old name "liver of sulphur"), but from absorption of oxygen soon changes to green, and ultimately becomes white and useless. It is occasionally employed in the form of ointment (*Unguentum Potassæ Sulphuratæ*, B. P.).

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In preparing large quantities of sulphurated potash, the test-tube is replaced by an earthenware vessel termed a crucible (from *crux*, a cross). Originally a cross was impressed upon the melting-pot, as used by alchemists and goldsmiths: others derive the word from crux, an instrument of torture (sense symbolical).

Crucibles of a few ounces' capacity may be heated in an ordinary grate-fire. Larger ones require a stove with a good draught—that is, a furnace. Even the smaller ones are more conveniently and quickly heated in a furnace. Half-ounce or one-ounce experimental porcelain crucibles may be heated in a spirit or gas-flame; the air-gas flame already described being generally the most suitable.

Third Synthetical Reaction.—Place twenty or thirty grains of carbonate of potassium in a small dish, and add acetic acid drop by drop until effervescence ceases; the resulting liquid is a strong solution of acetate of potassium. Evaporate most of the water, and a white salt remains which fuses on the further application of heat; this is the officinal Acetate of Potash (*Potassæ Acetas*, B. P.), or Acetate of Potassium as it is more correctly called.

$$\underset{\text{Carbonate of potassium.}}{K_2CO_3} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} = \underset{\text{Acetate of potassium.}}{2KC_2H_3O_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid.}}{CO_2}$$

The formula for acetic acid (the acetate of hydrogen) is $HC_2H_3O_2$, and of acetate of potassium $KC_2H_3O_2$. The grouping, $C_2H_3O_2$, is characteristic of all acetates; it is univalent, and may be shortly, though less instructively, written $\bar{A}$. The student will notice that the quantivalence of the constituent elements in these acidulous groupings still asserts itself; indeed it is by the amount of affinity expressed by the quantivalence that the atoms of a molecule are held together. Thus in carbonate of potassium, K_2CO_3, the grouping CO_3 has two units of affinity ("bonds," Frankland) in excess of those necessary for binding together the atoms of the grouping (C= iv, O_3=vi), and it is this excess which probably gives it its bivalent character. So, on adding up the units of affinity, or the numbers expressing the quantivalence of each of the atoms of the grouping $C_2H_3O_2$, it will be found that there is one unit in excess of those uniting the constituents of the grouping together, one bond engaging the bond of some univalent atom, forming a whole, an acetate.

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When two molecules of acetic acid ($2H\bar{A}$) and one of carbonate of potassium (K_2CO_3) react, two molecules of acetate of potassium ($2K\bar{A}$) and one of carbonic acid (H_2CO_3) are produced, the latter at once splitting up into water (H_2O) and carbonic acid gas (CO_2), as already shown in the equation.

Evaporation of water from a liquid is best conducted in wide shallow vessels rather than in narrow deep ones, as the steam can thus quickly diffuse into the air and be rapidly conveyed away; hence a small round-bottomed basin is far more suitable than a test-tube for such operations. On the manufacturing scale, iron, or iron lined with enamel or semi-porcelain; copper, tinned copper, or solid tin pans are used. Up to 12 or 18 inches diameter, pans, basins, or dishes, made of Wedgwood ware or porcelain composition, may be employed.

The above reaction has a general as well as a special synthetical interest. It represents one of the commonest methods of forming salts, namely, the saturation of an acid with a carbonate. Carbonates added to acetic acid yield acetates, to nitric acid nitrates, to sulphuric acid sulphates. Many illustrations of this general process occur in pharmacy.

Fourth Synthetical Reaction.—Make a strong solution of carbonate of potassium by heating in a test-tube a mixture of a few grains of the salt with an equal weight of water. Through the cooled solution pass carbonic acid gas; after a few minutes a white crystalline precipitate of Acid Carbonate of Potassium ($KHCO_3$), the *Bi*carbonate of Potash of the Pharmacopœia (*Potassæ Bicarbonas*, B. P.), will be formed.

K_2CO_3	+	H_2O	+	CO_2	=	$2KHCO_3$
Carbonate of potassium.		Water.		Carbonic acid.		Acid carbonate of potassium.

The carbonic acid gas necessary for this operation might be obtained from any carbonate. Thus the previous synthetical reaction could be made available for this purpose, the carbonic gas evolved on the addition of the acetic acid to the carbonate of potassium being conducted into a strong solution of more carbonate of potassium by a glass tube bent and fitted as described when treating of oxygen gas. But motives of economy induce the use of carbonate of calcium, the form known as

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marble being always employed. Economy and convenience also cause hydrochloric acid to be used in preference to acetic or any other.

Generate the carbonic acid gas by adding hydrochloric acid, diluted with twice its bulk of water, to a few fragments of marble contained in a test-tube, and conduct the gas into the solution of carbonate of potassium by a glass tube bent to a convenient angle or angles, and fitted to the test-tube by a cork in the usual way.

Acid carbonate of potassium is to a certain extent soluble in water; but as it is less so than the carbonate of potassium, and as a *saturated* solution of the latter has been used, a precipitation of a part of the acid carbonate inevitably occurs. In other words, the quantity of water present is sufficient to keep the carbonate, but insufficient to retain the equivalent quantity of acid carbonate in solution.

A solution of 30 grains of acid carbonate of potassium in one pint of water, charged with carbonic acid gas under pressure, constitutes the ordinary "potash-water," the so-called *Liquor Potassæ Effervescens*, B. P.

Note on Nomenclature.—Salts whose specific name end in the syllable "*ate*" are in general conventionally so termed when they contain the acidulous radical, or characteristic elements, of an acid whose name ends in "*ic*," and from which acid they have been or may be formed. Thus, the syllable "*ate*" in the words sulph*ate*, nitr*ate*, acet*ate*, carbon*ate*, &c., indicate that the respective salts were each made from, or, at least, contain the characteristic elements of an acid whose name ended in *ic*, the previous syllables, sulph-, nitr-, acet-, carbon-, indicating what that acid was—sulphuric, nitric, acetic, or carbonic. Occasionally a letter or syllable is dropped from or added to a word to render the name more euphonious; thus sulphuric acid forms sulphates, not sulphurates.

Fifth Synthetical Reaction.—Dissolve a few grains of citric acid ($H_3C_6H_5O_7$) in water, and add carbonate of potassium so long as effervescence occurs. The resulting liquid is a solution of

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citrate of potassium ($K_3C_6H_5O_7$ or $K_3\overline{Ci}$). Evaporated to dryness a granular residue is obtained, which is the officinal *Potassæ Citras.*

$$\underset{\text{Carbonate of potassium.}}{3K_2CO_3} + \underset{\text{Citric acid.}}{2H_3C_6H_5O_7} = \underset{\text{Citrate of potassium.}}{2K_3C_6H_5O_7} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Carbonic acid gas.}}{3CO_2}$$

The citric radical or group of elements which with three of hydrogen forms citric acid, and with three of potassium citrate of potassium, is a trivalent grouping; hence the three atoms of potassium in a molecule of the citrate. The full chemistry of citric acid will be subsequently described.

Nitrate of potassium (KNO_3) (*Potassæ Nitras*, B. P.), and sulphate of potassium (K_2SO_4) (*Potassæ Sulphas*, B. P.), could obviously also be made by saturating nitric acid (HNO_3), and sulphuric acid (H_2SO_4), respectively, by carbonate of potassium. But practically they are not made in that way,—the nitrate occurring, as already stated, in nature, and the sulphate as a bye-product in many operations. Both salts will be hereafter alluded to in connexion with nitric acid.

Sixth Synthetical Reaction.—Place a few grains of acid tartrate of potassium ($KHC_4H_4O_6$ or $KH\overline{T}$) in a test-tube with a little water, and add carbonate of potassium till there is no more effervescence; a solution of neutral tartrate of potassium ($K_2\overline{T}$) results, the *Potassæ Tartras* of the British Pharmacopœia.

$$\underset{\text{Acid tartate of potassium.}}{2KHC_4H_4O_6} + \underset{\text{Carbonate of potassium.}}{K_2CO_3} = \underset{\text{Neutral tartrate of potassium.}}{2K_2C_4H_4O_6} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

$C_4H_4O_6$ are the elements characteristic of all tartrates: they form a bivalent grouping; hence the formula of the hydrogen tartrate, or tartaric acid, is $H_2C_4H_4O_6$; that of the potassium tartrate $K_2C_4H_4O_6$; of the intermediate salt, the acid potassium tartrate (cream of tartar), $KHC_4H_4O_6$. If the acid tartrate of one metal and the carbonate of another react, a neutral double tartrate results, as seen in Rochelle Salt ($KNaC_4H_4O_6$) (p. 41).

Seventh Synthetical Reaction.—To a little warm solution of potash add a small quantity of solid iodine. The deep colour of

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the iodine disappears entirely. This is due to the formation of the colourless salts, iodide of potassium (KI) and iodate of potassium (KIO_3), which remain dissolved in the liquid. Continue the addition of iodine so long as its colour disappears; when this point is reached, the whole of the potash in the solution of potash has been converted into the salts mentioned.

$$\underset{\text{Hydrate of potassium.}}{6KHO} + \underset{\text{Iodine.}}{3I_2} = \underset{\text{Iodide of potassium.}}{5KI} + \underset{\text{Iodate of potassium.}}{KIO_3} + \underset{\text{Water.}}{3H_2O}$$

Evaporate the solution to dryness. If both salts were required, the solid mixture might be digested in spirit of wine, which dissolves the iodide, but not the iodate. But the iodide only is used in medicine. Mix the residue, therefore, with a few grains of charcoal, and gently heat in a test-tube until deflagration ensues*.

$$\underset{\text{Iodate of potassium.}}{KIO_3} + \underset{\text{Carbon.}}{C_3} = \underset{\text{Iodide of potassium.}}{KI} + \underset{\text{Carbonic oxide.}}{3CO}$$

Under these circumstances the iodide remains unaffected, but the iodate loses all its oxygen, and is thus also reduced to the state of iodide. Treat the mass with a little water, and filter to separate excess of charcoal; a solution of pure iodide of potassium results.

This is the process mentioned in the British Pharmacopœia (*Potassii Iodidum*). Solution of iodate of potassium is also officinal as a test-liquid.

On the large scale, crystals of the iodide are obtained by evaporating much of the water, and setting aside the strong solution; when cold, crystals will deposit if the liquid has been concentrated to the right degree.

The addition of charcoal in the above process is simply to

* Deflagration means violent burning, from *flagratus*, burnt (*flagro*, I burn), and *de*, a prefix augmenting the sense of the word to which it may be attached. Paper thrown into a fire simply burns, nitre deflagrates. *Detonate* is a precisely similar word, meaning to explode with violent noise.

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facilitate the removal of the oxygen of the iodate of potassium. Iodate of potassium (KIO_3) is analogous in constitution, and in composition, so far as the atoms of oxygen are concerned, to chlorate of potassium ($KClO_3$), which has already been stated to be more useful than any other salt for the actual preparation of oxygen gas itself. Hence the removal of the oxygen of the iodate might be accomplished by heating the residue without charcoal. In that case the student would detect the liberated oxygen by inserting the incandescent extremity of a strip of wood into the mouth of the test-tube in which the mixture of iodide and iodate had been heated. The charcoal, however, burns out the oxygen more quickly, and thus economizes heat.

Iodate of potassium remaining as an impurity in iodide of potassium may be detected by adding to a solution some tartaric acid, shaking, and then adding mucilage of starch; blue "iodide of starch" is formed if a trace of iodate be present, but not otherwise. The tartaric acid liberates iodic acid (HIO_3) and hydriodic acid (HI), and these reacting give free iodine, which combines with the starch.

$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

Note on Nomenclature.—The syllable *ide* attached to the syllable *iod* in the name "iodide of potassium," indicates that the element *iodine* is combined with the potassium. An iod*ate*, as already explained, is a salt containing the characteristic elements of iod*ic* acid. Salts, one of whose names end in *ide*, are those which are, or may be, formed from elements. The names of salts which are, or may be, formed from acids include other syllables, *ate* being one (see page 32). The only other syllable is *ite*, which is included in the names of salts which are, or may be, formed from acids whose names end in *ous*: thus hyposulph*ite* of sodium, &c. To recapitulate, sulph*ide* relates to sulphur, sulph*ite* to sulphurous acid, sulph*ate* to sulphuric acid, and so with all other "ides," "ites," or "ates."

Chlorate of Potassium (*Potassæ Chloras*, B. P.) is made by a method similar to that just described for iodide and iodate of potassium, but differing in detail, as will be shown hereafter in connexion with chloric acid. The action of heat upon it gives first perchlorate of potassium ($2KClO_3 = KClO_4 + O_2 + KCl$), and then chloride of potassium ($KClO_4 = KCl + O_4$).

Bromide of Potassium (*Potassii Bromidum*, B. P.). This salt is identical in constitution with iodide of potassium, and is made in exactly the same way, bromine being substituted for iodine. All

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that has been said of iodide and iodate of potassium is applicable to bromide and bromate of potassium (KBr and $KBrO_3$).

$$\underset{\text{Hydrate of potassium.}}{6KHO} + \underset{\text{Bromine}}{3Br_2} = \underset{\text{Bromide of potassium.}}{5KBr} + \underset{\text{Bromate of potassium.}}{KBrO_3} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\text{Bromate of potassium.}}{KBrO_3} + \underset{\text{Carbon.}}{C_3} = \underset{\text{Bromide of potassium.}}{KBr} + \underset{\text{Carbonic oxide.}}{3CO}$$

Eighth Synthetical Reaction.—Place a fragment of solid caustic potash (KHO), with about the same quantity of chlorate of potassium ($KClO_3$), and of black oxide of manganese (MnO_2), on a piece of platinum foil. Hold the foil, by a small pair of forceps or tongs, in the flame of a blowpipe for a few minutes until the fused mixture has become dark green. This colour is that of manganate of potassium (K_2MnO_4).

Permanganate of Potassium ($K_2Mn_2O_8$) (*Potassæ Permanganas*, B. P.), which is purple, is obtained, or rather a solution of it, on placing the foil and its adherent mass in water, and boiling for a short time.

$$\underset{\text{Hydrate of potassium.}}{6KHO} + \underset{\text{Chlorate of potassium.}}{KClO_3} + \underset{\text{Black oxide of manganese.}}{3MnO_2} = \underset{\text{Manganate of potassium.}}{3K_2MnO_4} + \underset{\text{Chloride of potassium.}}{KCl} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\text{Manganate of potassium.}}{3K_2MnO_4} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Permanganate of potassium.}}{K_2Mn_2O_8} + \underset{\text{Hydrate of potassium.}}{4KHO} + \underset{\text{Black oxide of manganese.}}{MnO_2}$$

On the large scale, the potash set free in the reaction is neutralized by sulphuric or carbonic acid, and the solution evaporated to the crystallizing point.

Solutions of manganate or permanganate of potassium so readily yield their oxygen to organic matter, that they are used on the large scale as disinfectants, under the name of "Condy's Disinfecting Fluids."

Synthetical Reactions bringing under consideration the remaining officinal compounds (namely, bichromate, arsenite, cyanide, ferrocyanide, and ferridcyanide of potassium) are deferred at present.

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(*b*) *Reactions having Analytical Interest.*

Note.—These are reactions utilized in searching for small quantities of potassium in a solution.

First Analytical Reaction.—To a solution of any salt of potassium (chloride*, for example) add solution of perchloride of platinum ($PtCl_4$), and stir the mixture with a glass rod; a yellow precipitate of the double chloride of platinum and potassium ($PtCl_4 2KCl$) will be precipitated.

This salt is, practically, insoluble in water. It is for this reason that a very small quantity of any soluble potassium salt (or, rather, of the potassium in that salt) is thrown out of solution by perchloride of platinum.

Experiments with such expensive reagents as perchloride of platinum are economically performed in watch-glasses, drops of the liquids being operated on. When the precipitate is long in forming, it is sometimes of an orange-yellow colour. If iodide of potassium happen to be the potassium salt under examination, some iodide of platinum (PtI_4) will also be formed, giving a red colour to the solution.

It is the chloride of potassium only that forms this characteristic precipitate; hence, if the potassium salt in the solution is known not to be a chloride, or if its composition is unknown, a few drops of hydrochloric acid must be added, otherwise some of the perchloride of platinum will be utilized for its chlorine only, the platinum being wasted. Thus, if nitrate of potassium (KNO_3) be present, a few drops of hydrochloric acid enable the potassium to assume the form of chloride when the perchloride of platinum is added, nitric acid (HNO_3) being set free.

Second Analytical Reaction.—To a solution of any salt of potassium add some strong solution of tartaric acid ($H_2C_4H_4O_6$), and shake or well stir the mixture; a white granular precipitate of acid tartrate of potassium ($KHC_4H_4O_6$) will be formed.

* A few fragments of carbonate of potassium, two or three drops of hydrochloric acid, and a small quantity of water, give a solution of chloride of potassium at once, $K_2CO_3+2HCl=2KCl+H_2O+CO_2$.

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Acid tartrate of potassium is soluble in about 180 parts of cold and in 6 parts of boiling water. Hence, in applying the tartaric test for potassium, the solutions must not be hot. Even if cold, no precipitate will be obtained if the solutions are very dilute. This test, therefore, is of far less value than the first mentioned. The acid tartrate of potassium is less soluble in diluted alcohol than in water; so that the addition of spirit of wine renders the reaction somewhat more delicate.

This precipitate is the *Potassæ Tartras Acida* of the British Pharmacopœia, though the officinal preparation is not formed in the above manner; on the contrary, the acid is derived from the salt, which occurs naturally in the juice of many plants. Our supplies of the salt are from the crusts that form in wine-casks (argal, or crude cream of tartar), deposited because less soluble in the diluted alcohol of the fermented liquid than in the unfermented juice.

When the tartaric acid is added to the salt of potassium, and the acid tartrate formed, the acid whose chief elements were previously with the potassium is set free; and in such acid solutions the acid tartrate is somewhat soluble. To obviate this, acid tartrate of sodium, which is a much more soluble salt than the acid tartrate of potassium, may be used as a test instead of tartaric acid (Plunkett). The sodium uniting with the acidulous radical, thus gives a neutral instead of an acid solution. But this advantage is of less importance from the fact that more water is introduced by the saturated solution of acid tartrate of sodium than by a saturated solution of tartaric acid.

Third Analytical Reaction.—The *flame*-test. Dip the looped end of a platinum wire into a solution containing a potassium salt, and introduce the loop into a spirit-flame, the flame of a mixture of gas and air, a blowpipe flame, or other slightly coloured flame. A violet tint will be produced highly characteristic of salts of potassium.

Fourth Analytical Fact.—Salts of potassium are not volatile. Place a fragment of carbonate, nitrate, or any other potassium salt, on a piece of platinum foil, and heat the latter in the flame of a lamp; the salt will fuse to a transparent liquid, and flow freely over the foil, but otherwise will be unaffected by the heat. This is a valuable negative property, as will be evident further on.

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SODIUM.

Symbol Na. Atomic weight 23.

Memoranda.—Most of the sodium salts met with in Pharmacy are directly obtained from carbonate of sodium, which is now manufactured on an enormous scale from chloride of sodium (common salt, sea-salt, or rock-salt), the natural source of the sodium salts. Besides the direct and indirect use of carbonate of sodium, or carbonate of soda, as it is commonly called, in medicine, it is largely used for household cleansing-purposes, and in the manufacture of soap. Nitrate of sodium also occurs in nature, but it is valuable for its nitric constituents rather than for its sodium.

Sodium is prepared by a process similar to that for potassium, but with less difficulty.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Reactions having Synthetical Interest.*

First Synthetical Reaction.—The formation of solution of hydrate of sodium or caustic soda, NaHO (*Liquor Sodæ*, B. P.). This operation resembles that of making solution of potash, as described on page 28.

The student should refer to the remarks already made concerning solution of potash, applying them to solution of soda. He may perform the corresponding experiments or omit them, as he considers he does or does not clearly comprehend all they are designed to teach.

Na_2CO_3	+	Ca2HO	=	2NaHO	+	$CaCO_3$
Carbonate of sodium.		Hydrate of calcium.		Hydrate of sodium.		Carbonate of calcium.

Second Synthetical Reaction.—The reaction of sulphur and carbonate of sodium at a high temperature resembles that of sulphur and carbonate of potassium; but as the product is not used in medicine, nor otherwise interesting, the experiment may be omitted.

Third Synthetical Reaction.—Add the powder or fragments of carbonate of sodium (Na_2CO_3) to some strong acetic acid in a test-

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tube as long as effervescence occurs, and then evaporate a little of the water. When the solution is cold, crystals of acetate of sodium ($NaC_2H_3O_2$) (*Sodæ Acetas*, B. P.), will be deposited.

$$\underset{\text{Carbonate of sodium.}}{Na_2CO_3} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} = \underset{\text{Acetate of sodium.}}{2NaC_2H_3O_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

The salt contains water in a loose state of combination, water of crystallization ($NaC_2H_3O_2$, $3H_2O$).

Fourth Synthetical Reaction.—The action of carbonic acid (H_2CO_3), or carbonic acid gas (CO_2) and water (H_2O), on carbonate of sodium (Na_2CO_3). This resembles that of carbonic acid on carbonate of potassium, and is carried out in the same manner. The result is acid carbonate of sodium ($NaHCO_3$) (*Sodæ Bicarbonas*, B. P.).

$$\underset{\text{Carbonate of sodium.}}{Na_2CO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2} = \underset{\text{Acid carbonate of sodium.}}{2NaHCO_3}$$

A *crystal* of carbonate of sodium is carbonate of sodium plus water; on heating it, more or less of the water is evolved, and anhydrous carbonate of sodium is partially or wholly produced (*Sodæ Carbonas Exsiccata*, B. P.).

$$\underset{\text{Crystallized carbonate of sodium.}}{Na_2CO_3,10H_2O} - \underset{\text{Water.}}{10H_2O} = \underset{\text{Dried carbonate of sodium.}}{Na_2CO_3}$$

The water in crystallized carbonate of sodium is in the solid condition. By far the larger number of crystalline salts possess such *water of crystallization*, so termed. Many of these salts, when dissolved in water, give a very cold solution. This is because some of their solid water is then converted into liquid water, the difference between the solid and liquid water being heat. Take away from water some of its heat, the result is ice. Give to ice more heat than it contains already, the result is water. The only difference between ice and the water in such crystals as carbonate of sodium, is that ice is solid water in the free, and water of crystallization solid water in the combined state. The former can only exist at freezing, the latter at ordinary temperatures. In chemical formulæ, the symbols representing water are usually separated by a comma from those representing salts.

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A solution of acid carbonate of sodium in water charged with carbonic acid gas under pressure constitutes the ordinary "soda-water" (the *Liquor Sodæ Effervescens*, B. P.).

Acid carbonate of sodium may also be medicinally administered in the form of lozenge (*Trochisci Sodæ Bicarbonatis*, B. P.).

Fifth Synthetical Reaction.—To some hot strong solution of carbonate of sodium in a test-tube add acid tartrate of potassium till no more effervescence occurs; when the solution is cold, crystals of double tartrate of potassium and sodium (*Soda Tartarata*, B. P.), the old *Rochelle Salt*, will be found in the solution.

$$Na_2CO_3 + 2KHC_4H_4O_6 = 2KNaC_4H_4O_6 + H_2O + CO_2$$

Carbonate of sodium. | Acid tartrate of potassium. | Double tartrate of potassium and sodium. | Water. | Carbonic acid gas.

Tartaric acid ..... HH $C_4H_4O_6$
Acid tartrate of potassium..... KH $C_4H_4O_6$
Tartrate of potassium and sodium.. KNa $C_4H_4O_6$

The student will notice the analogy in the constitution of these salts. When the other tartrates come under notice it will be found they also have a similar constitution. The crystals of the above double tartrate contain water ($KNaC_4H_4O_6$, $4H_2O$).

Sixth Synthetical Reaction.—Pass chlorine (*vide* page 12) into a solution of carbonate of sodium. The result is a bleaching and disinfecting liquid, which, when made of prescribed strength, is the Solution of Chlorinated Soda (*Liquor Sodæ Chlorinatæ*) of the Pharmacopœia. It is said to contain chloride of sodium (NaCl) and hypochlorite of sodium (NaClO), with some undecomposed acid carbonate of sodium.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

Blk. oxide of manganese. | Hydrochloric acid. | Chloride of manganese. | Water. | Chlorine.

$$Na_2CO_3 + Cl_2 = NaCl, NaClO + CO_2$$

Carbonate of sodium. | Chlorine. | Chlorinated soda. | Carbonic acid gas.

The student may perform a bleaching experiment with this liquid similar to that described under chlorine (p. 13).

Synthetical Reactions portraying the chemistry of the remain-

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ing officinal compounds (namely, nitrate, sulphate, hyposulphite, phosphate, arseniate and valerianate of sodium) are deferred. The officinal citro-tartrate (*Sodæ Citro-tartras Effervescens*) is a mixture of bicarbonate of sodium, citric acid, and tartaric acid, heated until the particles aggregate to a granular condition. When required for medicinal use, a dose of the mixture is placed in water; escape of carbonic acid gas at once occurs, and an effervescing liquid results. In the manufacture of carbonate of sodium from chloride, the latter is first converted into sulphate, the sulphate is then roasted with coal and limestone, and the resulting *black-ash* lixiviated (*lixivia*, from *lix*, lye—water impregnated with alkaline salts). The lye evaporated to dryness, yields crude carbonate of sodium (soda-ash). This process will be further described in connexion with Carbonates.

Other Synthetical Reactions might be described similar to those given under potassium, and thus citrate, iodide, bromide, iodate, bromate, chlorate, manganate, and permanganate of sodium, and many other salts be formed. But enough has been stated to show how chemically analogous sodium is to potassium. Such analogies will constantly present themselves. In few departments of knowledge is order and method more perceptible; in few is there as much natural law, as much *science*, as in chemistry.

It will probably occur to the student, if he has really grasped the facts concerning potassium and sodium, that sodium salts being cheaper than potassium salts, the former might be economically substituted. That one is employed rather than the other, is unquestionably often merely a result due to accident or fashion. But it must be borne in mind that in some cases a potassium salt will crystallize more readily than its sodium analogue, or that a sodium salt is stable when perhaps the corresponding potassium salt has a tendency to absorb moisture, or one may be more soluble than the other, or the two may have different medicinal effects. For these or similar reasons, a potassium salt has come to be used in medicine or commerce, instead of the corresponding sodium salt, and *vice versâ*.

(*b*) *Reactions having Analytical Interest.*

1. *The chief analytical reaction* for sodium is *the flame-test.* When brought into contact with a flame in the manner described under potassium (page 38), an intensely yellow colour is communicated to the flame by any salt of sodium. This is a highly

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characteristic test—indeed, almost too delicate; for if the point of the wire be touched by the fingers, enough salt (which is contained in the moisture of the hand) adheres to the wire to communicate a distinct sodium reaction to the flame. The student should experimentally verify these statements, using chloride, sulphate, or any other salt of sodium.

2. Sodium is the only metal whose common salts are all soluble in water. Hence no ordinary reagent can be added to a solution containing a sodium salt which shall give a precipitate containing the sodium. A neutral or alkaline solution of a sodium salt gives, however, a granular precipitate if well stirred or shaken with a solution of *antimoniate of potassium* ($K_2H_2Sb_2O_7$). But the reagent is liable to decompose and become useless.

Antimoniate of potassium is made by adding, gradually, finely-powdered metallic antimony to nitrate of potassium fused in a crucible so long as deflagration continues. The resulting mass is boiled with a large quantity of water, the solution filtered and preserved in a well-stoppered bottle; for the carbonic gas in the air is rapidly absorbed by the solution, antimonic acid being deposited.

3. Sodium salts, like those of potassium, are not volatile. Prove this fact by the means described when treating of the effect of heat on potassium salts (p. 38).

AMMONIUM.

Symbol NH_4 or Am. Atomic weight 18.

Memoranda.—The elements nitrogen and hydrogen, in the proportion of one atom to four (NH_4), are those characteristic of all the compounds about to be studied, just as potassium (K) and sodium (Na) are the characteristic elements of the potassium and sodium compounds. Ammonium is a nucleus, like potassium or sodium, and the ammonium compounds closely resemble those of potassium or sodium. In short, if, for an instant, potassium or sodium be imagined to be compounds, the analogy between these three series of salts is complete. Yet ammonium never having been isolated, its existence remains a matter of assumption.

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The source of nearly all the ammoniacal salts met with in commerce is ammoniacal gas (NH_3) obtained in distilling coals in the manufacture of ordinary illuminating gas. It is doubtless derived from the nitrogen of the plants from which the coal has been produced.

When this gas (NH_3) comes into contact with water (H_2O) hydrate of ammonium (NH_4HO, or AmHO) is believed to be formed, the analogue of hydrate of potassium (KHO) or sodium (NaHO). The grounds for this belief are,—that the solution does not always give the same reaction as the gas itself, the observed analogy of the well-known ammoniacal salts to those of potassium and sodium, the similarity of action of solutions of potash, soda, and ammonia on salts of metals, and the existence of crystals of an analogous sulphur salt (AmHS).

The "ammoniacal liquor" of the gas-works is usually neutralized by hydrochloric acid, by which chloride of ammonium (sal-ammoniac) is produced,

$$AmHO + HCl = AmCl + H_2O;$$

and from this salt the others used in pharmacy are directly or indirectly made.

The purest form of ammonia is that met with in volcanic districts, and obtained as a by-product in the manufacture of borax.

Reactions having (*a*) General, (*b*) Synthetical, and (*c*) Analytical Interest.

(*a*) *General Reaction.*—To forty or fifty grains of mercury in a test-tube, add one or two small pieces of dry sodium, and amalgamate by gently warming the tube. To this amalgam, when cold, add some fragments of chloride of ammonium and a strong solution of the same salt. The sodium amalgam soon begins to swell and rapidly increase in bulk, probably overflowing the tube. The light spongy mass produced is the so-called ammonium amalgam, and the reaction is usually adduced as evidence of the existence of ammonium; the sodium of the amalgam unites with the chlorine of the chloride of ammonium, while the ammonium is supposed to form an amalgam with the mercury.

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(*b*) *Reactions having Synthetical interest.*

First Synthetical Reaction.—The action of slaked lime (Ca2HO) on chloride of ammonium. This operation, and the solution of the resulting gas in water, has already been described (p. 23).

$2NH_4Cl$	+	$Ca2HO$	=	$CaCl_2$	+	$2H_2O$	+	$2NH_3$
Chloride of ammonium.		Hydrate of calcium.		Chloride of calcium.		Water.		Ammonia gas.

NH_3	+	H_2O	=	NH_4HO or AmHO
Ammonia gas.		Water.		Hydrate of ammonium (ammonia).

Solutions of ammonia, prepared by this process on a large scale and in suitable apparatus, are met with in pharmacy—the one containing 32·5 per cent., the other 10 per cent. by weight of ammonia gas, NH_3, or 66·9 and 20·6 of ammonia, AmHO (*Liquor Ammoniæ Fortior* and *Liquor Ammoniæ*, B. P.).

Second Synthetical Reaction.—To acetic acid and water in a test-tube add powdered commercial carbonate of ammonium until effervescence ceases; the resulting liquid is Solution of Acetate of Ammonium ($NH_4C_2H_3O_2$, or $Am\bar{A}$) (*Liquor Ammoniæ Acetatis*, B. P.).

$AmHCO_3$	+	Am_2CO_3	+	$3H\bar{A}$	=	$3Am\bar{A}$	+	$2H_2O$	+	$2CO_2$
Acid carbonate of ammonium.		Normal carbonate of ammonium.		Acetic acid.		Acetate of ammonium.		Water.		Carbonic acid.

Commercial carbonate of ammonium is made by heating a mixture of chalk and sal-ammoniac; chloride of calcium ($CaCl_2$) is produced, ammonia gas (NH_3) and water (H_2O) escape, and the ammoniacal carbonate sublimes in cakes (*Ammoniæ Carbonas*, B. P.). The salt is probably a mixture of two molecules of acid carbonate of ammonium ($2AmHCO_3$) and one of a salt termed carbamate of ammonium ($AmNH_2CO_2$). The latter belongs to an important class of salts known as carbamates, but is the only one of interest to the pharmaceutical student. Cold water extracts it from the commercial carbonate of ammonium, leaving the acid carbonate of ammonium undissolved if the amount of liquid used be very small. In water it soon changes into neutral carbonate of ammonium,

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$$NH_4NH_2CO_2 + H_2O = CO_32NH_4 \text{ or } Am_2CO_3;$$

so that an aqueous solution of commercial carbonate of ammonium contains both acid carbonate and neutral carbonate of ammonium. If to such a solution some ordinary solution of ammonia be added, a solution of neutral carbonate of ammonium is obtained; and this is the common reagent always found on the shelves of the analytical laboratory.

$$AmHCO_3 + AmHO = Am_2CO_3 + H_2O.$$

Neutral carbonate of ammonium is the salt formed on adding strong solution of ammonia to the commercial carbonate in preparing a pungent mixture for toilet smelling-bottles; but it is unstable, and on continued exposure to air is reduced to a mass of crystals of the acid carbonate.

Sal Volatile (*Spiritus Ammoniæ Aromaticus*, B. P.) is a spirituous solution of ammonia (AmHO), neutral carbonate of ammonium, (Am_2CO_3) and the oils of nutmeg and lemon. Fetid spirit of ammonia (*Spiritus Ammoniæ Fœtidus*, B. P.) is an alcoholic solution of the volatile oil of assafœtida mixed with solution of ammonia.

Third Synthetical Reaction.—To solution of citric acid ($H_3C_6H_5O_7$ or $H_3\overline{Ci}$) add solution of ammonia (AmHO) until the liquid is neutral to test-paper; the product is Solution of Citrate of Ammonium ($Am_3\overline{Ci}$) (*Liquor Ammoniæ Citratis*, B. P.).

Phosphate of Ammonium (Am_2HPO_4) (*Ammoniæ Phosphas*, B. P.), and Benzoate of Ammonium ($AmC_7H_5O_2$) (*Ammoniæ Benzoas*, B. P.), are also made by adding solution of ammonia to phosphoric acid (H_3PO_4) and benzoic acid ($HC_7H_5O_2$) respectively.

$H_3C_6H_5O_7$	+	$3AmHO$	=	$Am_3C_6H_5O_7$	+	$3H_2O$
Citric acid.		Ammonia.		Citrate of ammonium.		Water.
H_3PO_4	+	$2AmHO$	=	Am_2HPO_4	+	$2H_2O$
Phosphoric acid.		Ammonia.		Phosphate of ammonium.		Water.
$HC_7H_5O_2$	+	$AmHO$	=	$AmC_7H_5O_2$	+	H_2O
Benzoic acid.		Ammonia.		Benzoate of ammonium.		Water.

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Fourth Synthetical Reaction.—Pass sulphuretted hydrogen gas (H_2S) through a small quantity of solution of ammonia in a test-tube, until a portion of the liquid no longer causes a white precipitate in solution of sulphate of magnesium (Epsom salt); the product is solution of sulphydrate of ammonium, AmHS (*Sulphide of Ammonium*, B. P.), a most valuable chemical reagent, as will presently be apparent.

$$AmHO + H_2S = AmHS + H_2O.$$

Crystals of sulphydrate of ammonium (AmHS) may be obtained on bringing ammonia gas (NH_3) and sulphuretted hydrogen (H_2S) together at a low temperature. They are soluble in water without decomposition.

Sulphuretted hydrogen is a compound of noxious odour; hence the above operation, and many others, described further on, in which this gas is indispensable, can only be performed in the open air, or in a cupboard so contrived that deleterious gases and vapours shall escape into a chimney in connexion with the external air. In the above experiment, the small quantity of gas required can be made in a test-tube, after the manner of hydrogen itself. To two or three fragments of sulphide of iron (FeS), add water and then sulphuric acid; the gas is at once evolved, and may be conducted by a tube into the solution of ammonia.

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

The iron remains dissolved in the water in the state of sulphate of iron.

As no heat is necessary in this operation, the test-tube may be advantageously replaced by a bottle, especially when larger quantities of the gas are required. In analytical operations, the gas should be purified by passing it through water contained in a second bottle.

Sulphuretted-hydrogen Apparatus.—The most convenient arrangement for general use is prepared as follows:—Two common wide-mouth bottles are selected, the one having a capacity of about half a pint, the other a quarter pint; the former may be called the generating-bottle, the latter the wash-bottle. Fit two

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corks to the bottles. Through each cork bore two holes by a round file or other instrument, of such a size that glass tubing of about the diameter of a quill pen shall fit them tightly. Through one of the holes in the cork of the generating-bottle pass a funnel-tube, so that its extremity may nearly reach the bottom of the bottle. Such "funnel-tubes" may be purchased at the usual shops; or, if the student has access to a table-blowpipe, and the advantage of a tutor to direct his operations, they may be made by himself. To the other hole adapt a piece of tubing, 6 inches long, and bent in the middle to a right angle. A similar "elbow-tube" is fitted to one of the holes in the cork of the wash-bottle, and another elbow-tube, one arm of which is long enough to reach to near the bottom of the wash-bottle, fitted to the other hole. Removing the corks, two to three ounces of water are now poured into each bottle, an ounce or two of sulphide of iron put into the generating-bottle, and the corks replaced. The elbow-tube of the generating-bottle is now attached by a short piece of india-rubber tubing to the long-armed elbow-tube of the wash-bottle, so that gas coming from the generator may pass through the water in the wash-bottle. The delivery-tube of the wash-bottle is then lengthened by attaching to it, by india-rubber tubing, a straight piece of glass tubing, three or four inches long. The apparatus is now ready for use. Strong sulphuric acid is poured down the funnel-tube in small quantities at a time, until brisk effervescence is established, and more added from time to time as the evolution of gas becomes slow. The gas passes through the tubes into the wash-bottle, where, as it bubbles up through the water, any trace of sulphuric acid, or other matter mechanically carried over, is arrested, and thence flows out at the delivery-tube into any vessel or liquid that may be placed there to receive it. The generator must be occasionally dismounted, and the sulphate of iron washed out.

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(*c*) *Reactions having Analytical Interest.*

First Analytical Reaction.—To a solution of any salt of ammonium (the chloride, for example) add solution of caustic soda (or solution of potash, or a little slaked lime); ammonia gas is at once evolved, recognized by its well-known odour.

$$NH_4Cl + NaHO = NH_3 + H_2O + NaCl.$$

Though ammonium itself cannot exist in the free state, its compounds are stable. Ammonia is easily expelled from those compounds by action of the stronger alkalies, caustic potash, soda, or lime. As a matter of exercise, the student should here draw out equations in which acetate ($Am\bar{A}$), sulphate (Am_2SO_4), nitrate ($AmNO_3$), or any other ammoniacal salt not already having the odour of ammonia, is supposed to be under examination; also equations representing the use of the other hydrates, potash ($\bar{K}HO$) or slaked lime (Ca2HO).

The odour of ammonia gas is perhaps the best means of recognizing its presence; but the following tests are occasionally useful. Into the test-tube in which the ammonia gas is evolved insert a glass rod moistened with hydrochloric acid (that is, with the solution of hydrochloric acid gas, conventionally termed hydrochloric acid, the *Acidum Hydrochloricum* of the Pharmacopœia); white fumes of chloride of ammonium will be produced.

$$NH_3 + HCl = NH_4Cl.$$

Hold a piece of moistened red litmus paper in a tube in which ammonia gas is present; the red colour will be changed to blue.

Litmus is a blue vegetable pigment, exceedingly sensitive to the action of acids, which turn it red. When thus reddened, alkalies (potash, soda, and ammonia) and other soluble hydrates readily turn it blue. The student should here test for himself the delicacy of this action by experiments with paper soaked in solution of litmus and dipped into very dilute solutions of acid, alkalies, and such neutral salts as nitrate of potassium, sulphate of sodium, chloride of ammonium, &c.

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Second Analytical Reaction.—To a few drops of a solution of an ammonium salt add a drop or two of hydrochloric acid and a like small quantity of solution of perchloride of platinum ($PtCl_4$); a yellow crystalline precipitate of the double chloride of platinum and ammonium ($PtCl_4 2AmCl$) will be produced, similar in appearance to the corresponding salt of potassium, the remarks concerning which (p. 37) are equally applicable to the precipitate under notice.

Third Analytical Reaction.—To a moderately strong solution of an ammonium salt add a strong solution of tartaric acid, and shake or well stir the mixture; a white granular precipitate of acid tartrate of ammonium will be formed.

For data from which to draw out an equation representing this action, see the remarks and formulæ under the analogous salt of potassium (p. 37).

Fourth Analytical Fact.—Evaporate a few drops of a solution of an ammonium salt to dryness, or place a fragment of a salt in the solid state on a piece of platinum-foil, and heat the latter in a flame; the salt is readily *volatilized*. As already noticed, the salts of potassium and sodium are *fixed* under these circumstances.

The student may now briefly review the operations he has performed. He should be able, without the aid of the book, to state how the various officinal preparations of potassium, sodium, and ammonium may be made, and to write down equations descriptive of the reactions which take place in the production of those preparations. These equations should be submitted to a tutor or other authority for correction.

With regard to those experiments which are useful rather as means of detecting the presence of potassium, sodium, and ammonium, than as illustrating the preparation of salts, the student should proceed to apply them to certain solutions * of any

* Such solutions are prepared in educational laboratories by a tutor. They should, under other circumstances, be mixed by a friend, as it is not

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of the salts of potassium, sodium, and ammonium with the view of ascertaining which metal is present; that is, proceed to practical analysis. A little thought will enable him to apply these reactions in the most suitable order and to the best advantage for the contemplated purpose; but the following is perhaps as good an arrangement as can be devised.

APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A SALT OF ONE ONLY OF THE METALS, POTASSIUM, SODIUM, AMMONIUM.

Heat a portion with caustic soda; the odour of ammonia gas at once reveals the presence of an ammonium salt.

If ammonium is not present, apply the perchloride-of-platinum test; a yellow precipitate proves the presence of a potassium salt.

(It will be observed that potassium can only be detected in the absence of ammonium.)

The flame-test is sufficient for the recognition of the presence of a sodium salt.

APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE, TWO, OR ALL THREE OF THE ALKALI METALS.

Commence by testing a small portion of the solution for an ammonium salt. If present, make a memorandum to that effect, and then proceed to get rid of the ammoniacal compound to make way for the detection of potassium. Evaporate the original solution to dryness in a small basin, transfer the solid residue to a porcelain crucible, and heat the latter to low redness, or until no more fumes escape. This operation should be

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desirable to know previously what is contained in the substance about to be analyzed.

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conducted in a fume-cupboard, to avoid contamination with the air of the apartment. When the crucible is cold, dissolve out the solid residue with a small quantity of water, and test the solution for potassium by the perchloride-of-platinum test, and for sodium by the flame-test.

If ammonium is proved to be absent, the original solution may, of course, be at once tested for potassium and sodium.

The violet tint imparted to flame by potassium salts may be seen when masked by the intense yellow colour due to sodium if the flame be observed through a piece of dark-blue glass, a medium which absorbs the yellow rays of light.

Note on the Classification of Elements.—The compounds of potassium, sodium, and ammonium have many analogies. Their carbonates, phosphates, and most other salts are soluble in water. The atoms of the radicals themselves are univalent, that is, replace or are replaced by one atom of hydrogen. In fact they constitute by their similarity in properties a distinct group or family. All the elements thus naturally fall into classes—a fact the student should constantly bear in mind, and evidence of which he should always seek. It would be impossible for the memory to retain the details of chemistry without a system of classification and leading principles. Classification is also an important feature in the art as well as in the science of chemistry; for without it practical analysis would be impossible.

BARIUM, CALCIUM, MAGNESIUM.

These three elements have many analogies. Their atoms are bivalent.

BARIUM.

Symbol Ba. Atomic weight 137.

The analytical reactions only of this metal are of interest to the general student of pharmacy. The chloride ($BaCl_2$) (Chloride of Barium, B.P.) and nitrate ($Ba2NO_3$) are the soluble salts in common use in analysis; and these and others are made by dis-

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solving the native carbonate ($BaCO_3$), the mineral *witherite*, in acids, or by heating the other common natural compound of barium, the sulphate or *heavy spar* ($BaSO_4$), with coal—

$$BaSO_4 + C_4 = 4CO + BaS,$$

and dissolving the resulting sulphide in acids. When the nitrate is strongly heated it is decomposed, the oxide of barium or *baryta* (BaO) remaining. The latter is tolerably soluble, yielding *baryta-water;* and from this solution crystals of hydrate of barium (Ba2HO) are obtained on evaporation.

The operations above described may all be performed in test-tubes and small porcelain crucibles, heated by the gas-flame, if they have special interest for any student.

Reactions having Analytical Interest.

First Analytical Reaction.—To the solution of any soluble salt of barium (nitrate or chloride, for example) add dilute sulphuric acid; a white precipitate is obtained. Set the test-tube aside for two or three minutes, and when some of the precipitate has fallen to the bottom pour away most of the supernatant liquid, add strong nitric acid, and boil; the precipitate is insoluble.

The production of a white precipitate by sulphuric acid, insoluble even in hot nitric acid, is highly characteristic of barium.

In cases of poisoning by soluble barium salts, sulphates of magnesium, sodium, &c. (Epsom salt, Glauber's salt, alum) would be obvious antidotes.

Second Analytical Reaction.—To a barium solution add solution of the yellow chromate of potassium (K_2CrO_4); a pale yellow precipitate ($BaCrO_4$) falls. Add acetic acid to a portion of the chromate of barium; it is insoluble. Add hydrochloric or nitric acid to another portion; it is soluble.

Other Analytical Reactions.—To a barium solution add a soluble carbonate (carbonate of ammonium (Am_2CO_3) will generally be rather more useful than others); a white precipitate of carbonate of barium ($BaCO_3$) results.——To more of the solution

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add an alkaline phosphate or arseniate (phosphate of sodium (Na_2HPO_4) is the most common of these chemically analogous salts, but arseniate of ammonium (Am_2H,AsO_4) will subsequently have the preference); white phosphate of barium ($BaHPO_4$), insoluble in pure water, but soluble in aqueous solutions of salts, or arseniate of barium ($BaHAsO_4$), both soluble even in acetic and other weak acids, are precipitated.——To another portion add oxalate of ammonium ($Am_2C_2O_4$); white oxalate of barium (BaC_2O_4) is precipitated, soluble in the strong acids, and sparingly so in acetic acid.——The silico-fluoride of barium ($BaSiF_6$) is insoluble, and falls readily if an equal volume of spirit of wine be added to the solution under examination after the addition of hydrofluosilicic acid (H_2SiF_6).——Barium salts, moistened with hydrochloric acid, impart a greenish colour to flame.

Write out equations descriptive of each of the foregoing reactions.

CALCIUM.

Symbol Ca. Atomic weight 40.

Calcium compounds form a large proportion of the crust of our earth. Carbonate of calcium is met with as chalk, marble, limestone, calc-spar, &c., the sulphate as gypsum or plaster of paris, alabaster, &c., the silicate in many minerals, the fluoride of calcium as fluor-spar. The phosphate is also a common mineral. The element itself is only isolated with great difficulty.

Reactions having Synthetical Interest.

First Synthetical Reaction.—To some hydrochloric acid add carbonate of calcium (chalk or, the purer form, white marble, *Marmor Album*, B. P.) ($CaCO_3$) until effervescence ceases, filter; solution of chloride of calcium ($CaCl_2$) (*Calcii Chloridum*, B. P.), the most common soluble salt of calcium, is formed.

$CaCO_3$	+	$2HCl$	=	$CaCl_2$	+	H_2O	+	CO_2
Carbonate of calcium.		Hydrochloric acid.		Chloride of calcium.		Water.		Carbonic acid gas.

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Solution of chloride of calcium evaporated to a syrupy consistence readily yields crystals. These are too deliquescent (that is, absorbent of moisture, from *deliquescens*, melting away) to be useful. Evaporated to dryness, and the residue strongly heated, solid anhydrous chloride of calcium is obtained in a porous form, much used for drying gases, and for freeing certain liquids from water.

Marble often contains ferrous carbonate ($FeCO_3$), which in the above process becomes converted into ferrous chloride, rendering the chloride of calcium impure:—

$FeCO_3$	+	$2HCl$	=	$FeCl_2$	+	H_2O	+	CO_2
Ferrous carbonate.		Hydrochloric acid.		Ferrous chloride.		Water.		Carbonic acid gas.

If absolutely pure chloride of calcium is required, the solution should be tested for iron (by adding sulphydrate of ammonium, which gives a black precipitate with salts of iron), and, if the latter is present, chlorinated lime and slaked lime be added, whereby iron is peroxidized; on filtering, a pure solution of chloride of calcium is obtained:—

$4FeCl_2$	+	$Ca2ClO$	+	$4CaH_2O_2$	+	$2H_2O$	=	$2Fe_26HO$	+	$5CaCl_2$
Ferrous chloride.		Hypochlorite of calcium.		Hydrate of calcium.		Water.		Ferric hydrate.		Chloride of calcium.

This is the officinal process, and may be imitated on the small scale by adding a particle of iron to a fragment of the marble before dissolving in acid.

Second Synthetical Reaction.—Place a small piece of chalk in a strong fire and heat until a fragment no longer effervesces on the addition of acid; caustic lime, CaO (*Calx*, B. P.), remains.

$CaCO_3$	=	CaO	+	CO_2
Carbonate of calcium (chalk).		Oxide of calcium (lime).		Carbonic acid gas.

Etymologically considered, this action is analytical (*ἀναλύω*, *analuo*, I resolve) and not synthetical (*σύνθεσις*, *sūnthesis*, a putting together); but conventionally it is synthetical, and not analytical; for in this, the usual sense, synthesis is the application

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of chemical action with the view of producing something, analysis the application of chemical action with the view of finding out the composition of a substance. In the etymological view of the matter there is scarcely an operation performed either by the analyst or by the manufacturer but includes both analysis and synthesis.

When cold, add to the lime a few drops of water, and notice the evolution of steam and other evidence of strong action; the product is *slaked* lime, hydrate of calcium (Ca2HO) (*Calcis hydras*, B. P.).

CaO	+	H_2O	=	Ca2HO
Lime.		Water.		Hydrate of calcium (slaked lime).

The evolution of steam is due to the solidification of a portion of the water and liberation of the natural heat which kept that water in the liquid condition; this surplus heat acting on another portion produces the usual effect of heat on water, conversion into steam.

Place the hydrate of calcium in water: in a short time a saturated solution (11 or 12 grains of CaO in one pint), known as *lime-water* (*Liquor Calcis*, B. P.), results.

Slaked lime is much more soluble in aqueous solution of sugar than in pure water. The *Liquor Calcis saccharatus*, B. P., is such a solution, containing 2 ounces of sugar and 142 grains of lime (CaO) in 1 pint.

Third Synthetical Reaction.—To a solution of chloride of calcium add carbonate of sodium; a white precipitate of carbonate of calcium (*Calcis Carbonas præcipitata*, B. P.) ($CaCO_3$) results.

$CaCl_2$	+	Na_2CO_3	=	$CaCO_3$	+	2NaCl
Chloride of calcium.		Carbonate of sodium.		Carbonate of calcium.		Chloride of sodium.

If the student were preparing this *precipitated chalk* for use in medicine it would have to be washed—that is, the precipitate and accompanying liquid placed on a paper or other filter, allowed to drain, and then pure water passed through the filter.

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Filtering-paper is simply good unsized paper made from the best white rags—white blotting-paper, in fact, of unusually good quality. Students' or analysts' filters, on which to collect precipitates, are round pieces of this paper, from three to six inches in diameter, twice folded, and then opened out so as to form a hollow cone. The cone is supported by a glass or earthenware funnel.

Precipitates may also be washed by allowing them to settle, pouring off the supernatant liquid, agitating with water, again allowing to settle, and so on. This is washing by decantation (*de*, from, *canthus*, a brim).

Prepared carbonate of calcium (*Creta præparata*, B. P.) is merely washed chalk (*Creta*, B. P.) or *whiting*, only that in Pharmacy fashion demands that the chalk be in little conical lumps, about the size of thimbles, instead of in the larger rolls characteristic of "whiting." Wet whiting pushed, portion by portion, through a funnel, and each separately dried, gives the conventional *Creta præparata*.

Fourth Synthetical Reaction.—Dissolve a few grains of bone-ash (bones burnt till all animal matter has been removed, impure phosphate of calcium (*Os Ustum*, B. P.)) in hydrochloric acid in a test-tube.

$$\underset{\text{Phosphate of calcium (impure).}}{Ca_3 2PO_4} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Acid phosphate of calcium.}}{CaH_4 2PO_4} + \underset{\text{Chloride of calcium.}}{2CaCl_2}$$

Filter, boil, and when cold add excess of solution of ammonia; the phosphate of calcium, now pure (*Calcis Phosphas*, B. P.), is reprecipitated.

$$\underset{\text{Acid phosphate of calcium.}}{CaH_4 2PO_4} + \underset{\text{Chloride of calcium.}}{2CaCl_2} + \underset{\text{Ammonia.}}{4AmHO} = \underset{\text{Phosphate of calcium (pure).}}{Ca_3 2PO_4} + \underset{\text{Chloride of ammonium.}}{4AmCl} + \underset{\text{Water}}{4H_2O}$$

Bone-black, or *Animal Charcoal* (*Carbo Animalis*, B. P.), is the residue of bones which have been exposed to a red heat without access of air. The student may imitate the operation by heating a few fragments of bone in a covered porcelain crucible in a fume-chamber until smoke and vapour ceases to be evolved. Purified Animal Charcoal (*Carbo Animalis purificatus*, B. P.) is

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obtained on digesting animal charcoal in equal parts of hydrochloric acid and water, filtering, thoroughly washing, drying, and igniting the product in a closely covered crucible. The acid dissolves out phosphate of calcium, according to the previous reaction, decomposes and dissolves carbonate of calcium and sulphide of calcium, the carbon remaining unacted on. Wood Charcoal (*Carbo Ligni*, B. P.) is wood similarly ignited without access of air.

Phosphate of calcium is converted into phosphate of sodium (*Sodæ Phosphas*, B. P.) ($Na_2HPO_4, 12H_2O$) as follows:—Treat for some time with sulphuric acid, dilute, filter, add carbonate of sodium, boil, filter, evaporate, crystallize. This is the B. P. and the ordinary process.

$$\underset{\text{Phosphate of calcium.}}{Ca_3 2PO_4} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Acid phosphate of calcium.}}{CaH_4PO_4} + \underset{\text{Sulphate of calcium.}}{2CaSO_4}$$

$$\underset{\text{Acid phosphate of calcium.}}{CaH_4 2PO_4} + \underset{\text{Carbonate of sodium.}}{2Na_2CO_3} = \underset{\text{Carbonate of calcium.}}{CaCO_3} + \underset{\text{Phosphate of sodium.}}{2Na_2HPO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Fifth Synthetical Reaction.—Pass chlorine, generated as already described, into damp slaked lime contained in a piece of wide tubing, open at the opposite end to that in which the delivery-tube is fixed. (A test-tube, the bottom of which has been accidentally broken, is very convenient for such operations.) The product is ordinary *bleaching-powder*, said to be a mixture of hypochlorite and chloride of calcium, commonly called chloride of lime, the *Calx chlorata* of the British Pharmacopœia.

$$\underset{\text{Blk. oxide of manganese.}}{MnO_2} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Chloride of manganese.}}{MnCl_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{Cl_2}$$

$$\underset{\text{Hydrate of calcium.}}{2CaH_2O_2} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorinated lime.}}{\underset{\text{Hypochlorite of calcium.}}{CaCl_2O_2} , \underset{\text{Chloride of calcium.}}{CaCl_2}}$$

Digest the powder in water, in which the bleaching compound is soluble, filter from the undissolved lime, &c., and test the

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bleaching-powers of the liquid (*Liquor Calcis chloratæ*, B. P.) by adding a few drops to a decoction of logwood slightly acidulated.

Gummate of Calcium is the only officinal calcium salt that remains to be noticed. This compound is, in short, the ordinary Gum-Acacia or Gum-Arabic (*Acaciæ Gummi*, B. P.). A solution of gum-arabic in water (*Mucilago Acaciæ*, B. P.) yields a white precipitate of oxalate of calcium on the addition of solution of oxalate of ammonium. Or a piece of gum burnt to an ash in a porcelain crucible yields a calcareous residue, which, dissolved in dilute acids, affords characteristic reactions with any of the analytical reagents for calcium. These statements should be experimentally verified by the student.

Reactions having Analytical Interest.

First Analytical Reaction.—Add sulphuric acid, highly diluted, to a calcium solution; sulphate of calcium ($CaSO_4$) is formed, but is *not* precipitated.

Second Analytical Reaction.—Add yellow chromate of potassium (K_2CrO_4) to a calcium solution slightly acidified with acetic acid; chromate of calcium ($CaCrO_4$) is probably formed, but is *not* precipitated.

These two negative reactions are most valuable in analysis, as every precipitant of calcium is also a precipitant of barium; but the above two reagents are precipitants of barium only. Hence calcium, which when alone can be readily detected by the following reactions, cannot by any reaction be detected in the presence of barium. But by the sulphuric or chromic test barium is easily removed, and then either of the following reagents will throw down the calcium.

Other Analytical Reactions.—Add carbonate of ammonium, phosphate of sodium, arseniate of ammonium, and oxalate of ammonium to calcium solutions as described under the analytical reactions of barium, and write out descriptive equations. The

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precipitates correspond in appearance to those of barium; their constitution is also identical, hence their correct formulæ can be easily deduced by the student.——Calcium compounds impart a reddish colour to flame.

MAGNESIUM.

Symbol Mg. Atomic weight 24.

Magnesium is abundant in nature in the form of mountain limestone, or *dolomite*, a double carbonate of magnesium and calcium in common use as a building-stone (*e. g.* the Houses of Parliament, and the School of Mines in London), and *magnesite*, a tolerably pure carbonate of magnesium, though too "stony" for direct use in medicine, even if very finely powdered. Chloride of magnesium and sulphate of magnesium (Epsom salt) also occur in sea-water, and the water of many springs.

Magnesium may be obtained from the chloride by the action of sodium. It burns readily in the air, emitting a dazzling light due to the white heat to which the resulting particles of magnesia (MgO) are exposed. The evolution of so much heat is explained in the usual way. All bodies contain heat; it is a natural property of magnesia to contain less heat than its constituents oxygen and magnesium, hence when those elements combine, much of the heat naturally existing in them escapes, becomes evident to the senses, recognizable by the thermometer. Probably some of the liberated heat is converted into light, for neither force nor matter can be created by man.

Reactions having Synthetical Interest.

First Synthetical Reaction.—To a few drops of sulphuric acid and a little water in a test-tube, add carbonate of magnesium (preferably the native carbonate *magnesite* ($MgCO_3$)) until effervescence ceases, subsequently boiling to aid in the expulsion of the carbonic acid gas. The filtered liquid is a solution of sulphate of magnesium ($MgSO_4$), crystals of which, *Epsom salt* ($MgSO_4$, $7H_2O$) (*Magnesiæ Sulphas*, B. P.) may be obtained on evaporating most of the water, and setting the concentrated solution aside to cool. This is an ordinary manufacturing process.

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Second Synthetical Reaction.—To solution of sulphate of magnesium add solution of carbonate of sodium and boil; the resulting precipitate is *light* carbonate of magnesium (*Magnesiæ Carbonas levis*, B. P.), a mixture of carbonate and hydrate of magnesium ($3MgCO_3, Mg2HO, 4H_2O$). A denser precipitate of similar chemical composition (*Magnesiæ Carbonas*, B. P.) is obtained on mixing strong solutions of the above salts, evaporating to dryness, and then washing out the sulphate of sodium in the usual way.

$$4MgSO_4 + 4Na_2CO_3 + H_2O = 3MgCO_3,Mg2HO + 4Na_2SO_4 + CO_2$$

Sulphate of magnesium. | Carbonate of sodium. | Water. | Officinal carbonate of magnesium. | Sulphate of sodium. | Carbonic acid gas.

Third Synthetical Reaction.—Heat some of the above light dry carbonate in a porcelain crucible till it ceases to effervesce on adding, to a small portion, water and acid; the residue is light magnesia (MgO) (*Magnesia levis*, B. P.). The same operation on the heavy carbonate yields heavy magnesia (MgO) (*Magnesia*, B. P.). Both are sometimes spoken of as "calcined magnesia."

$$3MgCO_3,Mg2HO = 4MgO + H_2O + 3CO_2$$

Officinal carbonate of magnesium. | Oxide of magnesium. | Water. | Carbonic acid gas.

A trace only of magnesia is dissolved by pure water. Moisten a grain or two of magnesia with water, and place the paste on a piece of red litmus-paper; the wet spot, after a time, becomes blue, showing that the magnesia is slightly soluble.

Fourth Synthetical Reaction.—Pass carbonic acid gas, generated as described on page 32, into a mixture of water and carbonate of magnesium contained in a test-tube. After some time, separate undissolved carbonate by filtration; the filtrate contains carbonate of magnesium dissolved by carbonic acid. When of a strength of about 13 grains in one ounce, the solution constitutes the *Fluid Magnesia* (*Liquor Magnesiæ carbonatis*, B. P.).

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Heat the solution; ter-hydrated monocarbonate of magnesium ($MgCO_3, 3H_2O$) is precipitated.

The same salt is deposited in crystals by the spontaneous evaporation of the solution of carbonate of magnesium.

Reactions having Analytical Interest.

First Analytical Reaction.—Add solution of hydrate or carbonate of ammonium to a magnesium solution (sulphate for example) and boil; the precipitation of part only of the magnesium as hydrate (Mg2HO) or carbonate ($MgCO_3$) occurs. Add now solution of chloride of ammonium; the precipitate is dissolved.

This is an important reaction, the presence of chloride of ammonium enabling the analyst to throw out from a solution barium and calcium by an alkaline carbonate, magnesium being retained. The cause of this reaction is the tendency of magnesium to form soluble double salts with potassium, sodium, ammonium, &c.

Second Analytical Reaction.—To some of the solution resulting from the last reaction, add solution of phosphate of sodium; phosphate of magnesium and ammonium ($MgAmPO_4$) is precipitated.——*3rd.* To another portion add arseniate of ammonium; arseniate of magnesium and ammonium ($MgAmAsO_4$) is precitated.

Barium and calcium are also precipitated by alkaline phosphates and arseniates. (*Vide* pages 54 and 59.) The other precipitants of magnesium are also precipitants of barium and calcium. In other words, there is no *direct* test for magnesium. Hence the analyst always removes any barium or calcium by an alkaline carbonate, as indicated above; the phosphate of sodium or arseniate of ammonium then become very delicate tests of the presence of magnesium. In speaking of magnesium tests, the absence of barium and calcium salts is to be understood.

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Here again, and at the end of each succeeding group of substances, the student should review his operations, as directed in connexion with the first group of elements (p. 50).

APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A SALT OF *ONE* OF THE METALS, BARIUM, CALCIUM, AND MAGNESIUM.

Add yellow chromate of potassium; a precipitate indicates barium.

If no barium is present, add chloride and carbonate of ammonium, and boil; a precipitate indicates calcium.

If barium and calcium are proved to be absent, add chloride of ammonium, ammonia, and then either phosphate of sodium or arseniate of ammonium; a white granular precipitate indicates magnesium.

Ammonia is here added to yield the necessary elements to ammonio-magnesian phosphate or ammonio-magnesian arseniate, both of which are highly characteristic precipitates; and chloride of ammonium is added to prevent a mere partial precipitate of the magnesium by the ammonia.

APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE, TWO, OR ALL THREE OF THE METALS OF THE ALKALINE EARTHS.

Add chromate of potassium; barium, if present, is precipitated. Filter, if necessary, and add chloride, hydrate, and carbonate of ammonium, and boil; calcium, if present, is precipitated. Filter, if requisite, and add phosphate of sodium; magnesium, if present, is precipitated.

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APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS CONTAINING ANY OR ALL OF THE METALLIC ELEMENTS HITHERTO CONSIDERED.

Add AmCl, AmHO, Am_2CO_3; boil and filter.

<table>
<tr><td colspan="2">Precipitate
Ba Ca.
Wash, dissolve in $HC_2H_3O_2$, add K_2CrO_4, and filter.</td><td colspan="2">Filtrate
Mg Am Na K.
Add Am_2HPO_4, shake, filter.</td></tr>
<tr><td>Precipitate
Ba.</td><td>Filtrate
Ca.
Test by $Am_2C_2O_4$.</td><td>Precipitate
Mg.</td><td>Filtrate
Am Na K.
Evap. to dryness, ignite, dissolve residue in water.
Test for K by $PtCl_4$
,, Na ,, flame.
Test original solution for Am.</td></tr>
</table>

In the above, and in subsequent charts of analytical processes, the leading precipitants will be found to be ammonium salts. These, being volatile, can be got rid of towards the end of the operations, and thus the detection of potassium and sodium be in no way prevented—an advantage which could not be had if chromate of potassium, phosphate of sodium, &c. were the group-precipitants employed.

Acetic, and not hydrochloric or nitric, acid is used in dissolving the barium and calcium carbonates, because chromate of barium, on the precipitation of which the detection of barium depends, is soluble in the stronger acids, and therefore could not be thrown down in their presence.

Note on Classification.—The compounds of barium, calcium, and magnesium, like those of the alkali metals, have many analogies; the carbonates, phosphates, and arseniates of each are insoluble, which sufficiently distinguishes them from the members of the class first studied. They possess, moreover, well-marked differences, so that their separation from each other is easy. The solubility of their hydrates in water mark their connexion with the alkali metals; the slightness of that solubility, diminishing as we advance further and further from the alkalies, baryta being most and magnesia least soluble in water, points to their

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connexion with the next class of metals, the hydrates of which are insoluble in water. These considerations must not, however, be over-valued. Though the solubility of their hydrates places barium nearest and magnesium furthest from the alkali metals the solubility of their sulphates gives them the opposite order, magnesium-sulphate being most soluble, calcium-sulphate next, strontium-sulphate third (strontium is a rarer element, which will be mentioned subsequently), and barium-sulphate insoluble in water. These metals are sometimes spoken of as the alkaline earths.

ZINC, ALUMINIUM, IRON.

These three elements are classed together for analytical convenience rather than for more general analogies. The atom of zinc is bivalent (Zn^{II}), aluminium quadrivalent (Al^{IV}), and iron sexivalent (Fe^{VI}).

ZINC.

Symbol Zn. Atomic weight 65.

Zinc is tolerably abundant in nature as sulphide (ZnS) or *blende*, and carbonate ($ZnCO_3$) or *calamine* (from *calamus*, a reed, in allusion to the appearance of the mineral). The ores are roasted to expel sulphur, carbonic acid gas, and some impurities, and the resulting oxide distilled with charcoal, when the metal vaporizes and readily condenses. Its use as a metal is familiar; alloyed with nickel it yields german silver; with twice its weight of copper forms common brass, and as a coating on iron (the so-called *galvanized* iron) greatly retards the formation of rust. Most of the salts of zinc are prepared, directly or indirectly, from the metal (*Zincum*, B. P.).

Reactions having (*a*) Synthetical and (*b*) Analytical Interest.

(*a*) *Synthetical Reactions.*

First Synthetical Reaction.—Boil zinc with water and sulphuric acid in a test-tube until gas ceases to be evolved; solution of sulphate of zinc ($ZnSO_4$) results. Concentrate the solution in a

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small evaporating dish; on cooling, crystals of Sulphate of Zinc ($ZnSO_4, 7H_2O$) are deposited (*Zinci Sulphas*, B. P.).

This reaction affords hydrogen and sulphate of zinc; it also gives electricity. Of several methods of evolving hydrogen, it is the most convenient; of the two or three means of preparing sulphate of zinc it is that most commonly employed; and of the many reactions which may be utilized in the development of dynamic electricity it is at present the cheapest and most manageable. The apparatus in which the reaction is effected differs according to the requirements of the operator; if the sulphate of zinc alone is wanted, an open dish is all that is necessary, the action being, perhaps, accelerated by heat; if hydrogen, a closed vessel, delivery-tube, &c.; if electricity, square vessels called cells and certain complementary materials, forming altogether what is termed a battery. In each operation for one product the other two are commonly wasted. It would not be difficult for the student, as a matter of amusement, to construct an apparatus in which all three products should be collected.

Impure sulphate of zinc may be purified as described in the next reaction.

Second Synthetical Reaction.—Dissolve zinc in hydrochloric acid in a test-tube; the resulting solution contains chloride of zinc. Evaporate the solution till no more steam escapes; Chloride of Zinc ($ZnCl_2$) in a state of fusion remains, and, on cooling, is obtained as a white opaque solid (*Zinci Chloridum*, B. P.).

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Chloride of zinc.}}{ZnCl_2} + \underset{\text{Hydrogen.}}{H_2}$$

This reaction is analogous to that previously described. The process and product are those of the British Pharmacopœia. Burnett's disinfecting liquid is solution of chloride of zinc.

Zinc sometimes contains traces of iron and lead; and these, like zinc, are dissolved by most acids, with formation of soluble salts: they may be recognized in the liquids by the tests described hereafter. Should either be present in the above solutions, a little chlorine water is added to the liquid till the odour of chlorine is permanent, and then the whole well shaken with some carbonate of zinc. In this way iron is precipitated as ferric hydrate, and lead as peroxide:—

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$$\underset{\text{Ferrous chloride.}}{2FeCl_3} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Ferric chloride.}}{Fe_2Cl_6}$$

$$\underset{\text{Ferric chloride.}}{Fe_2Cl_6} + \underset{\text{Carbonate of zinc.}}{3ZnCO_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Ferric hydrate.}}{Fe_2 6HO} + \underset{\text{Chloride of zinc.}}{3ZnCl_2} + \underset{\text{Carbonic acid gas.}}{3CO_2}$$

$$\underset{\text{Chloride of lead.}}{PbCl_2} + \underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Carbonate of zinc.}}{2ZnCO_3} = \underset{\text{Peroxide of lead.}}{PbO_2} + \underset{\text{Chloride of zinc.}}{2ZnCl_2} + \underset{\text{Carbonic acid gas.}}{2CO_2}$$

In the British Pharmacopœia the presence of impurities in the zinc is assumed, and the process of purification just described incorporated with the process of preparation of *Zinci Chloridum*, *Liquor Zinci Chloridi*, and *Zinci Sulphas*.

Third Synthetical Reaction.—To solution of sulphate of zinc in a test-tube, add an equal quantity of solution of carbonate of sodium and boil; the resulting precipitate is Carbonate of Zinc ($ZnCO_3$) (*Zinci Carbonas*, B. P.), or, rather, a mixture of carbonate ($ZnCO_3$) and hydrate (Zn2HO), in the proportion of one molecule of the former and two of the latter, together with a molecule of water (H_2O).

$$\underset{\text{Sulphate of zinc.}}{3ZnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Carbonate of sodium.}}{3Na_2CO_3} = \underset{\text{Officinal carbonate of zinc.}}{ZnCO_3, 2ZnH_2O_2} + \underset{\text{Carbonic acid gas.}}{2CO_2} + \underset{\text{Sulphate of sodium.}}{3Na_2SO_4}$$

Fourth Synthetical Reaction.—Collect on a filter the precipitate obtained in the last reaction, wash with distilled water, and dissolve a small portion in acetic acid; the resulting solution contains acetate of zinc ($Zn2C_2H_3O_2$), and, on evaporation, yields crystals ($Zn2C_2H_3O_2, 2H_2O$). This is the process for *Zinci Acetas*, B. P.

$$\underset{\text{Officinal carbonate of zinc.}}{ZnCO_3, 2ZnH_2O_2} + \underset{\text{Acetic acid.}}{6HC_2H_3O_2} = \underset{\text{Acetate of zinc.}}{3(Zn2C_2H_3O_2)} + \underset{\text{Water.}}{5H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Fifth Synthetical Reaction.—Dry the remainder of the precipitated carbonate (by placing the open filter on a plate over a dish of water kept boiling), and then heat it in a small crucible till it ceases to effervesce on the addition of water and acid (to trial

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samples taken out of the crucible from time to time); the product is Oxide of Zinc (*Zinci Oxidum*, B. P.), much used in the form of ointment (*Unguentum Zinci*, B. P.).

$$\underset{\text{Officinal carbonate of zinc.}}{ZnCO_3, 2ZnH_2O_2} = \underset{\text{Oxide of zinc.}}{3ZnO} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}.$$

This oxide is of a very pale yellow or buff tint, not nearly so white as oxide prepared by the combustion of zinc in air. The latter variety can be obtained in commerce under the name of Hubbuck's oxide of zinc. Its preparation can only be practically accomplished on the large scale, but the student may observe the chief features of the action by heating a piece of zinc in a small porcelain crucible till it burns; flocks escape from the crucible, float about in the air, and slowly fall. These are the old *Flores Zinci, Lana Philosophica*, or *Nihilum Album*.

Sixth Synthetical Reaction.—Valerianate of Zinc ($Zn2C_5H_9O_2$) (*Zinci Valerianas*, B. P.) is prepared by mixing strong solutions of sulphate of zinc and valerianate of sodium.

$$\underset{\text{Sulphate of zinc.}}{ZnSO_4} + \underset{\text{Valerianate of sodium.}}{2NaC_5H_9O_2} = \underset{\text{Sulphate of sodium.}}{Na_2SO_4} + \underset{\text{Valerianate of zinc.}}{Zn2C_5H_9O_2}$$

The compounds of zinc described in the above six reactions are the only ones mentioned in the British Pharmacopœia; the processes are also those of that work.

(*b*) *Reactions having Analytical Interest.*

First Analytical Reaction.—To solution of a zinc salt (sulphate for example) add solution of sulphydrate of ammonium (AmHS); white sulphide of zinc (ZnS) is precipitated, insoluble in acetic, but soluble in the stronger acids.

This is the only white sulphide the student will meet with. Its formation on the addition of the sulphydrate of ammonium is therefore highly characteristic of zinc. Hydrate of aluminium, which is also white and precipitated by sulphydrate of ammonium, is the only substance sulphide of zinc is likely to be mistaken for, and *vice versâ*; but, as will be seen immediately, there are satisfactory means of distinguishing these from each other.

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Second Analytical Reaction.—To solution of a zinc salt add solution of ammonia; white hydrate of zinc (Zn2HO) is precipitated. Add now excess of ammonia; the precipitate is redissolved.

This reaction at once distinguishes a zinc salt from an aluminium salt, hydrate of aluminium being insoluble in ammonia.

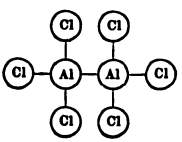
Other Analytical Reactions.—The fixed alkali hydrates afford a similar reaction to that just mentioned, the hydrate of zinc redissolving if the alkali is free from carbonate.——Carbonate of ammonium yields a white precipitate of carbonate and hydrate, soluble in excess.——The fixed alkaline carbonates give a similar precipitate, which is not redissolved if the mixed solution and precipitate is well boiled.

Antidotes.—There are no efficient chemical means of counteracting the poisonous effects of zinc. Large doses, fortunately, act as powerful emetics. If vomiting has not occurred, or apparently to an insufficient extent, solution of carbonate of sodium (common washing soda) immediately followed by white of egg and demulcents may be administered.

ALUMINIUM.

Symbol Al. Atomic weight 27·5.

In the formulæ of salts of aluminium, it will be observed that to one atom of metal there are three atoms of other univalent radicals; hence, apparently, the atom of aluminium is trivalent. But in reality it is a tetrad, the atom is quadrivalent; for one molecule of aluminium compounds includes two atoms of the metal, three-fourths only of whose power is exerted in retaining the other constituents of the molecule, the remaining fourth enabling the aluminium atoms themselves to keep together. This is graphically shown in the following formula of chloride of aluminium from Frankland's 'Lecture Notes for Chemical Students,'



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which represents each aluminium atom as a body having four arms or bonds, three of which are engaged in grasping the arms of univalent chlorine atoms, while the fourth grasps the corresponding arm of its brother aluminium atom. Such graphic formulæ, as they are called, are exceedingly useful in aiding the student to obtain a correct idea of the constitution of chemical substances, especially if he avoids the error of supposing that they are pictures either of the shape, position, or absolute power of atoms in a molecule, or, indeed, the true representation of a molecule at all; for on this point man knows nothing. Frankland says, "The lines connecting the different atoms of a compound are but crude symbols of the bonds of union between them; and it is scarcely necessary to remark that no such material connexions exist, the bonds which actually hold together the atoms of a compound being in all probability, as regards their nature, much more like those which connect the members of our solar system."

Aluminium is very abundant in nature, chiefly as silicate, in clays, slate, marl, granite, basalt, and a large number of minerals. The sapphire and ruby are almost pure oxide of aluminium. The metal is obtained near Newcastle, from the double chloride of aluminium and sodium, by the action of metallic sodium, the source of the chloride being the mineral *bauxite*. Aluminium-bronze is an alloy of ten parts of aluminium with ninety of copper.

Alum (*Alumen*, B. P.), a double sulphate of aluminium and ammonium ($Al_2 3SO_4, Am_2SO_4, 24H_2O$), is obtained from aluminous slate or shale by exposure to air; oxidation and chemical change produces sulphate of aluminium, sulphate of iron, and silica, from the silicate of aluminium and bisulphide of iron (iron pyrites) originally present in the shale. The sulphate of aluminium is dissolved out of the mass by water and sulphate of ammonium added to it. There are several *alums*, iron or chromium replacing aluminium, and potassium or sodium taking the place of ammonium, all crystallizing in one, eight-sided, form, the octahedron—a sort of double pyramid. They are, apparently, alike in chemical constitution, and their general formula (M = either metal) is $M'''_2 3SO_4, M'_2SO_4, 24H_2O$. The student may prepare alum by boiling a small quantity of powdered pipeclay (silicate of aluminium) with sulphuric acid in a test-tube, dissolving out the resulting sulphate of aluminium by water, and adding to the solution sulphate of ammonium; on evaporating, crystals of alum are obtained. Dried alum (*Alumen Exsiccatum*, B. P.) is alum from which the water of crystallization has been expelled by heat.

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REACTIONS HAVING ANALYTICAL INTEREST.

First Analytical Reaction.—To a solution of an aluminium salt (alum, for example, which contains sulphate of aluminium) add sulphydrate of ammonium (AmHS); a gelatinous white precipitate of hydrate of aluminium falls:—

$$Al_2 3SO_4 + 6AmHS + 6H_2O = Al_2 6HO + 3Am_2SO_4 + 6H_2S.$$

Second Analytical Reaction.—To solution of alum add ammonia AmHO; hydrate of aluminium falls: add now excess of ammonia; the precipitate is insoluble.

This precipitated hydrate of aluminium or alumina has great affinity for vegetable colouring-matters, and also for the fibre of cloth, &c. Again perform the above experiment, but before adding the ammonia introduce some decoction of logwood, solution of cochineal, or other similar coloured liquid, into the test-tube. Add now the ammonia, and set the tube aside for the alumina to fall; the latter takes down all the colouring principle with it. In dye-works, the cloths, &c., are passed through liquids holding the alumina but weakly in solution, and then through the colouring liquids; from the first bath the fibres abstract alumina, and from the second the alumina abstracts colouring-matter. Some other metallic oxides resemble alumina in this property; they are all termed *mordants* (from *mordens*, biting); the substances they form with colouring-matters have the name of *lakes* (probably from the root of *lay*, literally, to throw down).

Third Analytical Reaction.—To the alum add solution of potash; again hydrated alumina falls. Add now excess of the potash, and agitate; the precipitate dissolves.

Alumina may be precipitated from this solution in potash by neutralizing the latter with hydrochloric acid, and adding ammonia until, after mixing, the liquid smells ammoniacal, or, by adding solution of chloride of ammonium to the potash liquid. But the former way is the better; for it is difficult to know

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when a sufficiency of the chloride of ammonium has been poured in, whereas test-paper at once enables the operator to know when a sufficiency of hydrochloric acid and ammonia have been added.

Alkaline carbonates, phosphates, arseniates, and salts of other acidulous radicals also decompose aluminium salts and produce insoluble compounds of that metal, but the resulting precipitates are of no general interest to the student of pharmacy.

IRON.

Symbol Fe. Atomic weight 56.

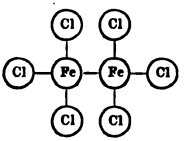
Compounds of iron are very abundant in nature. *Magnetic Iron Ore*, or *Loadstone* (*Lodestone* or *Leadstone*, from the Saxon *lædan*, to lead, in allusion to its use, or, rather, of magnets made from it, in navigation) is the chief ore from which Swedish iron is made; it is a mixture of ferrous and ferric oxide (FeO,Fe_2O_3). Much of the Russian iron is made from *Specular Iron Ore* (from *speculum*, a mirror, in allusion to the lustrous nature of the crystals of this mineral). This and *Red Hæmatite* (from αἷμα, *aima*, blood, so named from the colour of its streak), an ore raised in Lancashire, are composed of ferric oxide only (Fe_2O_3). *Brown Hæmatite*, a hydrated ferric oxide, is the source of much of the French iron. *Spathic Iron Ore* (from *spatha*, a slice, in allusion to the lamellar structure of the ore) is a ferrous carbonate ($FeCO_3$). An impure ferrous carbonate forms the *Clay Ironstone*, whence most of the English iron is derived. The chief Scotch ore is also an impure carbonate, containing much bituminous matter; it is known as *Black Band*. *Iron Pyrites* (from πῦρ, *pūr*, fire, in allusion to the production of sparks when sharply struck) (FeS_2) is a yellow lustrous mineral, of use only for its sulphur.

Iron is obtained from its ores by processes of roasting, and reduction with coal or charcoal in the presence of chalk, the latter uniting with the sand, clay, &c. to form a fusible slag. The resulting *cast iron* is converted into *wrought iron* by burning out the carbon, silicon, and other impurities present, by an operation termed *puddling*. *Steel* is wrought iron impregnated with from one to two per cent. of carbon by heating bars &c. in charcoal.

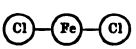
Iron combines with other elements and radicals in two proportions; those salts in which the other radicals are in the less amount are termed *ferrous*, the higher being *ferric* salts.

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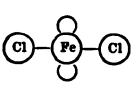
The atom of iron is considered to be sexivalent, on account of the analogy of its compounds with those of chromium, which is undoubtedly sexivalent. But in nearly all the ferric compounds two-sixths of the power of the atom is latent, two of its six bonds control one another's activity; and, indeed, of the other four, one is engaged by the corresponding bond of a second atom, so that each of the two atoms of iron in ferric salts is apparently trivalent, as is the case with aluminium salts. The ferric salts, therefore, may be expressed by graphic formulæ similar to those of the aluminium salts. Thus the ordinary ferric chloride or perchloride of iron :—



In the lower salts of iron, the ferrous salts, four-sixths of the quantivalence of the atom is latent; two pairs of bonds control one another's activity, leaving the atom in an apparently bivalent condition. The graphic formula for ferrous chloride will be,



The latent as well as the active quantivalence may be thus shown :—



Or the formula for ferric chloride may be written $'''Fe'''_2\ Cl'_6$, and ferrous chloride $''Fe''Cl_2$.

REACTIONS HAVING (*a*) SYNTHETICAL, AND (*b*) ANALYTICAL INTEREST.

(*a*) *Synthetical Reactions.*

FERROUS SALTS.

First Synthetical Reaction.—Place iron (a few small tacks) in dilute sulphuric acid in a test-tube, accelerating the action, if necessary, by heat.

$$\underset{\text{Iron.}}{Fe} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sulphate of}\\ \text{iron.}}}{FeSO_4} + \underset{\text{Hydrogen.}}{H_2}$$

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The solution contains sulphate of iron, and will yield crystals of that substance ($FeSO_4, 7H_2O$) (*Ferri Sulphas*, B. P.) on evaporation; or if the hot concentrated solution be poured into alcohol, the mixture being well stirred, the sulphate is at once thrown down in minute crystals (*Ferri Sulphas granulata*, B. P.). At a temperature of 400° F. ferrous sulphate loses six-sevenths of its water, and becomes the *Ferri Sulphas Exsiccata*, B. P.

In the laboratory sulphate of iron is often obtained as a by-product in making sulphuretted hydrogen,

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

In manufactories it occurs as a by-product in the decomposition of aluminous shale, as already noticed (p. 70).

Sulphate of iron is sometimes termed *green vitriol*. Vitriol (from *vitrum*, glass) was originally the name of any transparent crystalline substance, but afterwards restricted to the sulphates of zinc, iron, and copper, which were, and still are, occasionally known as white, green, and blue vitriol. *Copperas* (probably originally *Copper-rust*, a term applied to verdegris and other green incrustations of copper) is another name for sulphate of iron, sometimes distinguished as *green copperas*, sulphate of copper being blue copperas.

Sulphate of iron, when exposed to the air, gradually turns brown through absorption of oxygen, ferric compounds being formed.

Second Synthetical Reaction.—To some of the above solution of ferrous sulphate, boiling, add solution of carbonate of ammonium in recently boiled water; a white precipitate of ferrous carbonate ($FeCO_3$) is thrown down, rapidly becoming light green, bluish green, and finally red, through absorption of oxygen.

$FeSO_4$	+	Am_2CO_3	=	$FeCO_3$	+	Am_2SO_4
Ferrous sulphate.		Carbonate of ammonium.		Ferrous carbonate.		Sulphate of ammonium.

This precipitate, rapidly washed with hot well-boiled distilled water, and the moist powder mixed with sugar and quickly dried, forms the saccharated carbonate of iron (*Ferri Carbonas Saccharata*, B. P.). The same compound, mixed with a fourth its weight of Confection of Roses, is the *Pilula Ferri Carbonatis*, B. P.

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Carbonate of iron is said to be more easily dissolved in the stomach than any other iron preparation. It is so unstable and prone to oxidation, that it must be washed in water containing no dissolved air and mixed with the sugar (which protects it from oxidation) as quickly as possible. In making the officinal compound mixture of iron (*Mistura Ferri Composita*, B. P.), the various ingredients, including the carbonate of potassium, should be placed in a bottle of the required size, space being left for the solution of sulphate of iron, which should be added last, the bottle immediately filled up with rose-water, and securely corked.

$FeSO_4$	+	K_2CO_3	=	$FeCO_3$	+	K_2SO_4
Ferrous sulphate.		Carbonate of potassium.		Ferrous carbonate.		Sulphate of potassium.

Third Synthetical Reaction, by which arseniate of iron (*Ferri Arsenias*, B. P.) (Fe_32AsO_4), partially oxidized, is formed. This will be noticed again under Arsenicum.

Fourth Synthetical Reaction.—To solution of ferrous sulphate in a test-tube add a little acetate of sodium, then phosphate of sodium; phosphate of iron (Fe_32PO_4) is precipitated (*Ferri Phosphas*, B. P.).

$3FeSO_4$	+	$2Na_2HPO_4$	+	$2NaC_2H_3O_2$
Ferrous sulphate.		Phosphate of sodium.		Acetate of sodium.

=	Fe_32PO_4	+	$3Na_2SO_4$	+	$2HC_2H_3O_2$
	Ferrous phosphate.		Sulphate of sodium.		Acetic acid.

The use of the acetate of sodium is to ensure the occurrence of acetic acid in the solution, where otherwise would be free sulphuric acid. Sulphuric acid is a solvent of ferrous phosphate; acetic acid is not. It is impossible to prevent the separation of sulphuric acid, the only alternative, therefore, is to neutralize it as soon as formed, which the acetate of sodium does. Ferrous phosphate is white, but soon oxidizes and becomes blue.

The above reaction also occurs in making *Syrupus Ferri Phosphatis*, B. P.

Fifth Synthetical Reaction.—The formation of sulphide of iron (FeS). Strongly heat a fragment of sulphur with about twice its

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weight of iron filings in a test-tube; sulphide of iron is formed. When cold, add water, then a few drops of sulphuric acid; sulphuretted hydrogen gas (H_2S), known by its odour, is evolved.

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Sticks of sulphur pressed against a white-hot bar of cast iron give the purest form of sulphide of iron.

Sixth Synthetical Reaction.—The formation of iodide of iron (FeI_2). This has been described in connexion with iodine (p. 14).

Bromide of iron ($FeBr_2$), occasionally used in medicine, could be made, as might be expected, in the same way.

FERRIC SALTS.

Seventh Synthetical Reaction.—Pass chlorine (generated as usual, from black oxide of manganese and hydrochloric acid in a small flask or large test-tube) through sulphuric acid contained in a small bottle, and thence by the ordinary narrow glass tubing to the bottom of another test-tube containing twenty or thirty small iron tacks, the latter kept hot by a gas-flame; perchloride of iron (Fe_2Cl_6) is formed and condenses in the upper part of the tube as a mass of small dark iridescent crystals. When a tolerably thick mass of the salt is formed, break off the part of the tube containing it, being careful that the remaining corroded tacks are excluded, and place it in two or three ounces of water; the resulting solution, poured off from any pieces of glass, is a pure neutral solution of perchloride of iron, and will be serviceable to the student in performing analytical reactions.

The above experiment must be conducted in a cupboard having a draught outwards. In breaking up the tube, the student will notice the presence of small scales of a light buff colour adhering to the nails; they are crystals of ferrous chloride ($FeCl_2$). Solution of perchloride of iron evolves some hydrochloric acid on boiling, while a darker-coloured solution of peroxide of iron in perchloride of iron remains.

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Eighth Synthetical Reaction.—Dissolve iron tacks, in a test-tube, in hydrochloric acid; hydrogen escapes, and the solution on cooling, or on evaporation and cooling, deposits crystallized ferrous chloride ($FeCl_2, 4H_2O$).

Through a portion of the solution of ferrous chloride in a test-tube pass chlorine gas; the ferrous chloride becomes ferric chloride.

The excess of chlorine dissolved by the liquid in this experiment may be removed by ebullition; but the solution, though previously neutral, is more or less basic, for the reason just stated. The free chlorine may also be carried off by passing a current of air through the liquid for some time.

Ninth Synthetical Reaction.—To another portion of the solution of ferrous chloride, in a test-tube, add a little more hydrochloric acid; heat the liquid, and then drop in nitric acid until the black colour at first produced disappears; the resulting liquid is also solution of perchloride of iron.

$6FeCl_2$	+	$2HNO_3$	+	$6HCl$	=	$3Fe_2Cl_6$	+	N_2O_2	+	$4H_2O$
Ferrous chloride.		Nitric acid.		Hydrochloric acid.		Ferric chloride.		Nitric oxide.		Water.

This is the process for producing the *Liquor Ferri Perchloridi Fortior*, B. P. Diluted with 3 volumes of water this strong solution gives the *Liquor Ferri Perchloridi*, B. P.,—or with 3 volumes of rectified spirit the *Tinctura Ferri Perchloridi*, B. P. Practically it is impossible so to apportion the acids that a solution shall result containing neither excess of acid nor of metal, nor contain ferric nitrate. For most medicinal purposes, however, solution of perchloride of iron containing hydrochloric acid is said to be unobjectionable.

The black colour is due to solution of nitric oxide gas (N_2O_2) in a portion of the ferrous salt; it is decomposed by heat.

Tenth Synthetical Reaction.—Heat solution of ferrous sulphate with a few drops of sulphuric acid in a test-tube, and drop in nitric acid until the black colour first produced disappears; the resulting liquid, when made of a certain prescribed strength, is

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the solution of persulphate of iron (*Liquor Ferri Persulphatis*) of the British Pharmacopœia.

$$\underset{\text{Ferrous sulphate.}}{6FeSO_4} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Ferric sulphate.}}{3(Fe_2 3SO_4)} + \underset{\text{Nitric oxide.}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

The black colour, as in the eighth reaction, is due to a compound of ferrous salt with nitric oxide ($4FeSO_4 + N_2O_2$).

Eleventh Synthetical Reaction.—To a portion of the above solution of persulphate of iron, in a test-tube, add an alcoholic solution of acetate of potassium ($KC_2H_3O_2$), and well shake the mixture; a crystalline precipitate of sulphate of potassium (K_2SO_4) falls, and ferric acetate ($Fe_2 6C_2H_3O_2$) remains in solution, forming the *Tinctura Ferri Acetatis*, B. P.

$$\underset{\text{Ferric sulphate.}}{Fe_2 3SO_4} + \underset{\text{Acetate of potassium.}}{6KC_2H_3O_2} = \underset{\text{Sulphate of potassium.}}{3K_2SO_4} + \underset{\text{Ferric acetate.}}{Fe_2 6C_2H_3O_2}$$

Twelfth Synthetical Reaction.—To another portion of the above solution of persulphate of iron add excess of solution of soda; moist hydrated peroxide of iron is precipitated (*Ferri Peroxidum Humidum*, B. P.). Collect the precipitate on a filter, wash, and dry over hot water; the resulting powder (*Ferri Peroxidum Hydratum*, B. P.) is also peroxide of iron, but in a state of hydration differing from that of the moist oxide.

$$\underset{\text{Ferric sulphate.}}{Fe_2 3SO_4} + \underset{\text{Soda.}}{6NaHO} = \underset{\text{Ferric hydrate.}}{Fe_2 6HO} + \underset{\text{Sulphate of sodium.}}{3Na_2SO_4}$$

Either of the other alkalies (potash or ammonia) will produce a similar reaction; but soda is the one ordered in the British Pharmacopœia.

The *moist* oxide is an antidote to arsenic if administered directly after the poison has been taken. The nature of this action will be explained under Arsenicum.

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Moist hydrated peroxide of iron ($Fe_2 6HO$) loses water when dried and heated to low redness, peroxide of iron (Fe_2O_3) remaining,

$$Fe_2 6HO = Fe_2O_3 + 3H_2O,$$

the six univalent atoms of the HO, the characteristic elements of all hydrates, having been displaced by three bivalent oxygen atoms. But between the hydrate and oxide there obviously may be two compounds, oxy-hydrates, so to speak, ferric bodies in which 2HO is displaced by one of oxygen, O″, and in which 4HO is displaced by O''_2. The one, $Fe_2 04HO$, is a variety of brown iron ore; the other, $Fe_2O_2 2HO$, as well as occurring as an ore (needle iron ore), is the *Ferri Peroxidum Hydratum*, B. P.

"Ferri Peroxidum Humidum" ..	$'Fe'''_2$ 6HO
A variety of brown iron ore	$'Fe'''_2$ O″4HO
"Ferri Peroxidum Hydratum" ..	$'Fe'''_2$ $O''_2$2HO
Ferric oxide	$'Fe'''_2$ O''_3

The moist peroxide, when kept for some months, even under water, loses the elements of water, and is converted into an oxy-hydrate, having the formula ($Fe_4O_8 6HO$) (brown hæmatite), which is either a compound of the above oxy-hydrates ($Fe_2 04HO$)+ ($Fe_2O_2 2HO$), or is a definite intermediate oxy-hydrate: in the latter case we may yet expect to meet with oxy-hydrates having the formulæ $Fe_4 010HO$ and $Fe_4O_5 2HO$. These compounds may be thus formularized:—

Ferric hydrate (B. P.)	Fe_4 12HO
?	Fe_4 010HO
Brown iron ore	Fe_4 $O_2$8HO
Altered ferric hydrate.....	Fe_4 $O_3$6HO
Oxy-hydrate (B. P.)	Fe_4 $O_4$4HO
?	Fe_4 $O_5$2HO
Ferric oxide.....	Fe_4 O_6

Thirteenth Synthetical Reaction.—Repeat the previous reaction, introducing a little solution of citric or tartaric acid, or acid tartrate of potassium, before adding the alkali, and notice that now no precipitation of peroxide of iron occurs. This is due to the formation of double compounds, termed ammonio-citrate,

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potassio-citrate, ammonio-tartrate, and potassio-tartrate of iron. Such compounds, made with certain prescribed proportions of constituents, and the solutions evaporated to a syrupy consistence and spread on flat plates till dry, form the scaly preparations known as *Ferri et Ammoniæ Citras*, B. P., and *Ferri Potassio-tartras*, or, rather, *Ferrum Tartaratum*, B. P. A mixture of ferric citrate with citrate of quinine yields, by similar treatment, the well-known scales of *Ferri et Quinæ Citras*, B. P.

The above are the only officinal scaly preparations of iron. Many others of similar character might be formed. None crystallize or give other indications of definite chemical composition. Their properties are only constant so long as made with unvarying proportions of constituents. Their want of chemical compactness, the loose state in which the iron is combined, precludes their recognition as well-defined chemical compounds, yet possibly enables them to be more readily assimilated as medicines than some of the more definite salts of iron. *Vinum Ferri*, B. P., made by digesting iron wire in sherry wine, probably contains tartrate of potassium and iron, formed by action of the metal on the acid tartrate of potassium in presence of water. *Vinum Ferri Citratis*, B. P., is a solution of ammonio-citrate of iron in orange wine.

Fourteenth Synthetical Reaction.—To two-thirds of a small quantity of a solution of ferrous sulphate add a little sulphuric acid; warm, and gradually add nitric acid, as described in the tenth reaction, care being taken not to allow one drop more nitric acid than necessary to fall into the test-tube. Add now the other third of ferrous sulphate, and then precipitate with excess of an alkali; black oxide of iron (Fe_3O_4) in a hydrated state falls. It is so readily attracted by a magnet as to collect round the latter when immersed in the supernatant liquid. Hence the B. P. name, *Ferri Oxidum Magneticum*.

$$\underset{\text{Ferric sulphate.}}{Fe_2 3SO_4} + \underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Soda.}}{8NaHO} = \underset{\text{Blk. oxide of iron.}}{Fe_3O_4} + \underset{\text{Sulphate of sodium.}}{4Na_2SO_4} + \underset{\text{Water.}}{4H_2O}$$

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Fifteenth Synthetical Reaction.—Dissolve hydrated peroxide of iron in hydrochloric acid; solution of perchloride of iron is formed.

This is the old way of making solution of perchloride of iron; but, from the varying character of the acid and oxide as met with in commerce, the liquid is more likely to contain excess or deficiency of iron than the proper proportion.

Solution of perchloride of iron evaporated yields yellow crystals containing Fe_2Cl_6, $12H_2O$, or red crystals containing Fe_2Cl_6, $5H_2O$.

Sixteenth Synthetical Reaction.—Place a few iron tacks in dilute nitric acid and set aside; solution of pernitrate of iron is formed (Fe_26NO_3). This solution, made with care, and of a prescribed strength, forms the *Liquor Ferri Pernitratis*, B. P.

Fe_2	+	$8HNO_3$	=	Fe_26NO_3	+	$4H_2O$	+	N_2O_2
Iron.		Nitric acid.		Ferric nitrate.		Water.		Nitric oxide.

Seventeenth Synthetical Reaction.—Pass hydrogen gas, dried by sulphuric acid (in the manner described for chlorine, p. 76) over a small quantity of ferric oxide contained in a tube arranged horizontally, as in the fifth calcium synthetical reaction, p. 58, the oxide being kept hot by a gas-flame; oxygen is removed from the oxide by the hydrogen, steam escapes at the open end of the tube, and after a few minutes, when water ceases to be evolved, metallic iron, in a minute state of division, remains.

Fe_2O_3	+	H_6	=	Fe_2	+	$3H_2O$
Ferric oxide.		Hydrogen.		Iron.		Water.

While still hot throw the iron out into the air; it takes fire and falls to the ground as oxide.

$2Fe_2$	+	$3O_2$	=	$2Fe_2O_3$
Iron.		Oxygen.		Ferric oxide.

If the ferric oxide is reduced in a gun-barrel heated by a strong furnace, the particles of iron aggregate to some extent,

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and, when cold, are only slowly oxidized in dry air. This is *Fer réduit*, or *Quevenne's Iron*, the *Ferri pulvis*, or *Ferrum Redactum*, B. P. It is often administered in the form of lozenges (*Trochisci Ferri Redacti*, B. P.), gum and sugar protecting the iron from oxidation.

The spontaneous ignition of the iron in the above experiment is an illustration of the influence of minute division on chemical affinity. The action is the same as occurs whenever iron rusts, and the heat evolved and amount of oxide formed is not greater from a given quantity of iron; but the surface exposed to the action of the oxygen of the air is so enormous compared with the weight of the iron, that heat cannot be conducted away sufficiently fast to prevent elevation of temperature to a point at which the whole becomes incandescent. The amount of heat naturally existing in iron, oxygen, and oxide of iron, is, *cæteris paribus*, always the same, and the amount in the compound always less than in the same weight of its constituents; in the slow rusting of iron the escape of this heat occurs, but is not observed, because spread over a length of time; in the spontaneous ignition of reduced iron, the whole is evolved at one moment.

(*b*) *Reactions having Analytical Interest.*

(The iron occurring as a ferrous salt.)

First Analytical Reaction.—Pass sulphuretted hydrogen (H_2S) through a solution of a ferrous salt (*e. g.* ferrous sulphate) slightly acidulated by hydrochloric acid; no precipitate occurs.

This is a valuable negative fact, as will be evident presently.

Second Analytical Reaction.—Add sulphydrate of ammonium (AmHS) to solution of a ferrous salt; a black precipitate of ferrous sulphide (FeS) falls.

Third Analytical Reaction.—Add solution of ferrocyanide of potassium (yellow prussiate of potash) $K_4Fe''Cy_6$, or K_4Fcy'''', to solution of a ferrous salt; a precipitate ($K_2Fe''Fcy$) falls, at first white, but rapidly becoming blue, owing to absorption of oxygen.

Fourth Analytical Reaction.—To solution of a ferrous salt add ferridcyanide of potassium (red prussiate of potash), $K_6Fe'''_2Cy_{12}$,

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or K_6Fdcy, a precipitate (Fe''_3Fdcy) resembling prussian blue is thrown down.

Other Analytical Reactions.—The production of precipitates from ferrous solutions on the addition of alkaline carbonates, phosphates, and arseniates, as already described in the synthetical reactions of ferrous salts, are of course characteristic, and hence have a certain amount of analytical interest, but are inferior in this respect to the four reactions above mentioned.

The alkalies (solution of potash, soda, or ammonia) are incomplete precipitants of ferrous salts, and are therefore almost useless as tests. To solution of a ferrous salt add ammonia (AmHO); on filtering iron will still be found in the solution. To another portion of the ferrous solution add a few drops of nitric acid and boil; this converts the ferrous into ferric salt, and now alkalies will wholly remove the iron, as, indeed, has been already twice seen during the performance of the synthetical experiments.

In actual analysis, the separation of iron as ferric oxide is an operation of frequent performance. This is always accomplished by the addition of alkali, and, if the iron occurs as a ferrous salt, by previous ebullition with a little nitric acid.

(The iron occurring as a ferric salt.)

Sixth Analytical Reaction.—Through a ferric solution (perchloride, for example) pass sulphuretted hydrogen; a white precipitate of the sulphur of the sulphuretted hydrogen occurs, and the ferric is reduced to a ferrous salt, the latter remaining wholly in solution.

$$2Fe_2Cl_6 + 2H_2S = 4FeCl_2 + 4HCl + S_2$$

Seventh Analytical Reaction.—Add sulphydrate of ammonium to a ferric solution; the latter is reduced to the ferrous state, and black ferrous sulphide (FeS) is precipitated as in the second reaction, sulphur being set free.

Eighth Analytical Reaction.—To a ferric solution add ferro-

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cyanide of potassium (K_4FeCy_6, or K_4Fcy''''); a precipitate of prussian blue occurs ($Fe'''_4 3Fe''Cy_6$, or $Fe'''_4Fcy''''_3$).

Ninth Analytical Reaction.—To a ferric solution add solution of ferridcyanide of potassium; no precipitate occurs, but the liquid is darkened to a greenish or olive hue, according to the strength.

Tenth Analytical Reaction.—This is the production of a red precipitate of ferric hydrate, on the addition of alkalies to ferric salts, and is identical with the twelfth synthetical reaction.

This reaction illustrates the conventional character of the terms synthesis and analysis. It is of equal importance to the manufacturer and the analyst, and is synthetical or analytical according to the intention with which it is performed.

Other ferric reactions have occasional analytical interest. In neutral ferrie solutions the tannic acid in *tincture of galls* occasions a bluish-black inky precipitate, the basis of ordinary writing ink.——(The *Mistura Ferri Aromatica* of the British Pharmacopœia, made by digesting metallic iron in an infusion of various vegetable substances, contains tannate, or rather tannates of iron: it is commonly known in Ireland by the name of Heberden's Ink, after the physician by whom it was first used.)—— *Sulphocyanide of Potassium* (KCyS) causes the formation of ferric sulphocyanide, which is of a deep blood-red colour.——There is no ferric carbonate; alkaline carbonates cause the precipitation of ferric oxide, while carbonic acid escapes.

Cyanogen (NC or Cy'), ferro-cyanogen (FeC_6N_6, or $FeCy_6$, or simply FCy''''), ferridcyanogen (Fe_2Cy_{12}, or $Fdcy^{VI}$), and sulphocyanogen (NCS, or CyS, or Scy') are radicals which play the part of non-metallic elements, just as ammonium in its chemical relations resembles the metallic elements. They will be again referred to.

The student must on no account omit to write out equations or diagrams expressive of each of the reactions of iron. It is

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presumed that this has already been done immediately after each reaction has been performed.

APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS CONTAINING ONE OF THE METALS, ZINC, ALUMINIUM, IRON.

Add solution of ammonia gradually:—

A dirty-green precipitate indicates iron in the state of a ferrous salt.

A red precipitate indicates iron in the state of a ferric salt.

A white precipitate, insoluble in excess, indicates the presence of an aluminium salt.

A white precipitate, soluble in excess, shows zinc.

The result may be confirmed by the application of some of the other tests to fresh portions of the solution.

APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE, TWO, OR ALL THREE OF THE METALS, ZINC, ALUMINIUM, IRON.

Boil about half a test-tubeful of the solution with a few drops of nitric acid. This ensures the conversion of ferrous into ferric salts. Add now excess of ammonia, and shake the mixture. Filter.

<table>
<tr><td colspan="2">Precipitate
Al Fe,
Dissolve in HCl, add excess of KHO,
stir, filter.</td><td>Filtrate
Zn.
Test by AmHS,
white ppt.</td></tr>
<tr><td>Ppt.
Fe
(red ppt.).</td><td>Filtrate
Al.
Neutralize by HCl, and
then add excess of AmHO
(white ppt.).</td><td></td></tr>
</table>

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If iron is present, portions of the original solution must be tested by ferridcyanide of potassium for ferrous, and by ferrocyanide for ferric salts; dark-blue precipitates with both indicate both salts.

If no ferrous salt is present, ebullition with nitric acid is unnecessary. It is, perhaps, therefore advisable always to determine this point by previously testing a little of the original solution with ferridcyanide; if no precipitate occurs, the nitric-acid treatment may be omitted.

The following Table (*vide* Table opposite) is perhaps the best, but not the only adaptation of the ordinary reactions to systematic analysis. The student will notice that it is little else than the addition of the analytical scheme for the third group to that of the first two groups.

When a test gives no reaction, absence of the body sought for may be fairly inferred. If group-tests (that is, tests which precipitate a group of substances) give no reaction, the analyst is saved the trouble of looking for either member of that group.

ARSENICUM, ANTIMONY.

These two elements resemble metals in appearance and in the character of some of their compounds. But they are still more closely allied to the non-metals, especially to phosphorus and nitrogen. They are quinquivalent (As^{V}, Sb^{V}), but usually exert trivalent activity only ($^{II}As^{III}$, $^{II}Sb^{III}$). A few preparations of these elements are used in medicine; but all are more or less powerful poisons, and hence have considerable toxicological interest for the medical and pharmaceutical student.

ARSENICUM.

Symbol As. Atomic weight 75.

Arsenical ores are frequently met with in nature, the commonest being the arsenide and sulphide of iron (FeSAs). This mineral is roasted in a current of air, the oxygen of which, combining with the arsenicum, forms common white arsenic (As_2O_3) (*Acidum Arseniosum*, B. P.), which is condensed in chambers or long flues. *Realgar* (red algar) is the red native sulphide

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APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ANY OR ALL OF THE METALLIC ELEMENTS HITHERTO CONSIDERED.

Add AmCl; AmHO; AmHS; stir, filter.

<table>
<tr><td colspan="3">Precipitate
Fe Al Zn.
Wash, dissolve in HCl, boil with HNO_3, add KHO, stir, filter.</td><td colspan="4">Filtrate
Ba Ca Mg Am Na K.
Add Am_2CO_3, boil, filter.</td></tr>
<tr><td rowspan="2">Ppt.
Fe
(test orig. sol. by K_4FCy and K_6Fdcy).</td><td colspan="2">Filtrate
Al Zn.
Neutralize with HCl, add AmHO, stir, filter.</td><td colspan="2">Ppt.
Ba Ca.
Dissolve in $HC_2H_3O_2$, add K_2CrO_4, filter.</td><td colspan="2">Filtrate
Mg Am Na K.
Add Am_2HPO_4, stir, filter.</td></tr>
<tr><td>Ppt.
Al
(white).</td><td>Filtrate
Zn
add AmHS
(white ppt.).</td><td>Ppt.
Ba
(white).</td><td>Filtrate
Ca
add $Am_2C_2O_4$
(white ppt.).</td><td>Ppt.
Mg
(white).</td><td>Filtrate
Am Na K.
Evap., ignite, dissolve.
Na by flame; K by $PtCl_4$; orig. sol. for Am.</td></tr>
</table>

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(As_2S_2), and orpiment (*auripigmentum*, the golden pigment) the yellow native sulphide (As_2S_3) of arsenicum.

Reactions having (*a*) Synthetical and (*b*) Analytical Interest.

(*a*) *Reactions having Synthetical Interest.*

First Synthetical Reaction.—Boil a grain or two of powdered arsenic (As_2O_3) in water containing a little carbonate of potassium, and, if necessary, filter. This solution, when coloured with compound tincture of lavender, and containing 4 grains of arsenic per ounce, forms the *Liquor Arsenicalis*, B. P.

The arsenic does not decompose the carbonate of potassium in the above reaction, or only after long boiling. From concentrated solutions carbonic acid is more quickly eliminated. This solution may be preserved for analytical reactions.

Second Synthetical Reaction.—Boil arsenic with dilute hydrochloric acid. Such a solution made with prescribed proportions of acid and water, and containing 4 grains of arsenic (As_2O_3) per ounce, forms the *Liquor Arsenici hydrochloricus*, B. P.

No decomposition occurs in this experiment. The liquid is simply a solution of arsenic in dilute hydrochloric acid. This solution also may be preserved for analytical operations.

The student should boil arsenic in water only, and thus have an acid, alkaline, and aqueous solution for analytical comparison.

Third Synthetical Reaction.—Place a grain or two of arsenic at the bottom of a narrow test-tube, cover it with about half an inch or an inch of small fragments of dry charcoal, and hold the tube, nearly horizontally, in a flame, the mouth being loosely covered by the thumb. At first let the bottom of the tube project slightly beyond the flame, so that the charcoal may become nearly red-hot; then heat the bottom of the tube. The arsenic will sublime, become deoxidized by the charcoal, carbonic oxide

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being formed, and arsenicum deposited in the cool part of the tube as a dark mirror-like metallic incrustation.

There is a characteristic odour, resembling garlic, emitted during this operation, probably due to the trace of arsenicum which escapes from the tube, and which no doubt undergoes partial oxidation; for arsenic alone does not give this odour.

Metallic arsenicum may be obtained in large quantities by the above process if the operation be conducted in vessels of commensurate size. But performed with great care, in narrow tubes, using not charcoal alone, but *black flux* (a mixture of charcoal and carbonate of potassium obtained by heating acid tartrate of potassium in a test-tube or other closed vessel till no more fumes are evolved), the reaction has considerable analytical interest, the garlic odour and the formation of the mirror-like ring being highly characteristic of arsenicum. Compounds of mercury and antimony, however, give sublimates which may be mistaken for arsenicum.

Fourth Synthetical Reaction.—Boil a grain or two of arsenic with a few drops of nitric acid until red fumes cease to be evolved; evaporate the solution in a small dish to dryness, to remove excess of nitric acid; dissolve the residue in water: the product is Arsen'ic acid (H_3AsO_4).

Arsenic acid, when strongly heated, loses the element of water, and arsenic anhydride remains (As_2O_5).

Arsenic anhydride readily absorbs water and becomes arsenic acid (H_3AsO_4). Possibly arsenious anhydride (common white arsenic) does the same when dissolved in water, giving true arsenious acid (H_3AsO_3).

Salts analogous to arsenic acid are termed *arseniates*, and have the general formula R_3AsO_4. The ammonium arseniate ($Am_2H AsO_4$) has already been mentioned, p. 54.——Arsenic acid is used as an oxidizing agent in the manufacture of the well-known dye, magenta.

Salts analogous to arsenious acid are termed *arsenites*, and have the general formula R_3AsO_3. Arsenite and arseniate of sodium are used in the cleansing-operations of the calico-printer.

Fifth Synthetical Reaction.—Fuse a minute fragment of com-

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mon white arsenic (As_2O_3) with nitrate of sodium ($NaNO_3$) and carbonate of sodium (Na_2CO_3) on platinum foil; arseniate of sodium (Na_2HAsO_4) results.

$$\underset{\text{Arsenic.}}{3As_2O_3} + \underset{\text{Nitrate of sodium.}}{4NaNO_3} + \underset{\text{Carbonate of sodium.}}{4Na_2CO_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Arseniate of sodium.}}{6Na_2HAsO_4} + \underset{\text{Nitric oxide.}}{2N_2O_2} + \underset{\text{Carbonic acid gas.}}{4CO_2}.$$

Dissolved in water and crystallized the salt has the formula ($Na_2HAsO_4, 7H_2O$) (*Sodæ Arsenias*, B. P.). Heated to 300° F. the salt loses its water. A solution of the anhydrous salt (Na_2HAsO_4) in water forms the *Liquor Sodæ Arseniatis*, B. P.

Sixth Synthetical Reaction.—To solution of arseniate of sodium add solution of ferrous sulphate and a little acetate of sodium; a precipitate of ferrous arseniate occurs (Fe_32AsO_4) (*Ferri Arsenias*, B. P.).

$$\underset{\text{Arseniate of sodium.}}{2Na_2HAsO_4} + \underset{\text{Ferrous sulphate.}}{3FeSO_4} + \underset{\text{Acetate of sodium.}}{2NaC_2H_3O_2} = \underset{\text{Ferrous arseniate.}}{Fe_32AsO_4} + \underset{\text{Sulphate of sodium.}}{3Na_2SO_4} + \underset{\text{Acetic acid.}}{2HC_2H\,O_2}$$

Acetate of sodium is used here for a reason already given in connexion with phosphate of iron (p. 75).

(*b*) *Reactions having Analytical Interest.*

First Analytical Reaction.—Cut or break off portions of the tube containing the sublimate of arsenicum obtained in the third synthetical reaction, put them into a test-tube and heat the bottom of the latter, holding it nearly horizontally, and covering the mouth loosely with the finger or thumb; the arsenicum will absorb oxygen from the air in the tube, and the resulting arsenious anhydride be deposited on the cool part of the tube in characteristic octahedral crystals, more or less perfect.

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Prove that the crystals are identical in form with those of common white arsenic, by heating a grain or less of the latter in another test-tube, examining the two sublimates by a good lens or compound microscope.

The production of arsenicum and its subsequent oxidation are reactions perhaps not quite so delicate as some that follow, requiring more material for their satisfactory performance; yet the form of the crystals is characteristic, no other volatile body being likely to be mistaken for them; and in toxicological cases it is desirable to obtain the arsenicum in a similar state to that in which probably it originally exerted its effects; the processes alluded to are, therefore, of considerable importance. Moreover arsenicum, ready for sublimation to crystalline arsenic, is easily obtained from solution by the following reaction:—

Second Analytical Reaction.—Place a thin piece of copper, about a quarter inch wide and half inch long, in an acidified solution of arsenic, and boil; the arsenicum and an equivalent portion of the copper change places, the arsenicum being deposited on the plate in a metallic condition. Pour off the supernatant liquid from the copper, wash once or twice with water, dry the piece of metal by holding in the fingers and passing through a flame, and finally place it at the bottom of a clean dry narrow test-tube; sublime as described in the last reaction, again noticing the form of the resulting crystals.

This is commonly known as Reinsch's test for arsenicum. The tube may be reserved for subsequent comparison with an antimonial sublimate.

Copper itself frequently contains arsenicum, a fact that may not, perhaps, much trouble the student so long as he is performing operations in practical chemistry merely for educational purposes; but when he engages in the analysis of bodies of unknown composition, he must assure himself that neither his apparatus nor materials already contain the element of which he is in search.

Third Analytical Reaction—Marsh's test.—Generate hydrogen in the usual way from water by zinc and sulphuric acid, a bottle of about four or six ounces capacity being used, and a funnel-

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tube and short delivery-tube passing through the cork in the manner described on page 48. Dry the escaping hydrogen (except in rough experiments, when it is unnecessary) by adapting to the delivery-tube, by a pierced cork, a short piece of wider tubing containing fragments of chloride of calcium. To the opposite end of the wide tube fit a piece of narrow glass tubing eight or ten inches long, made of hard German glass, and having its aperture narrowed by drawing out in the flame of the blowpipe. When the hydrogen has been escaping sufficiently fast and for a sufficient number of minutes to warrant the operator in concluding that all the air originally existing in the bottle has been expelled, set light to the jet, and then pour eight or ten drops of the aqueous solution of arsenic, or three or four drops of the acid or alkaline solution of arsenic, previously prepared, into the funnel-tube, washing the liquid into the generating bottle with a little water. The arsenic is at once reduced to the state of arsenicum, and the latter combines with some of the hydrogen to form arseniuretted hydrogen gas (AsH_3). Immediately hold a piece of earthenware or porcelain (the lid of a porcelain crucible, if at hand) in the hydrogen jet at the extremity of the delivery-tube; a brown spot of condensed arsenicum is deposited. Collect several of these spots, and retain them for future comparison with antimonial spots.

The separation of arsenicum in the flame is due to the decomposition of the arseniuretted hydrogen by the heat of combustion. The cool porcelain at once condenses the arsenicum, and thus prevents its oxidation to white arsenic, which would otherwise take place at the outer edge of the flame.

Hold a small beaker or wide test-tube over the flame for a few minutes; a white film of arsenic will be slowly deposited, and may be further examined presently in contrast with a similar antimonial film.

During these experiments the student will have noticed the

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effect produced by the arsenical vapours on the colour of the hydrogen flame, giving it a dull livid bluish tint. This is characteristic.

Apply the flame of a gas-lamp to the middle of the hard glass delivery-tube; the arseniuretted hydrogen, as before, is decomposed by the heat, but the liberated arsenicum immediately condenses in the cool part of the tube beyond the flame, forming a dark metallic mirror. The tube may be removed and kept for comparison with an antimonial deposit.

Zinc, like copper, frequently itself contains arsenicum. When a specimen free from arsenicum is met with, it should be reserved for analytical experiments, or a quantity of guaranteed purity should be purchased of the chemical-apparatus maker. Sulphuric acid is more easily obtained free of arsenic.

In delicate and important applications of Marsh's test, magnesium may be substituted for zinc with safety, as arsenicum has not yet been, nor is it likely to be, found in magnesium. Magnesium in rods is convenient for this purpose, and may be obtained from most dealers in chemicals.

Arseniuretted hydrogen is decomposed by strong sulphuric acid; hence chloride of calcium is used in drying the gas.

Fourth Analytical Reaction—Fleitmann's test.—Generate hydrogen by heating to near the boiling-point a strong solution of caustic soda or potash and some pieces of zinc. Drop into the test-tube a little arsenical solution, and spread over the mouth of the tube a cap of filter-paper moistened with one drop of solution of nitrate of silver. Again heat the tube, taking care that the liquid itself shall not spurt up on to the cap; the arsenic is reduced to arsenicum, the latter uniting with the hydrogen as in Marsh's test, and the arseniuretted hydrogen passing up through the cap reacts on the nitrate of silver, causing the production of a purplish-black spot.

This reaction is particularly valuable, enabling the analyst to quickly distinguish arsenicum in the presence of its sister element antimony, which, although it combines with the hydrogen

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evolved from dilute acid and zinc, does not combine with the hydrogen evolved from solution of alkali and zinc, and therefore does not give the reaction just described.

The foregoing reactions are those of arsenicum, whether existing in the arsenious or arsenic condition, though from the latter the element is not generally eliminated so quickly as from the former. Of the following reactions, that with nitrate of silver at once distinguishes arsenious from arsenic acid.

Fifth Analytical Reaction.—Through an acidified solution of arsenious acid pass sulphuretted hydrogen; a yellow precipitate of sulphide of arsenicum or arsenious sulphide (As_2S_3) quickly falls. Add an alkaline hydrate or sulphydrate to the precipitate, it readily dissolves. The precipitate consequently would not be obtained on passing sulphuretted hydrogen through an alkaline solution of arsenic.

The only other metal which gives a yellow sulphide in an acid solution by action of sulphuretted hydrogen is cadmium; but this sulphide is insoluble in alkaline liquids.

Sixth Analytical Reaction.—Through an acidified solution of arsenic acid pass sulphuretted hydrogen; a yellow precipitate of arsenic sulphide (As_2S_5) slowly falls. This also is soluble in alkaline hydrates and sulphydrates.

The solubility of arsenious and arsenic sulphide in alkaline solutions is good evidence of the close chemical analogy between them and the corresponding oxygen compounds of arsenicum. The potassium arsenite and sulph-arsenite, arseniate and sulph-arseniate, have the composition represented by the following formulæ:—

$$K_3AsO_3 \qquad K_3AsO_4$$
$$K_3AsS_3 \qquad K_3AsS_4;$$

and the corresponding ammonium and sodium salts have a similar composition:—

$$6AmHS + As_2S_3 = 2Am_3AsS_3 + 3H_2S$$
$$6AmHS + As_2S_5 = 2Am_3AsS_4 + 3H_2S.$$

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Seventh Analytical Reaction.—To an aqueous solution of arsenic add a few drops of solution of sulphate of copper, and then cautiously add dilute solution of ammonia, drop by drop, until a green precipitate is obtained. The production of this precipitate is characteristic of arsenicum. To a portion of the precipitate add an acid; it dissolves. To another portion add alkali; it dissolves. These two experiments show the advantage of testing a suspected arsenical solution by litmus-paper before applying this reaction, and, if acid, cautiously adding alkali, and if alkaline, adding acid till neutrality is obtained.

The precipitate is arsenite of copper ($Cu''HAsO_3$) or Scheele's green. More or less pure, or mixed with acetate or, occasionally, carbonate of copper, it is very largely used, under many names, as a pigment, by painters, paper-stainers, and others.

Eighth Analytical Reaction.—Apply the test just described to solution of arsenic acid; a somewhat similar precipitate of arseniate of copper is obtained.

Ninth Analytical Reaction.—Repeat the seventh reaction, substituting nitrate of silver for sulphate of copper: in this case *yellow* arsenite of silver (Ag_3AsO_3) falls, also soluble in acids and alkalies.

Tenth Analytical Reaction.—Apply the test to a solution of arsenic acid; a *chocolate*-coloured precipitate of arseniate of silver (Ag_3AsO_4) falls.

While many reagents may be used for the detection of arsenicum, only nitrate of silver will readily indicate in which state of oxidation the arsenicum exists; for the two sulphides and the two copper precipitates, though differing in composition, resemble each other in appearance, whereas the two silver precipitates differ in colour as well as in composition.

The last four reactions may be performed with increased delicacy and certainty of result if the copper and silver reagents be previously prepared in the following manner:—To solution of sulphate of copper add ammonia until the precipitate at first

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formed is nearly all redissolved; filter and preserve the liquid as an arsenicum reagent, labelling it *ammonio-sulphate of copper*. Treat solution of nitrate of silver in the same way, and label it *ammonio-nitrate of silver*.

Soluble arseniates also give insoluble arseniates with barium, calcium, zinc, and some other metallic solutions.

Antidote.—In cases of poisoning by arsenic or arsenical preparations, the most effective antidote is recently precipitated moist hydrated peroxide of iron (*Ferri Peroxidum Humidum*, B. P.). It is perhaps best administered in the form of a mixture of solution of perchloride of iron (*Liquor Ferri Perchloridi*, B. P) with carbonate of sodium—two to three ounces of the former to about one ounce of the crystals of the latter. Instead of the carbonate of sodium about a quarter of an ounce of calcined magnesia (*Magnesia*, B. P.) may be used. These quantities will render at least ten grains of arsenic insoluble. Emetics should also be given, and the stomach-pump applied as quickly as possible.

The student should verify the above statements regarding the antidote for arsenic by mixing the various substances together, filtering, and testing the filtrate for arsenicum.

The action of the carbonate of sodium or the magnesia is to precipitate ferric hydrate ($Fe_2 6HO$), chloride of sodium (NaCl) or magnesium ($MgCl_2$) being formed, which are harmless, if not beneficial, under the circumstances. The reaction between the ferric hydrate and the arsenic results in the formation of insoluble ferrous arseniate.

$$\underset{\text{Ferric hydrate.}}{2(Fe_2 6HO)} + \underset{\text{Arsenic.}}{As_2 O_3} = \underset{\text{Ferrous arseniate.}}{Fe_3 2AsO_4} + \underset{\text{Water.}}{5H_2 O} + \underset{\text{Ferrous hydrate.}}{Fe2HO}.$$

Dried ferric hydrate (*Ferri Peroxidum Hydratum*, B. P) has no action on arsenic. Even the moist recently prepared hydrate ($Fe_4 12HO$) ceases to react with arsenic as soon as it has lost sufficient water to be wholly converted into the oxy-hydrate ($Fe_4 O_3 6HO$), a change which occurs though the hydrate be kept under water. According to T. and H. Smith this dehydration

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occurs gradually, but in an increasing ratio; so that after four months the power of the hydrate is reduced to one-half, and after five months to one-fourth.

ANTIMONY.

Symbol Sb (stibium). Atomic weight 122.

Antimony occurs in nature chiefly as sulphide, Sb_2S_3. The *crude* or *black antimony* of pharmacy is this native sulphide freed from earthy impurities by fusion: it has a striated, crystalline, lustrous fracture; subsequently powdered it forms the *Antimonium nigrum*, B. P. The metal is easily obtained from the sulphide by roasting, reducing with charcoal and carbonate of sodium. Metallic antimony is an important constituent of *Type-metal*, *Britannia metal* (tea and coffee pots, spoons, &c.), and the best varieties of *Pewter*. The old *pocula emetica*, or everlasting emetic cups, were made of antimony; wine kept in them for a day or two acquired a variable amount of emetic quality. The metal is not used in making the antimonial preparations of the Pharmacopœia, the sulphide alone being, directly or indirectly, employed for this purpose.

Antimony has very close chemical analogies with arsenicum.

Reactions having (*a*) Synthetical and (*b*) Analytical Interest.

(*a*) *Reactions having Synthetical Interest.*

First Synthetical Reaction.—Boil sulphide of antimony with hydrochloric acid in a test-tube; sulphuretted hydrogen is evolved and solution of chloride of antimony, $SbCl_3$, is obtained.

$$\underset{\text{Sulphide of antimony.}}{Sb_2S_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Chloride of antimony.}}{2SbCl_3} + \underset{\text{Sulphuretted hydrogen.}}{3H_2S}$$

This solution, cleared by subsidence, is what is commonly known as *Butter of antimony* (*Liquor Antimonii Chloridi*, B. P.). If pure sulphide has been used in its preparation the liquid is nearly colourless; but much of that met with in veterinary pharmacy is simply a by-product in the generation of sul-

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phuretted hydrogen from native sulphide of antimony and hydrochloric acid, and is more or less brown from the presence of chloride of iron. It not unfrequently darkens in colour on keeping; this is due to absorption of oxygen from the air and conversion of light-coloured ferrous into dark-brown ferric salt.

True butter of antimony ($SbCl_3$) is obtained on evaporating the above solution to a low bulk, and distilling the residue. The butter condenses as a white crystalline semitransparent mass in the neck of the retort; at the close of the operation it may be easily melted and run down into a bottle, which should be subsequently well stoppered.

Pentachloride of antimony ($SbCl_5$) also exists. It is a fuming liquid, obtained on passing chlorine over the lower chloride.

Second Synthetical Reaction.—Pour the solution of chloride of antimony produced in the last reaction into several ounces of water; a white precipitate of oxychloride of antimony ($2SbCl_3, 5Sb_2O_3$) is obtained, a small quantity of chloride of antimony remaining in the supernatant acid liquid.

$$\underset{\text{Chloride of antimony.}}{12SbCl_3} + \underset{\text{Water.}}{15H_2O} = \underset{\text{Oxychloride of antimony.}}{2SbCl_3, 5Sb_2O_3} + \underset{\text{Hydrochloric acid.}}{30HCl}$$

Well wash the precipitate with water, and then add solution of carbonate of sodium; the terchloride remaining with the oxide is thus decomposed, and oxide of antimony (Sb_2O_3) alone remains. This is *Antimonii Oxidum*, B. P. It is of a light buff colour.

$$\underset{\text{Oxychloride of antimony.}}{2SbCl_3, 5Sb_2O_3} + \underset{\text{Carbonate of sodium.}}{3Na_2CO_3} = \underset{\text{Oxide of antimony.}}{6Sb_2O_3} + \underset{\text{Chloride of sodium.}}{6NaCl} + \underset{\text{Carbonic acid gas.}}{3CO_2}$$

A higher oxide of antimony (Sb_2O_5), termed antimonic anhydride, corresponding with arsenic anhydride, is obtained on decomposing the pentachloride by water, or on boiling metallic antimony with nitric acid. The variety obtained from the chloride differs in saturating-power to that obtained from the metal, and is termed metantimonic acid (*μετὰ, meta*, beyond).

Third Synthetical Reaction.—Boil the oxide of antimony ob-

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tained in the previous reaction with about an equal quantity of cream of tartar and a little water, and filter; the resulting liquid contains the double tartrate of antimony and potassium ($KSbC_4H_4O_7$), potassio-tartrate of antimony, tartarated antimony, or tartar emetic (emetic, from ἐμέω, *emeo*, I vomit; tartar from Τάρταρος, *tartaros*, see page 27).

$$\underset{\text{Acid tartrate of potassium.}}{2KHC_4H_4O_6} + \underset{\text{Oxide of antimony.}}{Sb_2O_3} = \underset{\text{Tartar emetic.}}{2KSbC_4H_4O_7} + \underset{\text{Water.}}{H_2O}.$$

On evaporation the salt is obtained in crystals of the above composition, with a molecule of water of crystallization, forming the *Antimonium Tartaratum*, B. P.

Tartar emetic is soluble in water. Dissolved in sherry wine it forms the officinal *Vinum Antimoniale*, B. P. It may be externally applied as an ointment, *Unguentum Antimonii Tartarati*, B. P.

Fourth Synthetical Reaction.—Boil a few grains of sulphide of antimony with solution of soda in a test-tube, and filter; pour the filtrate into dilute sulphuric acid; a brownish-red precipitate of oxysulphide of antimony, the *Antimonium Sulphuratum*, B. P., falls. It is a mixture of sulphide of antimony (Sb_2S_3) with a small and variable amount of oxide (Sb_2O_3) and, occasionally, a higher sulphide (Sb_2S_5). The oxide results from the double decomposition of some of the sulphide of antimony and the soda.

This is one of the many varieties of *mineral kermes*, so called from their similarity in colour to the *insect kermes*. Kermes is the name, now obsolete, of the *Coccus Ilicis*, a sort of cochineal-insect, full of reddish juice, and used for dyeing from the earliest times.

The sulphides of antimony, like those of arsenicum, unite with metals to form soluble salts. In the hot solutions of these salts oxide and sulphide of antimony are soluble, and are partially re-precipitated in an indefinite state of combination on cooling, or wholly on the addition of an acid.

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$$\underset{\text{Sulphide of antimony.}}{2Sb_2S_3} + \underset{\text{Soda.}}{6NaHO} = \underset{\text{Sulph-antimonite of sodium.}}{2Na_3SbS_3} + \underset{\text{Oxide of antimony.}}{Sb_2O_3} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\text{Sulph-antimonite of sodium.}}{2Na_3SbS_3} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} = \underset{\text{Sulphate of sodium.}}{3Na_2SO_4} + \underset{\text{Sulphide of antimony.}}{Sb_2S_3} + \underset{\text{Sulphuretted hydrogen.}}{3H_2S}$$

These four synthetical reactions illustrate the officinal processes for the respective substances. The solution of chloride of antimony is only used in the preparation of oxide; the oxide, besides its use in the preparation of tartar emetic, is mixed with twice its weight of phosphate of lime to form *Pulvis Antimonialis*, B. P.

(*b*) *Reactions having Analytical Interest.*

First Analytical Reaction.—Dilute two or three drops of the solution of chloride of antimony with water; a precipitate of oxychloride occurs, the formation of which has been explained on page 98. The occurrence of this precipitate distinguishes antimony from arsenicum, but is a reaction that cannot be relied upon in analysis, because requiring the presence of too much material and the observance of too many conditions. Add now a sufficient quantity of hydrochloric acid to dissolve the precipitate, and boil a piece of copper in the solution as directed in the corresponding test for arsenicum (*vide* page 91); antimony is deposited on the copper. Wash, dry, and heat the copper in a test-tube as before; the antimony, like the arsenicum, is volatilized off the copper and condenses on the side of the tube as white oxide, but the sublimate, from its low degree of volatility, condenses close to the copper, and, moreover, is destitute of crystalline character, is amorphous (*a a*, without; *μορφὴ*, *morphē*, shape).

Shake out the copper and boil water in the tube for several minutes. Do the same with the arsenical sublimate similarly obtained. The deposit of arsenic slowly dissolves, and may be

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recognized in the solution by ammonio-nitrate of silver; the antimonial sublimate is insoluble.

Second Analytical Reaction.—Perform the experiments described under Marsh's test for arsenicum, carefully observing all the details there mentioned, but using a few drops of solution of chloride of antimony or tartar emetic instead of the arsenical solution. Antimoniuretted hydrogen (SbH_3), is formed and decomposed just as arseniuretted hydrogen was shown to be.

To one of the arsenicum spots on the porcelain lid add a drop of solution of "chloride of lime" (bleaching-powder); it quickly dissolves. Do the same with an antimony spot; it is unaffected.

Heat more quickly causes the volatilization of an arsenicum than an antimony spot; sulphydrate of ammonium more quickly dissolves the antimony than the arsenicum.

Boil water for several minutes in the beaker or wide test-tube containing the arsenious sublimate; it slowly dissolves and may be recognized in the solution by the yellow precipitate given on the addition of solution of ammonio-nitrate of silver. The antimonial sublimate, similarly treated, gives no similar reaction.

Pass a slow current of sulphuretted hydrogen through the delivery-tube removed from the Marsh's apparatus, and, when the air may be considered to have been expelled from the tube, gently heat that portion containing the deposit; the latter will be converted into a *yellow* sublimate of sulphide of arsenicum. Do the same with the antimony deposit; it is converted into *orange* sulphide of antimony, which, moreover, owing to inferior volatility, condenses nearer to the flame than sulphide of arsenicum does.

Pass dry hydrochloric acid gas through the two delivery-tubes. This is easily accomplished by adapting first one tube and then the other by a cork to a test-tube containing two or three lumps

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of common salt, on which a little sulphuric acid is poured, momentarily removing the cork for that purpose. The sulphide of antimony dissolves and disappears; the sulphide of arsenicum is unaffected.

Third Analytical Reaction.—Through an acidified antimonial solution pass sulphuretted hydrogen; an orange precipitate of amorphous sulphide of antimony falls. It has the same composition as the crystalline black sulphide (Sb_2S_3), into which, indeed, it is quickly converted by heat. Like sulphide of arsenicum, it is soluble in alkaline solutions.

A higher sulphide of antimony (Sb_2S_5), corresponding to the higher sulphide of arsenicum, exists. It is formed on passing sulphuretted hydrogen through an acidified solution of the higher chloride (Sb_2Cl_5), or on boiling black sulphide of antimony and sulphur with an alkali, and decomposing the resulting filtered liquid by an acid.

The arsenious and antimonious compounds only are employed in medicine. The arseniates and antimoniates are sometimes useful in analysis, and the antimonic chloride in chemical research. The higher compounds of both elements are noticed here chiefly to draw the attention of the student to the close analogy existing between arsenicum and antimony, an analogy carried out in the numerous other compounds of these elements.

The student should not omit to draw out equations or diagrams descriptive of each of the above reactions.

Antidote.—The introduction of poisonous doses of antimonials into the stomach is fortunately quickly followed by vomiting. If vomiting has not occurred, or apparently to an insufficient extent, any form of tannic acid may be administered (infusion of tea, nutgalls, cinchona, oak-bark, or other astringent solutions or tinctures), an insoluble tannate of antimony being formed, and absorption of the poison consequently somewhat retarded. The stomach-pump must be as quickly as possible applied.

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Recently precipitated moist hydrated peroxide of iron is also, according to T. and H. Smith, a perfect absorbent of antimony from its solutions, the chemical action being probably, they say, similar to that which takes place between arsenious acid and ferric hydrate. It may be given in the form of a mixture of perchloride of iron with either carbonate of sodium or magnesia.

The student should verify these statements by mixing together the various substances, filtering, and testing the filtrate for antimony in the usual manner.

APPLICATION OF THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ARSENICUM OR ANTIMONY ALONE.

Acidify the liquid with hydrochloric acid, and pass sulphuretted hydrogen through it:—

A *yellow* precipitate indicates arsenicum.

An *orange* precipitate indicates antimony.

The result may be confirmed by the application of other tests.

APPLICATION OF THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF BOTH ARSENICUM AND ANTIMONY.

If the precipitate by sulphuretted hydrogen is unmistakeably orange, antimony may be put down as present, and arsenicum only further searched for by the application of Fleitmann's test to the solution of the sulphides in aqua regia* freed from sulphur by boiling, or to the original solution.

Sulphide of antimony is far less readily soluble than sulphide

* *Aqua regia* is a mixture of two parts hydrochloric and one part nitric acid. It was so called, from its property of dissolving gold, the "king" of metals. Diluted with rather more than four times its bulk of water, it forms the *Acidum Nitro-hydrochloricum Dilutum*, B. P.

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of arsenicum in solution of carbonate of ammonium. But this fact is not of much analytical value; for the colour of the sulphides is already sufficient to distinguish the one from the other when they are unmixed; and when mixed, much sulphide of antimony will prevent a little sulphide of arsenicum from being dissolved by the alkaline carbonate, while much sulphide of arsenicum will carry a little sulphide of antimony into the solution. When the proportions are, apparently, from the colour of the precipitate, less wide, solution of carbonate of ammonium will be found useful in roughly separating the one sulphide from the other. On filtering and neutralizing the alkaline solution by an acid, the yellow sulphide of arsenicum is reprecipitated. The orange sulphide of antimony will remain on the filter.

If the precipitate by sulphuretted hydrogen is unmistakeably yellow, arsenicum may be put down as present, and any antimony detected by one of the following processes. These two processes are rather long, and require much care in their performance, but are indispensable, because at present we have no simple test for a small quantity of antimony in much arsenicum corresponding with Fleitmann's test for a small quantity of arsenicum in much antimony.

First process.—Generate hydrogen and pass it through a small wash-bottle containing solution of acetate of lead, to free the gas from any trace of sulphuretted hydrogen it may possess, and then through a dilute solution of nitrate of silver contained in a test-tube. When the apparatus is in good working order, pour into the generating-bottle the solution to be examined, adding it gradually to prevent violent action. After the gas has been passing for five or ten minutes, examine the contents of the nitrate-of-silver tube; arsenicum, if present, will be found in the solution,

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

while antimony, if present, will be found in the black precipitate that has fallen, according to the following equation:

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3.$$

The arsenicum may be detected in the clear, filtered, supernatant

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liquid by cautiously neutralizing with ammonia, yellow arsenite of silver being thrown out of solution. The antimony may be detected by washing the black precipitate, boiling it in an open dish with solution of tartaric acid, filtering, acidulating with hydrochloric acid, and passing sulphuretted hydrogen through the solution,—the orange sulphide of antimony being precipitated (Hofmann).

Second process.—Obtain the metallic deposit in the middle of the delivery-tube as already described under Marsh's test. Act on the deposit by sulphuretted hydrogen gas, and then by hydrochloric acid gas, as detailed in the second analytical reaction of antimony. If both arsenicum and antimony are present, the deposit, after the action of sulphuretted hydrogen, will be found to be of two colours, the yellow sulphide of arsenicum being usually further removed from the heated portion of the tube than the orange sulphide of antimony. Moreover the subsequent action of the hydrochloric acid gas causes the disappearance of the antimonial deposit, which is converted into chloride and carried off in the stream of gas.

The chief objection to this process is the liability of the operator mistaking sulphur, deposited from the sulphuretted hydrogen by heat, for sulphide of arsenicum. But the presence or absence of arsenicum is easily confirmed by Fleitmann's test, while the process is most useful for the detection of antimony.

The student may now proceed to the analysis of aqueous solutions of salts of any of the metallic elements hitherto considered. The method followed may be that for the separation of the previous three groups, sulphuretted hydrogen being first passed through the solution to throw out arsenicum and antimony. The whole scheme of analysis is given on the next page. Three or four solutions should be examined before proceeding to the last group of metals.

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APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ANY OR ALL OF THE METALLIC ELEMENTS HITHERTO CONSIDERED.

Acidify with HCl, and pass H_2S through the solution; filter.

<table>
<tr><td rowspan="4">Precipitate
As Sb.
Wash, separate by carb. ammon.; or dissolve in a few drops HCl and HNO_3, and examine as described on pages 104 and 105.</td><td colspan="4">Filtrate
Fe Al Zn Ba Ca Mg K Na Am.
Add Am Cl; Am HO; Am HS; stir; filter.</td></tr>
<tr><td colspan="2">Precipitate*
Fe Al Zn.
Wash, dissolve in HCl, boil with HNO_3, add KHO, stir, filter.</td><td colspan="2">Filtrate
Ba Ca Mg K Na Am.
Add Am_2CO_3, boil, filter.</td></tr>
<tr><td>Precipitate
Fe.
Examine orig. solution for ferrous or ferric state.</td><td>Filtrate
Al Zn.
Neut. by HCl, add AmHO, stir, filter.</td><td>Precipitate
Ba Ca.
Dissolve in H, $C_2H_3O_2$, add K_2CrO_4, filter.</td><td>Filtrate
Mg K Na Am.
Add Am_2HPO_4, shake, filter.</td></tr>
<tr><td>Ppt.
Al</td><td>Sol.
Zn</td><td>Precipitate
Ba</td><td>Filtrate
Ca</td><td>Precipitate
Mg</td><td>Filtrate
Am Na K (page 64).</td></tr>
</table>

* The student should carefully remember the colour of the various oxides, sulphides, &c. precipitated, as by so doing he may sometimes save much time. Thus, if the AmHS precipitate is white, iron cannot be present, and AmHO, for Al and Zn, may be at once added.

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COPPER, MERCURY, LEAD, SILVER.

These metals, like arsenicum and antimony, are precipitated from acidified solutions by sulphuretted hydrogen, in the form of sulphides; but the sulphides, unlike those of arsenicum and antimony, are insoluble in alkalies. The atoms of copper and mercury are bivalent, Cu″, Hg″; lead quadrivalent, Pb″″, frequently exerting only bivalent activity, ″Pb″; and silver univalent, Ag′.

COPPER.

Symbol Cu. Atomic weight 63·5.

The commonest ore of this metal is *copper pyrites*, a double sulphide of copper and iron; it is largely raised in Cornwall. Australia supplies *malachite*, a mixed carbonate and hydrate; much ore is also imported from South America. It is smelted in enormous quantities at Swansea, South Wales.

The alchemists termed this metal *Venus*, perhaps on account of the beauty of its lustre, and gave it the symbol ♀, a compound hieroglyphic indicating that they thought it a mixture of gold ☉ and a certain hypothetical substance called acrimony ✠, the corrosive nature of which was symbolized by the points of a Maltese cross. To this day the blue show-bottle in the shop-window of the chemist and druggist is occasionally ornamented by such a symbol, indicative, possibly, of the fact that the blue liquid in the vessel is a preparation of copper.

Sulphate of Copper (*Cupri Sulphas*, B. P.) ($CuSO_4$, $5H_2O$), *blue vitriol* or *bluestone*, is the only copper salt of much importance in Pharmacy. It is a by-product in silver-refining and in the roasting of copper pyrites. In the latter operation both the sulphide of iron and sulphide of copper are oxidized to sulphates; but the low red heat employed decomposes the sulphate of iron, while the sulphate of copper is unaffected. It is purified by crystallization from a hot aqueous solution. Sulphate of copper is also formed by dissolving in sulphuric acid the black oxide (CuO) obtained in annealing copper plates. The metal in the form of fine wire, about No. 25, is used in preparing *Spiritus Ætheris Nitrosi*, B. P.

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Reactions having (*a*) Synthetical and (*b*) Analytical Interest.

(*a*) *Synthetical Reactions.*

Beyond the formation of black oxide of copper by heating a piece of copper to redness in an open fire, of sulphate of copper by dissolving a few grains of black oxide of copper in two or three drops of sulphuric acid and a little water, and evaporation of the solution so that crystals may form on cooling, and the preparation of solution of ammonio-sulphate of copper, there are no copper-reactions having any synthetical interest for the medical or pharmaceutical student.

$$\underset{\text{Copper.}}{Cu_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Oxide of copper.}}{2CuO}$$

$$\underset{\text{Oxide of copper.}}{CuO} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sulphate of copper.}}{CuSO_4} + \underset{\text{Water.}}{H_2O}$$

(*b*) *Reactions having Analytical Interest.*

First Analytical Reaction.—Pass sulphuretted hydrogen through an acidified solution of a copper salt; black sulphide of copper (CuS) falls.

Second Analytical Reaction.—Add sulphydrate of ammonium to an aqueous copper solution; sulphide of copper is again precipitated, insoluble in excess.

Sulphide of copper is not altogether insoluble in sulphydrate of ammonium if free ammonia or much ammoniacal salt is present; it is quite insoluble in the fixed alkaline sulphides.

Third Analytical Reaction.—Immerse a piece of iron or steel, such as the point of a penknife or a piece of wire, in a few drops of a copper solution; the copper is deposited, of

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characteristic colour, an equivalent quantity of iron passing into solution.

By this reaction copper may be recovered on the large scale from waste solutions, old hoop iron &c. being thrown into the liquors.

Fourth Analytical Reaction.—Add ammonia to a copper solution; hydrate of copper (Cu2HO) of a light-blue colour is precipitated. Add now excess of ammonia; the precipitate is redissolved, forming a blue solution of ammonio-sulphate of copper, so deep in colour as to render ammonia an exceedingly delicate test for this metal.

Fifth Analytical Reaction.—Add solution of potash or soda to a copper solution; hydrate of copper is precipitated insoluble in excess. Boil the mixture in the test-tube; the hydrate loses the elements of water, and becomes the black anhydrous oxide (CuO).

Sixth Analytical Reaction.—Add solution of ferrocyanide of potassium (K_4Fcy) to an aqueous copper solution; a reddish-brown precipitate of ferrocyanide of copper (Cu_2Fcy) falls. This also is a delicate test for copper.

Seventh Analytical Reaction.—To a copper solution add solution of arsenic, and then cautiously neutralize with alkali; green arsenite of copper ($CuHAsO_3$) falls.

This precipitate has already been mentioned under arsenicum. An arsenicum salt is thus a test for copper, as a copper salt is for arsenicum,—a remark that may obviously be extended to most analytical reactions; for the body acted upon characteristically by a reagent is as good a test for the reagent as the reagent is for it; indeed it becomes a reagent when the other body is the object of search.

Antidotes.—In cases of poisoning by compounds of copper, iron filings should be administered, the action of which has just been explained (see third analytical reaction). Ferrocyanide of potas-

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sium may also be given (see sixth analytical reaction). Albumen forms, with copper, a compound insoluble in water; hence raw eggs should be swallowed, vomiting being induced or the stomach-pump applied as speedily as possible.

MERCURY.

Symbol Hg. Atomic weight 200.

Mercury occurs in nature as sulphide (HgS), forming the ore *cinnabar* (an Indian name expressive of something red), and is obtained from Spain, California, Eastern Hungary, China, Japan, and Peru. The metal is separated by roasting off the sulphur and then distilling, or distilling with lime, which combines with and retains the sulphur. The compounds of mercury used in medicine are all obtained from the metal. This rubbed with chalk or with confection of roses and powdered liquorice-root, or with lard and suet, until globules are no longer visible *to the eye*, is often used in medicine. The preparations are: the *Hydrargyrum cum Creta*, B. P., or "Grey Powder;" *Pilula Hydrargyri*, B. P., or "Blue Pill;" and *Unguentum Hydrargyri*, B. P., or "Blue Ointment." There is also a Compound Ointment, a Plaster of Mercury, a Plaster of Ammoniacum and Mercury, a Liniment and a Suppository, all Officinal. Their therapeutic effects are probably due to the black and red oxide which occur in them through the action of the oxygen of the air on the finely divided metal. The proportion of oxide or oxides varies according to the age of the specimen.

Mercury combines with other elements and radicals in two proportions: those salts &c. in which the other radicals are in the lesser amount are termed *mercurous*, the higher being *mercuric* compounds. Thus calomel (Hg_2Cl_2) is mercurous chloride, while corrosive sublimate ($HgCl_2$) is mercuric chloride. In every pair of mercury compounds the mercuric contains *twice* as much complementary radical, in proportion to the mercury, as the mercurous; or, which amounts to the same, a mercurous compound contains twice as much mercury to a given amount of other radical as the mercuric does to the same amount of radical. The atom of mercury is bivalent; in mercurous salts half of its power only is apparently exerted; but this will presently be explained.

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Reactions having (*a*) Synthetical and (*b*) Analytical Interest.

(*a*) *Synthetical Reactions.*

The two iodides.

First Synthetical Reaction.—Rub together a small quantity of mercury and iodine, controlling the rapidity of combination by adding a few drops of spirit of wine, which, by evaporation, carries off heat, and thus keeps down temperature. The product is either mercuric iodide, mercurous iodide, or a mixture of the two, as well as mercury or iodine if excess of either has been employed. If the two elements have been previously weighed in single atomic proportions, 200 of mercury to 127 of iodine (about 8 to 5), the mercurous or green iodide results, Hg_2I_2 (*Hydrargyri Iodidum Viride*, B. P.); if in the proportion of one atom of mercury to two atoms of iodine (200 to twice 127, or about 4 to 5), the mercuric or red iodide, HgI_2, results, an iodide that is also officinal, but made in another way.

Mercurous iodide is decomposed slowly by light, and quickly by heat, into mercuric iodide and mercury. Mercuric iodide is more stable, and may be sublimed in scarlet crystals without decomposition. In condensing, mercuric iodide is at first yellow, but soon acquires its characteristic scarlet colour. This may be shown by smearing or rubbing a sheet of white paper with the red iodide, and then holding the sheet before a fire or over a flame for a few seconds. As soon as the paper becomes hot the red instantly changes to yellow, and the salt does not quickly regain its red colour, even when cold, if the paper is carefully handled. But if a mark be made across the sheet by anything at hand, or the salt be pressed or rubbed in any way, the portions touched immediately return to the scarlet condition. According to Warington, this change is consequent upon rhomboidal crystals being converted into octohedra with a square base, and will serve as an illustration to the student of the influence of physical structure in causing colour. The yellow modification so acts on the rays of white light shining on its particles as to absorb the violet and reflect the

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complementary hue, the yellow, which entering the eye of the observer, strikes his retina, and thus conveys to the brain the impression of yellowness; and the red modification, though actually the same chemical substance, is sufficiently different in the structure of its particles as to absorb the green constituent of white light and reflect the complementary ray, the red.

Applying the atomic theory to the above iodides, the student will at once see why mercury and iodine should combine in the proportion of 200 of mercury with either 127 or 254 of iodine, and not with any intermediate quantity. For it is part of that theory that masses are composed of atoms, and that atoms are indivisible; and that the weight of the atom of mercury is to that of iodine as 200 is to 127. Mercury and iodine can only combine, therefore, in atomic proportions, atom to atom (which is the same as 200 to 127), or one atom to two atoms (which is the same as 200 to 254). To attempt to combine them in any intermediate proportion would be useless, a mere mixture of the two iodides would result. A higher proportion of mercury than 200 to 127 of iodine gives but a mixture of mercurous iodide and mercury; a higher proportion of iodine than 254 to 200 of mercury gives but a mixture of mercuric iodide and iodine. Or, for example, 200 grains of mercury mixed with, say, 200 of iodine would yield 139 grains of mercurous iodide, and 261 grains of mercuric iodide; for the 200 grains of mercury uniting with 127 grains of the iodine gives, for the moment, 327 grains of mercurous iodide and 73 grains of iodine still free. The 73 grains of iodine will immediately unite with 188 grains of the mercurous iodide (for if 127 of I require 327 of HgI to form HgI_2, 73 will require 188), and form 261 grains of mercuric iodide, diminishing the 327 grains of mercurous iodide to 139 grains.

THE TWO NITRATES.

Second Synthetical Reaction.—Mix a little nitric acid in a test-tube with four or five times its bulk of water, add a small globule of mercury, and set the tube aside for a few hours, applying no heat; solution of mercurous nitrate ($Hg_2 2NO_3$) will be formed, and nitric oxide (N_2O_2) evolved. The solution may be retained for subsequent analytical operations.

$$Hg_6 + 8HNO_3 = 3(Hg_2 2NO_3) + 4H_2O + N_2O_2.$$

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Third Synthetical Reaction.—Place mercury in strong nitric acid, and warm the mixture; mercuric nitrate is formed, and will be deposited in crystals as the solution cools. Retain the product for a subsequent experiment.

The mercuric nitrates vary somewhat in composition, according to the proportion, strength, and temperature of the acid used in their formation. A mercuric nitrate may be obtained having the formula $Hg2NO_3$.

Hg_3	+	$8HNO_3$	=	$3(Hg2NO_3)$	+	N_2O_2	+	$4H_2O$
Mercury.		Nitric acid.		Mercuric nitrate.		Nitric oxide.		Water.

The Pharmacopœia preparations of mercuric nitrate are *Liquor Hydrargyri Nitratis Acidus* and *Unguentum Hydrargyri Nitratis.*

THE TWO SULPHATES.

Fourth Synthetical Reaction.—Boil a few grains of mercury with a few drops of strong sulphuric acid in a test-tube; sulphurous acid gas (SO_2) is evolved, and mercuric sulphate (*Hydrargyri Sulphas*, B. P.) ($HgSO_4$) remains.

Hg	+	$2H_2SO_4$	=	$HgSO_4$	+	SO_2	+	$2H_2O$
Mercury.		Sulphuric acid.		Mercuric sulphate.		Sulphurous acid gas.		Water.

In chemical manufactories, secondary products, such as the sulphurous gas of the above reaction, are termed *by-products*, and, if of value, are utilized. In the present case the gas is of but little interest to the student, and is therefore allowed to escape. When pure sulphurous acid gas is required for experiments on the small scale, this would be the best method of making it, a delivery-tube being adapted by a cork to the mouth of the test-tube. The sulphate of mercury would then become the by-product.

The operation is completed and any excess of acid removed by evaporating the mixture of metal and acid to dryness, either in the open air or in a fume-chamber, sulphuric vapours being excessively irritating to the mucous membrane of the nose and throat; dry crystalline mercuric sulphate remains.

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Water decomposes mercuric sulphate into a soluble acid salt and an insoluble yellow oxysulphate ($Hg_3O_2SO_4$). The latter is called *Turpeth mineral*, from its resemblance in appearance to the powdered root of *Ipomea turpethum*, an Indian substitute for jalap. The yellow sulphate of mercury was formerly officinal, but is now seldom used.

Fifth Synthetical Reaction.—Rub a portion of the dry mercuric sulphate of the previous reaction with as much mercury as it already contains; the product, when the two have thoroughly blended, is mercurous sulphate (Hg_2SO_4): it may be retained for a subsequent experiment.

The exact proportion of mercury to sulphate is merely a matter of calculation; for the combining proportion of a compound is the sum of the combining proportions of its constituents. In other words, the combining weight of a molecule is simply the sum of the weights of its constituent atoms. In accordance with this rule, 296 of mercuric sulphate and 200 of mercury (about 3 to 2) are the exact proportions necessary to the formation of mercurous sulphate.

THE TWO CHLORIDES.

Sixth Synthetical Reaction.—Mix thoroughly a few grains of dry mercuric sulphate with about half its weight of chloride of sodium, and heat the mixture slowly in a test-tube; mercuric chloride ($HgCl_2$), or *corrosive sublimate* (*Hydrargyrum Perchloridum*, B. P.), sublimes and condenses in the upper part of the tube in crystals or a crystalline mass.

$HgSO_4$	+	$2NaCl$	=	$HgCl_2$	+	Na_2SO_4
Mercuric sulphate.		Chloride of sodium.		Mercuric chloride.		Sulphate of sodium.

If the mercuric sulphate contain any mercurous sulphate, some calomel will be formed. This result will be avoided if black oxide of manganese be previously mixed with the ingredients, the action of which is to eliminate chlorine from the excess of chloride of sodium used in the process, the chlorine converting any calomel into corrosive sublimate.

This operation must be conducted with care in a fume-

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chamber, as the vapour of corrosive sublimate is very acrid and poisonous. Its vulgar name is indicative of its properties. Ten grains of perchloride of mercury and the same quantity of chloride of ammonium in one pint of water, give the *Liquor Hydrargyri Perchloridi*, B. P.

Seventh Synthetical Reaction.—Mix a few grains of the mercurous sulphate of the fifth reaction with a fourth or a third of its weight of chloride of sodium, and sublime; mercurous chloride (Hg_2Cl_2) or calomel (*Hydrargyri Subchloridum*, B. P.) results.

$$\underset{\text{Mercurous sulphate.}}{Hg_2SO_4} + \underset{\text{Chloride of sodium.}}{2NaCl} = \underset{\text{Mercurous chloride.}}{Hg_2Cl_2} + \underset{\text{Sulphate of sodium.}}{Na_2SO_4}$$

The term calomel (καλὸς, *kalos*, good, and μέλας, *melas*, black) is said to relate to the use of the salt as a *good* remedy for *black* bile, but probably was simply indicative of the esteem in which black sulphide of mercury was held, the compound to which the name calomel was first applied.

If the mercurous sulphate contains mercuric sulphate, some mercuric chloride will also be formed. Corrosive sublimate is soluble in water, calomel insoluble; the presence of the former may therefore be detected by boiling the calomel in distilled water, filtering, and testing the filtrate by sulphuretted hydrogen or sulphydrate of ammonium as described hereafter. If corrosive sublimate is present, the whole bulk of the calomel must be washed with hot distilled water till the filtrate ceases to give any indications of mercury.

The above process is that of the British Pharmacopœia; but calomel may also be made by other methods. Calomel mixed with lard forms the *Unguentum Hydrargyri Subchloridi*, B. P., and with sulphurated antimony, guaiacum resin, and castor-oil the *Pilula Hydrargyri Subchloridi Composita*, B. P.

THE TWO OXIDES.

Eighth Synthetical Reaction.—Evaporate the mercuric nitrate of the third reaction to dryness in a small dish, and heat the residue till no more fumes are evolved; mercuric oxide (HgO),

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the Red Oxide of Mercury (*Hydrargyri Oxidum Rubrum*, B. P.), remains.

$$\underset{\text{Mercuric nitrate.}}{2(Hg2NO_3)} = \underset{\text{Mercuric oxide.}}{2HgO} + \underset{\text{Nitric peroxide.}}{2N_2O_4} + \underset{\text{Oxygen.}}{O_2}$$

The nitric constituents of the salt may be partially economized by previously thoroughly mixing with the dry mercuric nitrate as much mercury as it already contains, and then heating the mixture. In this case the free mercury is also converted into mercuric oxide. This is the officinal process.

$$\underset{\text{Mercuric nitrate.}}{(Hg2NO_3)} + \underset{\text{Mercury.}}{Hg} = \underset{\text{Mercuric oxide.}}{2HgO} + \underset{\text{Nitric peroxide.}}{N_2O_4}$$

Mercuric oxide mixed with yellow wax and oil of almonds yields the *Unguentum Hydrargyri Oxidi Rubri*, B. P. (1 part in 8).

Ninth Synthetical Reaction.—To solution of corrosive sublimate add solution of potash or soda, or lime-water; yellow oxide of mercury, or mercuric oxide (HgO), is precipitated.

$$\underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Hydrate of calcium.}}{Ca2HO} = \underset{\text{Mercuric oxide.}}{HgO} + \underset{\text{Chloride of calcium.}}{CaCl_2} + \underset{\text{Water.}}{H_2O}$$

Eighteen grains of corrosive sublimate to ten ounces of lime-water form the *Lotio Hydrargyri Flava*, B. P. The precipitate only differs physically from the red mercuric oxide; the yellow is in a more minute state of division than the red.

Tenth Synthetical Reaction.—To calomel add solution of potash or soda, or lime-water; black oxide of mercury, or mercurous oxide (Hg_2O), is produced.

Thirty grains of calomel to ten ounces of lime-water form the *Lotio Hydrargyri Nigra*, B. P.

$$\underset{\text{Mercurous chloride.}}{Hg_2Cl_2} + \underset{\text{Hydrate of calcium.}}{Ca2HO} = \underset{\text{Mercurous oxide.}}{Hg_2O} + \underset{\text{Chloride of calcium.}}{CaCl_2} + \underset{\text{Water.}}{H_2O}$$

(*b*) *Analytical Reactions.*

MERCUROUS OR MERCURIC SALTS.

First Analytical Reaction.—The Copper Test.—Deposition of

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mercury upon, and sublimation from copper. Place a small piece of bright copper, about half an inch long and a quarter of an inch broad, in a solution of any salt of mercury, mercurous or mercuric, and heat in a test-tube; the copper becomes coated with mercury in a fine state of division. Pour away the supernatant liquid from the copper, wash the latter once or twice by pouring water into, and then out of, the tube, remove the metal, take off excess of water by gentle pressure in a piece of filter-paper, dry the copper by passing it quickly through a flame holding it by the fingers; finally, place the copper in a dry narrow test-tube, and heat to redness in a flame; the mercury sublimes and condenses as a white sublimate of minute globules on the cool part of the tube outside the flame. The globules aggregate on gently pressing with a glass rod, and are especially visible where flattened between the rod and the side of the test-tube.

This is a valuable test, for several reasons:—It is very delicate when performed with care. It brings the element itself before the observer, being one which from its metallic lustre and fluidity cannot be mistaken for any other. It separates the element both from mercurous and mercuric salts. Mercury can in this way be readily eliminated in the presence of most other substances, organic or inorganic.

In performing the test the absence of any quantity of nitric acid must be ensured, or the copper itself will be dissolved. This may be avoided by adding an alkali until a slight permanent precipitate appears, and then reacidifying with a few drops of hydrochloric acid, or, if that acid cause a precipitate, with acetic acid; or, if acetic acid fail to redissolve the precipitate, with a very few drops of nitric acid.

MERCURIC SALTS.

Second Analytical Reaction.—To a few drops of a solution of a mercuric salt (corrosive sublimate, for example) add solution of iodide of potassium, drop by drop; a precipitate of mercuric iodide, HgI_2, forms, and at first quickly redissolves, but is

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permanent when sufficient iodide of potassium has been added. Continue the addition of iodide of potassium; the precipitate is once more redissolved.

This reaction has considerable synthetical interest. When first precipitated, mercuric iodide is yellowish red, but soon changes to a beautiful scarlet. It is soluble either in solution of the mercuric salt or in solution of iodide of potassium. Hence equivalent proportions of the two salts must be used in making this preparation ($HgCl_2=271$; $2KI=332$; about 4 to 5). This solubility renders the detection of a small quantity of a mercurial salt by iodide of potassium, or a small quantity of an iodide by a mercuric solution, difficult, and hence lessens the value of the reaction as a test. Mercuric iodide thus made has the same composition as that prepared by direct combination of its elements. The method by precipitation is the one adopted in the British Pharmacopœia (*Hydrargyri Iodidum Rubrum*, B. P.).

$HgCl_2$	+	$2KI$	=	HgI_2	+	$2KCl$
Mercuric chloride.		Iodide of potassium.		Mercuric iodide.		Chloride of potassium.

Precipitated red iodide of mercury mixed with white wax, lard, and oil forms the *Unguentum Hydrargyri Iodidi Rubri*, B. P.

Third Analytical Reaction.—To a solution of mercuric salt add solution of ammonia until the mixture, after well stirring, smells of ammonia; the body known as "white precipitate," the old ammonio-chloride, or "amido-chloride of mercury," falls.

Performed in a test-tube, this reaction is a very delicate test of the presence of a mercuric salt; performed in large vessels, the mercuric salt being corrosive sublimate, it is the usual and the Pharmacopœial process for the preparation of "white precipitate," now known as Ammoniated Mercury (*Hydrargyrum Ammoniatum*, B. P.). The precipitate is considered to be the chloride of mercuric ammonium ($NH_2Hg''Cl$)—that is, chloride of ammonium (NH_4Cl) in which two atoms of univalent hydrogen are replaced by one atom of bivalent mercury.

$HgCl_2$	+	$2NH_4HO$	=	$NH_2Hg''Cl$	+	NH_4Cl	+	$2H_2O$
Mercuric chloride.		Ammonia		"White precipitate."		Chloride of ammonium.		Water.

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An ointment of this compound is officinal (*Unguentum Hydrargyri Ammoniati*, B. P.).

The formation of "white precipitate" in the above manner is good evidence that aqueous solution of ammonia is not merely ammoniacal gas dissolved in water. For when ammoniacal gas combines with corrosive sublimate, an entirely different compound results, which moreover, by the subsequent action of water, does not simply yield "white precipitate." If not a mere solution, then it is probably a chemical combination of either one molecule of the gas with water to form AmHO,

$$NH_3+\left.\begin{matrix}H\\H\end{matrix}\right\}O=\left.\begin{matrix}NH_4\\H\end{matrix}\right\}O,$$

or of two molecules of the gas to form Am_2O,

$$2NH_3+\left.\begin{matrix}H\\H\end{matrix}\right\}O=\left.\begin{matrix}NH_4\\NH_4\end{matrix}\right\}O$$

Analogy with solution of potash (KHO) and soda (NaHO), and with solution of sulphydrate of ammonium (AmHS), leads to the belief that solution of ammonia contains AmHO.

$\left.\begin{matrix}K\\H\end{matrix}\right\}O$ Hydrate of potassium (potash). $\left.\begin{matrix}Na\\H\end{matrix}\right\}O$ Hydrate of sodium (soda). $\left.\begin{matrix}Am\\H\end{matrix}\right\}O$ Hydrate of ammonium (ammonia).

$\left.\begin{matrix}K\\H\end{matrix}\right\}S$ $\left.\begin{matrix}Na\\H\end{matrix}\right\}S$ $\left.\begin{matrix}Am\\H\end{matrix}\right\}S$ Sulphydrates of potassium, sodium, and ammonium.

Fourth Analytical Reaction.—Pass sulphuretted hydrogen through a mercuric solution; a black precipitate of mercuric sulphide (HgS) falls.

Sulphuretted hydrogen also precipitates mercurous sulphide (Hg_2S) from mercurous solutions; and in appearance the precipitates are alike; hence the reagent does not distinguish between mercurous and mercuric salts. But in the course of systematic analysis, mercuric salts are thrown down from solution as sulphide after mercurous salts have been otherwise removed; hence the necessity of noticing this reaction here. The sulphides are insoluble in sulphydrate of ammonium.

An insufficient amount of the gas gives a white or coloured precipitate of mixed sulphide and oxide.

Ethiop's Mineral, the *Hydrargyri Sulphuretum cum Sulphure*, is a mixture of sulphide of mercury and sulphur, obtained on

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triturating the elements in a mortar till globules are no longer visible. Its name is probably in allusion to its similarity in colour to the skin of the Æthiop. It was formerly officinal.

Vermilion is mercuric sulphide, prepared by sublimation.

MERCUROUS SALTS.

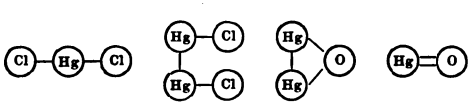
Fifth Analytical Reaction.—To a solution of a mercurous salt (the mercurous nitrate obtained in the second reaction, for example) add hydrochloric acid, or any soluble chloride; a white precipitate of calomel (Hg_2Cl_2) occurs.

This reaction was formerly officinal in the Dublin Pharmacopœia as a process for the preparation of calomel.

Sixth Analytical Reaction.—To solution of a mercurous salt add iodide of potassium; green mercurous iodide (Hg_2I_2) is precipitated.

Seventh Analytical Reaction.—To a mercurous salt, dissolved or undissolved (calomel), add ammonia; black chloride of mercurous ammonium ($NH_2Hg'_2Cl$) is formed.

The mercury in this black precipitate is doubtless in the same condition as in mercurous chloride, iodide, sulphide, or oxide, a condition which enables its atom to play an apparently univalent part. Instead of each of the atoms being independent and exerting bivalent activity, or of their affinities being wholly engaged with other atoms, they are united with each other to the extent of one-half of their affinities, the other half of each enabling the conjoined atoms to act as a single atom. The following imaginary picture of molecules of mercurous and mercuric salts (see also Frankland's 'Lecture Notes,' p. 168) will illustrate this matter:—



Mercuric chloride. Mercurous chloride. Mercurous oxide. Mercuric oxide.

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The elimination of mercury in the actual state of metal by the copper test, coupled with the production or non-production of a white precipitate on the addition of hydrochloric acid to the original solution, is usually sufficient evidence of the presence of mercury and its existence as a mercurous or mercuric salt. But other tests may sometimes be applied with advantage. Thus metallic mercury is deposited on placing a drop of the solution on a plate of gold (sovereign, half-sovereign, &c.), and touching the drop and the edge of the plate simultaneously with a key; an electric current passes, under these circumstances, from the gold to the key, and thence through the liquid to the gold, decomposing the salt, the mercury of which forms a white metallic spot on the gold, while the other elements go to the iron. This is called *the galvanic test*, and is useful for clinical purposes.—— Solution of stannous chloride ($SnCl_2$), from the readiness with which the salt forms stannic chloride ($SnCl_4$), gives a white precipitate of mercurous chloride in mercuric solutions, and quickly still further reduces this mercurous chloride or other mercuric salts to a greyish mass of finely divided mercury; this is the old *magpie test*, probably so called from the white and grey appearance of the precipitate.——Confirmatory tests for mercuric and mercurous salts will be found in the action of solution of potash, solution of soda, lime-water, solution of ammonia, and solution of iodide of potassium. (*Vide* pages 116 to 120.)—— The alkaline carbonates produce yellowish mercurous carbonate, and brownish-red mercuric carbonate, both of them unstable.——Alkaline bicarbonates give mercurous carbonate and mercuric oxychloride.——Yellow chromate of potassium (K_2CrO_4) gives, with mercurous salts, a red precipitate of mercurous chromate (Hg_2CrO_4).——All compounds of mercury are volatilized by heat.

Antidote.—Albumen gives a white precipitate with solution of mercuric salts; hence the importance of administering white of

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egg while waiting for a stomach-pump in case of poisoning by corrosive sublimate.

LEAD.

Symbol Pb. Atomic weight 207.

The ores of lead are numerous, but the one from which the metal is chiefly obtained is the sulphide of lead (PbS), or *galena* (from γαλέω, *galeō*, I shine, in allusion to the lustrous metallic appearance of the mineral). The ore is first roasted in a current of air; much sulphur is thus burnt off as sulphurous acid gas, while some of the metal is converted into oxide and a portion of the sulphide oxidized to sulphate. Oxidation being stopped when the mass presents certain appearances, the temperature is raised, and the oxide and sulphate, reacting on undecomposed sulphide, yield the metal and much sulphurous acid gas:—

$$2PbO + PbS = Pb_3 + SO_2$$
$$PbSO_4 + PbS = Pb_2 + 2SO_2.$$

The uses of lead are well known. Alloyed with arsenicum it forms common *shot*; with antimony gives *type-metal*; with tin *solder*; and in smaller quantities enters into the composition of *Britannia metal*, *pewter*, &c.

The salts of lead used in pharmacy and all other preparations of lead are obtained, directly or indirectly, from the metal itself. Heated in a current of air, lead combines with oxygen and forms oxide of lead (PbO) (*Plumbi Oxidum*, B. P.), a yellow powder (*massicot*), or, if fused and solidified, a brighter yellow, or reddish-yellow heavy mass of bright scales, termed *litharge* (from λίθος, *lithos*, a stone, and ἄργυρος, *arguros*, silver). It is from this oxide that the chief lead compounds are obtained. Oxide of lead, by further roasting in a current of air, yields *red lead* (or *minium*), Pb_3O_4, or $PbO_2 2PbO$. Both oxides are much used by painters, paper-stainers, and glass-manufacturers. *White lead* is a mixture of carbonate ($PbCO_3$) and hydrate of lead (Pb2HO) (commonly 2 molecules of the former to 1 of the latter), usually ground up with about 7 per cent. of linseed oil; it is made by exposing lead, cast in spirals or little gratings, to the action of air, acetic acid fumes, and carbonic acid, the latter generated from decaying vegetable matter (spent tan &c); basic acetate of lead slowly but continuously forms, and is as continuously decomposed by the carbonic acid with production of basic carbonate, or *dry*

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white lead (*Plumbi Carbonas*, B. P.). The latter is the active constituent of *Unguentum Plumbi Carbonatis*, B. P., the old *Unguentum Cerussæ*.

Lead compounds are poisonous, producing saturnine colic, or even paralysis. These effects are termed *saturnine* from an old name of lead, *Saturn*. The alchemists called lead Saturn, first, because they thought it the oldest of the seven then known metals, and it might therefore be compared to Saturn, who was supposed to be the father of the gods; and secondly, because its power of dissolving other metals recalled a peculiarity of Saturn, who was said to be in the habit of devouring his own children.

The atom of lead is quadrivalent (Pb''''); but in most of the compounds used in medicine it exerts bivalent activity only, one half of its energy being latent (''Pb'').

Reactions having (*a*) Synthetical and (*b*) Analytical Interest.

(*a*) *Synthetical Reactions.*

First Synthetical Reaction.—Place a few grains of oxide of lead in a test-tube, add about twice its weight of acetic acid, and boil; the oxide dissolves and forms a solution of acetate of lead ($Pb2C_2H_3O_2$). When cold, or on evaporation, crystals of acetate of lead ($Pb2C_2H_3O_2$, $3H_2O$) are deposited.

$$\underset{\text{Oxide of lead.}}{PbO} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} = \underset{\text{Acetate of lead.}}{Pb2C_2H_3O_2} + \underset{\text{Water.}}{H_2O}$$

This is the B. P. process for *Plumbi Acetas*. The salt is vulgarly termed *Sugar of Lead*, from its sweet taste. Besides its direct use in pharmacy, it forms three-fourths of the *Pilula Plumbi cum Opio*, B. P., is the chief constituent of *Unguentum Plumbi Acetatis*, and an ingredient in *Suppositoria Plumbi Composita*.

Second Synthetical Reaction.—Boil acetate of lead with about four times its weight of water and rather more than two-thirds its weight of oxide of lead; the resulting filtered liquid is solution of subacetate of lead, *Liquor Plumbi Subacetatis*, B. P.

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A similar solution was used by M. Goulard, who called it *Extractum Saturni*, and drew attention to it in 1770. It is now frequently termed *Goulard's Extract*. A more dilute solution, 1 in 80, is also officinal in the British Pharmacopœia, under the name of *Liquor Plumbi Subacetatis Dilutus*. The latter is commonly known as *Goulard Water*. The stronger solution is the chief ingredient in *Unguentum Plumbi Subacetatis Compositum*, B. P., a slight modification of the old *Goulard's Cerate*.

The officinal subacetate of lead is not a definite chemical salt. It is probably a mixture of two subacetates of lead, which are well-known crystalline compounds, and which the author is disposed to regard as having a constitution similar to that he has already indicated for some other salts (see Iron, Antimony, and Bismuth).

B. P.	Acetate of lead (3 molecules)	$Pb_3\ 6C_2H_3O_2$
	Pyro-oxyacetate of lead	$Pb_3O4C_2H_3O_2$
	Goulard's oxyacetate of lead	$Pb_3O2C_2H_3O_2$
	Oxide of lead (3 molecules)	Pb_3O_3

Third Synthetical Reaction.—Digest a few grains of red lead in nitric acid and water; nitrate of lead ($Pb2NO_3$) is formed, and remains in solution, while puce-coloured oxide of lead, or plumbic peroxide (PbO_2) is precipitated.

Nitrate of lead (*Plumbi Nitras*, B. P.) could be more directly made by dissolving litharge (PbO) in nitric acid; but the above reaction serves to bring before the student two other oxides of lead, namely red lead (Pb_3O_4) and peroxide of lead (PbO_2). In the latter oxide the quadrivalent character of lead is obvious. Nitrate of lead is used officinally in preparing iodide of lead.

Fourth Synthetical Reaction.—To solution of nitrate of lead add solution of iodide of potassium; a precipitate of iodide of lead (PbI_2) falls (*Plumbi Iodidum*, B. P.).

$Pb2NO_3$	+	$2KI$	=	PbI_2	+	$2KNO_3$
Nitrate of lead.		Iodide of potassium.		Iodide of lead.		Nitrate of potassium.

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Iodide of lead is the chief ingredient in *Emplastrum Plumbi Iodidi*, B. P., and *Unguentum Plumbi Iodidi*, B. P.

Heat the iodide of lead with the supernatant liquid, and, if necessary, filter; the salt is dissolved, and again separates in golden crystalline scales as the solution cools.

Fifth Synthetical Reaction.—Boil together in a small dish a few grains of very finely powdered oxide of lead, about two and a half times its weight of olive oil and some water, well stirring the mixture, and replacing water as it evaporates; the product is a white mass of oleate of lead (*Emplastrum Plumbi*, B. P.), glycerin remaining in solution in the water.

The action between the oxide of lead and olive-oil is slow, requiring several hours for its completion; but a sufficient amount of plaster to illustrate the operation is formed in a much shorter time. Lead plaster is a constituent of eleven of the fourteen plasters mentioned in the British Pharmacopœia.

The glycerin may be obtained by treating the aqueous product of the above reaction with sulphuretted hydrogen to remove a trace of lead, then digesting with animal charcoal, filtering, and evaporating. But on the large scale glycerin is now usually produced as a by-product in the manufacture of candles; for its elements are found in all vegetable and animal fats. Oils and fats are, apparently, almost as simple in constitution as ordinary inorganic salts. Just as potash (KHO) may be regarded as water (HHO) in which one atom of hydrogen is displaced by the univalent radical potassium, so glycerine may be regarded as a triple molecule of water ($H_3H_3O_3$), in which three atoms of hydrogen are displaced by the trivalent radical (C_3H_5) of glycerin. Or as the formula of potash is written KHO, and slaked lime Ca2HO, so glycerin may be written C_3H_53HO. And just as acetate of potassium is regarded as a compound of potassium with the characteristic elements of all acetates ($KC_2H_3O_2$), and oleate of potassium (soft soap) as a compound of potassium with the grouping characteristic of oleates ($KC_{18}H_{33}O_2$), and, similarly, acetate of calcium as having the formula $Ca2C_2H_3O_2$, and oleate of calcium as $Ca2C_{18}H_{33}O_2$, so olive-oil may be regarded as chiefly consisting of oleate of the trivalent radical C_3H_5, above referred to, and as having the formula $C_3H_53C_{18}H_{33}O_2$. Berthelot

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has succeeded in preparing this body artificially from oleic acid and glycerin; and it is said to be identical with the pure olein of olive- and of other fixed oils. Hard fats chiefly consist of stearin —that is, of tristearate of the glycerin-radical. Mr. Wilson, of Price's Candle Company, obtains stearic and oleic acids and glycerin by simply passing steam, heated to 500° or 600° F., through melted fat. Both the glycerin and fat acids distil over in the current of steam, the glycerin dissolving in the condensed water, the fat-acids floating on the aqueous liquid. Besides glycerin itself (*Glycerinum*, B. P.), there are several officinal preparations of glycerin, solutions of carbolic, gallic, and tannic acids, and borax in glycerin, and a sort of mucilage of starch in glycerin (*Glycerinum Acidi Carbolici*, *Glycerinum Acidi Gallici*, *Glycerinum Acidi Tannici*, *Glycerinum Amyli*, and *Glycerinum Boracis*).

Olive-oil boiled with solution of potash yields potassium soap, or *soft soap* (*Sapo Mollis*, B. P.); with soda, sodium soap, or *hard soap* (*Sapo Durus*, B. P.); mixed with ammonia, an ammonium soap (*Linimentum Ammoniæ*, B. P.); and with lime-water, a calcium soap (*Linimentum Calcis*, B. P.),—all oleates, chiefly, of the respective basylous radicals.

(*b*) *Reactions having Analytical Interest.*

First Analytical Reaction.—To solution of a lead salt (acetate, for example) add hydrochloric acid; a white precipitate of chloride of lead ($PbCl_2$) is obtained. Boil the precipitate with much water; it dissolves, but, on the solution cooling, is redeposited in small acicular crystals. Filter the cold solution, and pass sulphuretted hydrogen through it; a black precipitate (sulphide of lead, PbS) shows that the chloride of lead is soluble to some extent in cold water.

A white precipitate on the addition of hydrochloric acid, soluble in hot water, and blackened by sulphuretted hydrogen, sufficiently distinguishes lead salts from those of other metals, but the non-production of such a precipitate does not prove the absence of a small quantity of lead, chloride of lead being slightly soluble in cold water. Hydrochloric acid will presently be found to be a useful but not a delicate test for lead.

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Second Analytical Reaction.—Through a very dilute solution of a lead salt pass sulphuretted hydrogen; a black precipitate of sulphide of lead (PbS) occurs.

This is a very delicate test. Should a trace of lead be present in water used for drinking-purposes, sulphuretted hydrogen will detect it. On passing the gas through a pint of such water, a brownish tint, more or less deep, is produced. If the tint is scarcely perceptible, set the liquid aside for a day; the gas will become decomposed and a thin layer of sulphur be found at the bottom of the vessel, white, if no lead be present, but more or less brown if it contain sulphide of lead.

Third Analytical Reaction.—To solution of a lead salt add sulphydrate of ammonium; a black precipitate of sulphide of lead falls, insoluble in excess.

Fourth Analytical Reaction.—To solution of a lead salt add solution of chromate of potassium (K_2CrO_4); a yellow precipitate of chromate of lead ($PbCrO_4$) is formed, insoluble in weak acids.

This reaction has technical as well as analytical interest. The precipitate is the common pigment termed *chrome yellow*, or *lemon chrome*. Boiled with lime and water, a portion of the chromic elements are removed, and a lower chromate, of a bright red or orange colour (*orange chrome*), is produced.

Fifth Analytical Reaction.—To solution of a lead salt add dilute sulphuric acid, or solution of a sulphate; a white precipitate of sulphate of lead ($PbSO_4$) falls.

Sulphate of lead is slightly soluble in strong acids, and in solutions of alkaline salts.

The white precipitate always noticed in the bottles in which diluted sulphuric acid is kept, is sulphate of lead, derived from the leaden chambers in which the acid is made. Its solubility in strong acid and insolubility in weak, explains its appearance in the bottles.

Antidotes.—From the insolubility of sulphate of lead in water, the best *antidote* in a case of poisoning by the acetate or other soluble salt of lead, is a soluble sulphate, such as Epsom salt,

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sulphate of sodium, alum, &c., vomiting being also induced, or the stomach-pump applied as quickly as possible.

Other tests for lead will be found in the reaction with *iodide of potassium* (*vide* pp. 124–5); with *alkaline carbonates*, a white precipitate ($2PbCO_3 + Pb2HO$) insoluble in excess; with *alkalies*, a white precipitate ($Pb2HO$) more or less soluble in excess; with alkaline *phosphates, arseniates, ferrocyanides, cyanides*, &c., precipitates mostly insoluble, but of no special analytical interest. Insoluble salts of lead are decomposed by solutions of potash (KHO) or soda ($NaHO$).

The metal is precipitated in a beautifully crystalline state by metallic zinc and some other metals; the *lead tree* is thus formed. ——The *blowpipe-flame* decomposes solid lead compounds placed in a small cavity in a piece of charcoal, a soft malleable bead of metal being produced, and a yellowish ring of oxide deposited on the charcoal.

SILVER.

Symbol Ag. Atomic weight 108.

This element occurs in nature in the free state and as ore, the common variety being sulphide of silver (Ag_2S) in combination with much sulphide of lead, forming *argentiferous galena*. The metal from the latter ore is melted and slowly cooled; crystals of lead then separate and are raked out from the still fluid mass, and thus an alloy rich in silver is finally obtained: this is roasted in a current of air, whereby the lead is oxidized and removed as litharge, pure silver remaining. Other ores undergo various preparatory treatments according to their nature, and are then shaken with mercury, which amalgamate with and dissolve the particles of silver, the mercury being subsequently removed from the amalgam by distillation. Soils and minerals containing metallic silver are also treated in this way. An important improvement in the amalgamation process, by which the mercury more readily unites with the silver, consists in the addition of a small proportion of sodium to the mercury—a recent discovery, simultaneously made in England by Crookes, and in New York by Wurtz.

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Reactions having (*a*) Synthetical and (*b*) Analytical Interest.

(*a*) *Synthetical Reactions.*

First Synthetical Reaction.—Dissolve a silver coin in nitric acid; nitric oxide gas (N_2O_2) is evolved, and a solution of nitrates of silver and copper obtained.

Pure silver is too soft for use as coin, it is therefore hardened by alloying with copper. The silver money of England contains 7·5, of France 10, and of Prussia 25 per cent. of copper.

Second Synthetical Reaction.—To the above solution add hydrochloric acid or a soluble chloride; white chloride of silver (AgCl) is precipitated, copper still remaining in solution. Collect the precipitate on a filter and wash with water; it is pure chloride of silver.

The nitrates of silver and copper may also be separated by evaporating the solution to dryness and gently heating the residue, when the nitrate of copper is decomposed but the nitrate of silver unaffected. The latter may be dissolved from the residual oxide of copper by water.

Third Synthetical Reaction.—Dissolve the chloride of silver of the previous reaction in solution of ammonia, and immerse a piece of sheet copper in the liquid; metallic silver is precipitated, and after a time wholly removed from solution. Collect the precipitate on a filter and wash with water; it is pure metallic silver, and is readily fusible into a single button.

Chloride of silver may also be reduced by fusion, in a crucible, with about half its weight of carbonate of sodium.

Fourth Synthetical Reaction.—Dissolve the pure silver of the previous reaction in nitric acid, and remove excess of acid by evaporating the solution to dryness, slightly heating the residue;

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the product is pure nitrate of silver. Dissolve by heating with a small quantity of water; on the solution cooling, or on evaporation, crystals of nitrate of silver are obtained.

$$\underset{\text{Silver.}}{3Ag_2} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Nitric oxide.}}{N_2O_2} + \underset{\text{Nitrate of silver.}}{6AgNO_3} + \underset{\text{Water.}}{4H_2O}$$

The solution of pure or refined silver (*Argentum Purificatum*, B. P.) in nitric acid, evaporation, &c., is the process of the British Pharmacopœia for the preparation of the nitrate (*Argenti Nitras*, B. P.). The salt fused and poured into proper moulds, yields the sticks or rods commonly termed *lunar caustic*. (The alchemists called silver *Diana* or *Luna*, from its supposed mysterious connexion with the moon.) The specimen of nitrate of silver obtained in the above reaction, dissolved in water, will be found useful as an analytical reagent.

Silver salts are decomposed when in contact with organic matter, especially in the presence of light or heat, a black insoluble compound being formed. Hence the use of the nitrate in the manufacture of indelible ink for marking linen, &c.

Fifth Synthetical Reaction.—To a few drops of solution of nitrate of silver add solution of potash or soda or lime-water; a black precipitate of oxide of silver (Ag_2O) occurs.

The *Argenti Oxidum*, B. P., is thus made, lime-water being the precipitant employed.

$$\underset{\text{Nitrate of silver.}}{2AgNO_3} + \underset{\text{Hydrate of calcium.}}{Ca2HO} = \underset{\text{Oxide of silver.}}{Ag_2O} + \underset{\text{Nitrate of calcium.}}{Ca2NO_3} + \underset{\text{Water.}}{H_2O}$$

(*b*) *Reactions having Analytical Interest.*

First Analytical Reaction.—To a solution of a silver salt add hydrochloric acid or other soluble chloride; a white curdy precipitate of chloride of silver falls. Add nitric acid and boil; the precipitate does not dissolve. Pour off the acid and add solution of ammonia; the precipitate dissolves. Neutralize the ammoniacal solution by an acid; the chloride of silver is re-precipitated.

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This is the most characteristic test for silver. The precipitated chloride is also soluble in solutions of hyposulphite of sodium or cyanide of potassium—facts of considerable importance in photographic operations.

Other analytical reagents than the above are occasionally useful.——Sulphuretted hydrogen, or sulphydrate of ammonium, give a black precipitate, sulphide of silver (Ag_2S), insoluble in alkalies.——Solutions of potash or soda give a brown precipitate, oxide of silver (Ag_2O), converted into a fulminating compound by prolonged contact with ammonia.——Phosphate of sodium gives a pale yellow precipitate, phosphate of silver (Ag_3PO_4), soluble in nitric acid and in ammonia.——Arseniate of ammonium gives a chocolate-coloured precipitate, arseniate of silver (Ag_3AsO_4), already noticed in connexion with arsenic acid.——Iodide or bromide of potassium gives a yellowish-white precipitate, iodide or bromide of silver (AgI or AgBr), insoluble in acids and only slightly soluble in ammonia.——Cyanide of potassium gives a white precipitate, cyanide of silver (AgCy), soluble in excess, sparingly soluble in ammonia, insoluble in dilute nitric acid, soluble in boiling concentrated nitric acid.——Yellow chromate of potassium (K_2CrO_4) gives a red precipitate, chromate of silver (Ag_2CrO_4).——Red chromate of potassium also gives a red precipitate, acid chromate of silver (Ag_2CrO_4,CrO_3).——Many organic acids also yield insoluble salts of silver.——Several metals displace silver from solution, mercury forming in this way a crystalline compound known as the silver tree, or *Arbor Dianæ*.—— In the blowpipe flame, silver salts, placed on charcoal with a little carbonate of sodium, yield bright globules of metal, accompanied by no incrustation as in the corresponding reaction with lead salts.

Antidotes.—Solution of common salt, sal-ammoniac, or any other inert chloride should obviously be administered where large doses of nitrate of silver have been swallowed. A quantity of

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sea-water or brine would convert the silver into insoluble chloride, and at the same time produce vomiting.

APPLICATION OF THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE OF THE METALS COPPER, MERCURY (EITHER AS MERCUROUS OR MERCURIC SALT), LEAD, SILVER.

Add hydrochloric acid:—

Silver is indicated by a white curdy precipitate, soluble in ammonia.

Mercurous salts also by a white precipitate, turned black by ammonia.

Lead by a white precipitate, insoluble in ammonia. Confirm by boiling another portion of the hydrochloric precipitate in water; it dissolves.

If hydrochloric acid gives no precipitate, silver and mercurous salts are absent. Lead can only be present in very small quantity. Mercuric salts may be present. Copper may be present. Divide the liquid into three portions, and apply a direct test for each metal.

Lead is best detected by the sulphuric test; the tube being set aside for a time if the precipitate does not appear at once.

Mercury is best detected by the copper test. If present, it occurs as mercuric salt.

Copper betrays itself by the blue colour of the liquid under examination. Confirm by the ammonia test.

If the above reactions are not thoroughly conclusive, confirmatory evidence should be obtained by the application of some of the other reagents for copper, mercury, lead, or silver.

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APPLICATION OF THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ANY OR ALL OF THE METALS COPPER, MERCURY (EITHER MERCUROUS OR MERCURIC SALT, OR BOTH), LEAD, SILVER.

Add hydrochloric acid, filter, and wash the precipitate with a small quantity of cold water.

<table>
<tr><td colspan="2">Ppt.
Pb Hg Ag.
Wash with boiling water.</td><td rowspan="2">Filtrate
Cu Hg Pb.
Divide into three portions. Test for
Cu by AmHO; blue sol.
Hg (mercuric) by Cu; globules.
Pb by H_2SO_4; white ppt.</td></tr>
<tr><td colspan="2">Ppt.
Hg Ag.
Add AmHO.</td><td>Filtrate
Pb.
Add H_2SO_4, white ppt.</td></tr>
<tr><td>Precipitate
Hg.
(mercurous)
black.</td><td>Filtrate
Ag.
Add HNO_3, white ppt.</td><td></td></tr>
</table>

The student should now be able to analyze aqueous solutions containing any common metal. If his operations have hitherto only included—

One metal of the first group (p. 51),
One metal of the second group (p. 63),
One metal of the third group (p. 85),
One metal of the fourth group (p. 103),
One metal of the fifth group (p. 132),

he should proceed to examine solutions containing a salt of one metal of any of the groups (see next page).

If more time has enabled the student to analyze solutions containing—

One or more metals of the first group (p. 51),
One or more metals of the second group (p. 63),
One or more metals of the first two groups (p. 64),
One or more metals of the third group (p. 85),
One or more metals of the first three groups (p. 87),
One or both metals of the fourth group (p. 103),
One or more metals of the first four groups (p. 106),
One or more metals of the fifth group (p. 133),

he should complete this division of study by examining aqueous solutions containing salts of one or more of the metals of any or all of the groups (see next page but one).

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APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF ORDINARY SALTS OF ONE OF THE ELEMENTS HITHERTO CONSIDERED.

Add hydrochloric acid.

<table>
<tr>
<td>Ppt.
Hg(ous) Pb Ag.
Add AmHO.
Hg, black ppt.
Pb, ppt. still white.
Ag, ppt. dissolved.
If HCl gave no precipitate, neither Hg, Pb, nor Ag is present.
Hg obtained here must have existed in the solution as a mercurous salt.
Sb is also precipitated by HCl, but is dissolved on adding more HCl; the Hg, Pb, and Ag precipitates are not soluble in excess of HCl.</td>
<td colspan="2">If HCl gave no precipitate the metal is still in the liquid; pass H_2S through it.</td>
</tr>
<tr>
<td>Ppt.
Cu Hg(ic) Pb As Sb.
As, yellow ppt.
Sb, orange ppt.
Cu, Hg, Pb } black ppt.
Test original solution for Cu by AmHO; blue sol.
Hg by Cu; globules.
Pb by H_2SO_4; white ppt.
If H_2S gave no precipitate, neither Cu, Hg, Pb, As, nor Sb is present.</td>
<td colspan="2">If H_2S gave no precipitate the metal is still in the liquid; add AmCl, AmHO, and AmHS.</td>
</tr>
<tr>
<td></td>
<td>Ppt.
Fe Al Zn.
Fe, black ppt.
Test original solution for ferric salt by K_4Fcy (dark blue ppt.); ferrous salt by K_6Fdcy (dark blue ppt.).
Al, Zn } white ppt.
Test original solution by AmHO.
Al, white ppt. insoluble in excess.
Zn, white ppt. soluble in excess.</td>
<td>If AmHS, &c. gave no precipitate, the liquid may still contain either Ba, Ca, Mg, K, Na, or Am; add successively $KCrO_4$ for Ba, $Am_2C_2O_4$ for Ca, Na_2HPO_4 for Mg.
If neither Ba, Ca, or Mg is found, examine the original solution for Am by KHO, Na by the flame test, and K by $PtCl_4$.</td>
</tr>
</table>

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APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF ORDINARY SALTS OF ANY OR ALL OF THE ELEMENTS HITHERTO CONSIDERED.

Add hydrochloric acid, and filter.

Precipitate Hg(ous) Pb Ag. Wash, boil with water, filter.

Filtrate Cu Hg(ic) Pb As Sb Fe Al Zn Ba Ca Mg K Na Am. Pass H_2S through the liquid; filter.

Precipitate Hg Ag. Add AmHO.

- **Precipitate** Hg. Black precipitate.
- **Filtrate** Ag. Add HNO_3; white precipitate.

Filtrate Pb. Add H_2SO_4; white precipitate.

Precipitate Cu Hg Pb As Sb. Wash, digest in AmHS, filter.

- **Precipitate** Cu Hg Pb. Wash, dissolve in a few drops of HNO_3 and HCl; evap. nearly to dryness; redissolve in H_2O, divide into three, and test for
  - Cu by AmHO; blue solution.
  - Hg by Cu; globules.
  - Pb by H_2SO_4; white precip.
- **Filtrate** As Sb. Add $HC_2H_3O_2$, and boil; digest the precipitate in Am_2CO_3; filter.
  - **Precip.** Sb. Orange.
  - **Filtrate** As. Add $HC_2H_3O_2$. Yellow.

  Confirm by testing original solution by the H tests.

Filtrate Fe Al Zn Ba Ca Mg K Na Am. Add AmHO*, AmHS, and filter.

- **Precipitate** Fe Al Zn. Wash, dissolve in HCl, boil with a few drops of HNO_3; add KHO, stir, filter.
  - **Precipitate** Fe. ? Ferric or ferrous. Test original solution by yellow and red prussiate.
  - **Filtrate** Al Zn. Neutralize by HCl; add AmHO, stir, filter.
    - **Precipitate** Al. White precipitate.
    - **Filtrate** Zn. Add AmHS; white precipitate.
- **Filtrate** Ba Ca Mg K Na Am. Add Am_2CO_3; boil, filter.
  - **Precipitate** Ba Ca. Wash, dissolve in $HC_2H_3O_2$; add K_2CrO_4, filter.
    - **Precipitate** Ba. Yellow.
    - **Filtrate** Ca. Add $Am_2C_2O_4$; white precipitate.
  - **Filtrate** Mg K Na Am. Add Am_2HAsO_4; stir, filter.
    - **Precip.** Mg. White.
    - **Filtrate** K Na Am. Evap., ignite, dissolve in H_2O, and test for K by $PtCl_4$; yellow precipitate. Na by flame; yellow. Am in orig. sol. by NaHO.

* AmHO is to neutralize acid; this prevents the decomposition of the AmHS subsequently added, and at the same time forms with the acid of the solution an ammoniacal salt, which is useful in preventing any partial precipitation of Mg by the AmHO.

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OUTLINE OF THE PRECEDING TABLES.

H Cl	H_2S	Am H S	Am_2CO_3	Am_2HAsO_4	
Hg (as mercurous salt)	Cu	Zn	Ba	Mg	K
Pb	Hg (as mercuric salt)	Al	Ca		Na
Ag	Pb	Fe			Am
	As, Sb				

Insoluble in Am HS. Soluble in Am HS.

The student should practise the examination of solutions containing the above metals until he is able to analyze them with facility and accuracy. In this way he will best fix on his mind the peculiarities of each element and their general relations to each other. As the rarer metals are not included here, the tables are by no means complete analytical schemes; practical remarks concerning them, therefore, are, for the present, deferred.

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METALS OF MINOR PHARMACEUTICAL IMPORTANCE.

Thus far has been considered, somewhat in detail, the chemistry of the common metals, salts of which are frequently used in medicine or in testing medicinal substances. These are:—

Potassium,	Barium,	Zinc,	Arsenicum,	Mercury,
Sodium,	Calcium,	Aluminium,	Antimony,	Lead,
Ammonium (?),	Magnesium,	Iron,	Copper,	Silver.

There still remain eleven metals, eight of which are mentioned in the British Pharmacopœia, namely—

Lithium,	Chromium,	Gold,	Cadmium,
Manganese,	Tin,	Platinum,	Bismuth.

Compounds of the remaining three are sufficiently common to occasionally come under the notice of any student of chemistry:—

Strontium, Cobalt, Nickel.

These eleven metals of minor pharmaceutical interest may be shortly studied, a few only of the reactions of each being performed. When all have been thus treated, their respective positions in the analytical groups will be indicated and a tabular scheme be given by which an analysis of a solution containing any metal may be effected. Thus, step by step, we may learn how to analyze almost any substance that may occur, and know to what extent the presence of a rarer will interfere with the ordinary tests for a common element; additional illustrations of the working of chemical laws will be acquired, and the store of chemical and pharmaceutical facts increased. The opportunity thus afforded for improvement in habits of neatness in manipulation, precision, and classification is another and no mean reason why such experiments should be prosecuted, the direct value of which may not be considerable.

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LITHIUM.

Symbol L. Atomic weight 7.

Lithium is widely distributed in nature, but usually in minute proportions compared with other elements. A trace of it may be found in most soils and waters, a Cornish spring containing even considerable quantities as chloride. The salt chiefly used in medicine is the *Citrate* ($L_3C_6H_5O_7$) (*Lithiæ Citras*, B. P.), which is prepared by dissolving the *Carbonate* (L_2CO_3) in citric acid.

$$\underset{\text{Carbonate of lithium.}}{3L_2CO_3} + \underset{\text{Citric acid.}}{2H_3C_6H_5O_7} = \underset{\text{Citrate of lithium.}}{2L_3C_6H_5O_7} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Carbonic acid gas.}}{3CO_2}$$

The carbonate (*Lithiæ Carbonas*, B. P.) is obtained from the minerals which contain lithium—namely, lepidolite (from λεπὶς, *lepis*, a scale, and λίθος, *lithos*, a stone; it has a scaly appearance), triphane (from τρεῖς, *treis*, three, and φαίνω, *phainō*, I shine) or spodumene (from σποδόω, *spodöō*, to reduce to ashes, in allusion to its exfoliation in the blowpipe-flame), and petalite (from πέταλον, *petalon*, a leaf; its character is leafy and laminated). Each contains silicate of aluminium, with fluoride of potassium and lithium in the case of lepidolite, and silicate of sodium and lithium in the others. *Liquor Lithiæ Effervescens*, B. P., is a solution of carbonate of lithium in water charged with carbonic acid.

Urate * of lithium is more soluble than urate of sodium; hence lithium preparations are administered to gouty patients in the hope that urate of sodium, with which such systems are loaded, may be converted into urate of lithium and removed.

In chemical position lithium stands between the alkaline and the alkaline-earth metals, its hydrate, carbonate, and phosphate being slightly soluble in water. Its atom is univalent.

Analytical Reaction.—Moisten the end of a platinum wire with solution of a minute particle of solid lithium salt, and introduce it into an air gas- or other slightly coloured flame (spirit-lamp or blowpipe-flame); a magnificent crimson tinge is imparted to the flame.

The light emitted by ignited lithium vapour is of a purer scarlet

* Urates are salts of uric acid, which will be considered subsequently.

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than that given by strontium, the next element. When the flames are examined by spectrum analysis (physically analyzed by a prism), the red rays are, in the case of strontium, found to be associated with blue and yellow, neither of which are present in the lithium light.

STRONTIUM.

Symbol Sr. Atomic weight 87·5.

Strontium is not widely distributed in nature; but the carbonate ($SrCO_3$), known as strontianite, and the sulphate ($SrSO_4$), known as celestine (from *cælum*, the sky, in allusion to its occasional bluish colour), are by no means rare minerals.

Salts of strontium are not employed in medicine. They are chiefly used by firework-manufacturers in preparing red fire. The colour they impart to flame is a beautiful crimson—ignited strontium vapour emitting red rays, as already explained. Nitrate of strontium ($Sr2NO_3$) is best for pyrotechnic compositions, its oxygen enabling it to burn freely when mixed with charcoal, sulphur, &c. It, or any salts, may be obtained by dissolving the carbonate in the appropriate acid, or by igniting the cheaper sulphate with coal, whereby sulphide (SrS) is produced, and dissolving this in acid.

The position of strontium among the chemical elements is between barium and calcium; its sulphate is very sparingly soluble in water. Its atom, like those of barium and calcium, is bivalent (Sr″).

Analytical Reactions.

First Analytical Reaction.—To solution of a strontium salt ($Sr2NO_3$, $SrCl_2$, &c.) add carbonate of ammonium; a white precipitate of carbonate of strontium ($SrCO_3$) falls.

Second Analytical Reaction.—To a solution of a strontium salt add sulphuric acid previously so diluted that it will not precipitate calcium salts, or an equally dilute solution of a sulphate; a white precipitate of sulphate of strontium ($SrSO_4$) falls. The formation of this precipitate is promoted by stirring and by setting the liquid aside for some time.

Barium is precipitated immediately under similar circumstances.

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Third Analytical Reaction.—To a dilute solution of a strontium salt add yellow chromate of potassium; no precipitate falls.

Barium may be separated from strontium by chromate of potassium, that reagent at once precipitating barium from aqueous or acetic solutions.

Fourth Analytical Reaction.—Insert a fragment of a strontium salt in the blowpipe-flame, or other equally colourless flame, or hold the end of a platinum wire dipped into a strontium solution in the flame; a crimson colour is imparted.

Other Analytical Reactions.—Alkaline phosphates, arseniates, and oxalates give white insoluble precipitates with strontium as with barium and calcium.——Strontium, like calcium, but unlike barium, is not precipitated by hydrofluosilicic acid.

MANGANESE.

Symbol Mn. Atomic weight 55.

Manganese is a constituent of many minerals, and, as black oxide (MnO_2) (*Manganesii Oxidum Nigrum*, B. P.), or *pyrolusite* (from πῦρ, *pur*, fire, and λύσις, *lusis*, a loosing or resolving, in allusion to the readiness with which it is split up by heat into a lower oxide and oxygen), occurs frequently in abundance in the south-west of England, Aberdeenshire, and most of the countries of Europe.

The chemical position of manganese is close to iron and three other metals still to be considered—cobalt, nickel, and chromium. Its atom exhibits sexivalent affinities, four-sixths or two-sixths of its powers being occasionally latent, the pairs of bonds or affinities saturating each other instead of those of other atoms.

Metallic manganese is only used in alloy with iron in the manufacture of some varieties of steel. The black oxide is an important agent in the production of chlorine, the preparation of green and red disinfecting manganates, purple glass, and black glazes for earthenware.

Reactions having both Synthetical and Analytical Interest.

First Reaction.—Boil a few grains of black oxide of manganese

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with some drops of hydrochloric acid until chlorine ceases to be evolved; add water, and filter; the filtrate is a solution of manganous chloride ($MnCl_2$).

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

This is the reaction commonly applied in the preparation of chlorine gas. It is also a ready method of preparing a manganous salt for analytical experiments. Coupled with the employment of reagents to the filtrate, the reaction is that by which a black powder or mineral would be recognized as black oxide of manganese.

Second Reaction.—Heat a particle of a manganese compound with a grain or two of carbonate of sodium and a fragment of nitrate or chlorate of potassium on platinum foil in the blowpipe-flame; a green mass containing *manganate of potassium* (K_2MnO_4) results. Boil the foil in a little water; the green manganate dissolves and soon changes to solution of the purple *permanganate of potassium* ($K_2Mn_2O_8$).

This is a delicate analytical test for manganese.

The reaction is also similar to that by which permanganate of potassium (*Potassæ Permanganas*, B. P.) is directed to be prepared for use in volumetric analysis, and for the preparation of *Liquor Potassæ Permanganatis*, B. P. Equations showing the exact action which occurs in conducting the operation according to the process of the British Pharmacopœia have already been given in connexion with the salts of potassium (*vide* p. 36).

Bœttger's process for the preparation of permanganate of potassium is as follows:—Fuse together in an iron crucible four parts of hydrate of potassium and two parts of chlorate of potassium; and when oxygen begins to be evolved remove the crucible from the fire, and stir in gradually one part of black oxide of manganese. Heat again until the mixture solidifies, then boil it with eighty parts of water, and finally pass carbonic acid gas through the solution until it becomes red. The liquid is now decanted, filtered through gun-cotton, evaporated to one half, and set aside to cool. Large crystals of the permanganate may thus be obtained.

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Solutions of the manganates of potassium are in common use as disinfectants &c., under the name of Condy's fluid. They act by oxidizing organic matter, the manganic or permanganic acid being reduced to black manganic oxide, or even a lower oxide.

The changes in colour which the green mass of the above process undergoes when dropped into warm water procured for it the old name of *mineral chameleon.*

Third Reaction.—Heat a particle of a manganese compound on a borax bead in the blowpipe-flame; a bead of a violet or amethystine tint is produced.

This is a good analytical reaction. It also has synthetical interest, illustrating the use of black oxide of manganese in producing common purple-tinted glass.

Expose the bead to the reducing part of the flame, the part nearer to the blowpipe, where there are highly heated hydrocarbon gases greedy of oxygen; the colour disappears.

This is owing to the reduction of the manganic compound to a manganous condition, in which it no longer possesses peculiar colouring-power. This action also illustrates the use of black oxide of manganese in glass-manufacture. Glass when first made is usually of a green tint, owing to the presence of ferrous impurities; the addition of manganic oxide to the materials converts the ferrous into ferric compounds, which have comparatively little colorific power, it itself being thereby reduced to manganous oxide, which also gives but little colour. If excess of manganic oxide be added, a purple tint is produced.

Reactions having Analytical Interest only.

Fourth Reaction.—Through an acidified solution of a manganous salt pass sulphuretted hydrogen; no decomposition occurs. Add ammonia; the sulphydrate of ammonium thus formed causes the precipitation of a yellowish pink or flesh-tinted precipitate of manganous sulphide (MnS), in a hydrated state.

This reaction is characteristic, sulphide of manganese being

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the only flesh-coloured sulphide known. The salt used may be the manganous chloride obtained in the first reaction; but such crude solutions usually give a black precipitate with sulphydrate of ammonium, owing to the presence of iron. The latter element may be removed, however, on boiling the manganous solution with a little carbonate of sodium, which throws the ferric salt out of solution before the manganous. *Pure* manganous chloride may be similarly obtained on boiling the impure solution with manganous carbonate; the latter decomposes the ferric chloride with production of ferric oxide and more manganous chloride, and evolution of carbonic acid gas.

To the recently precipitated manganous sulphide add acetic acid; it is dissolved.

This solubility enables us to separate manganese from nickel, cobalt, and zinc, whose sulphides are insoluble in weak acetic acid. To express the fact in another way—manganese is not precipitated by sulphuretted hydrogen from a solution containing free acetic acid only.

Fifth Reaction.—To solution of a manganous salt add ammonia drop by drop; a white precipitate of manganous oxide (MnO), in a hydrated state, falls. Add excess of ammonia; the precipitate is dissolved.

The fixed alkalies give a similar precipitate *insoluble* in excess. The precipitate rapidly absorbs oxygen, becomes brown, and gradually passes into a higher oxide.

Many other reactions occur between manganese salts and various reagents, but are of no particular synthetical or analytical interest. A good method, proposed by Crum, for detecting minute quantities of manganese consists in adding diluted nitric acid and plumbic (puce-coloured) oxide to the solution, and then boiling; a red tint due to permanganic acid is imparted to the liquid.

COBALT.

Symbol Co. Atomic weight 58·8.

Cobalt occurs sparingly in nature as the arsenide ($CoAs_2$),

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or *tin-white cobalt*, and occasionally as a double arsenide and sulphide ($CoAs_2$, CoS_2), or *cobalt-glance* (from *Glanz*, brightness, in allusion to its lustre). Its chief use is in the manufacture of blue glass, the colour of which is due to a compound of cobalt. Cobalt is also the colouring constituent of *smalt* (from *smelt*, a corruption of *melt*), a finely ground sort of glass used as a blue pigment by paper-stainers and others, and employed also by laundresses to neutralize the yellowish appearance of washed linen. The salts of cobalt may be obtained from the oxide (CoO), and the oxide from *zaffre*, a mixture of sand and roasted ore.

Cobalt is a sexivalent element, but more often exhibits quadrivalent affinities, and still more often exerts only bivalent powers ($^{IV}Co^{II}$). It has analytical relations with zinc, nickel, and manganese, and may be regarded as a member of the iron group.

Analytical Reactions.

First Analytical Reaction.—Pass sulphuretted hydrogen through a solution of a salt of cobalt (the chloride ($CoCl_2$) or nitrate (Co2NO$_3$) for example); no decomposition occurs. Add ammonia; the sulphydrate of ammonium thus formed causes the precipitation of black sulphide of cobalt (CoS) in a hydrated condition.

The moist precipitate slowly absorbs oxygen from the air, becoming converted into sulphate of cobalt ($CoSO_4$).

Second Analytical Reaction.—Add ammonia gradually to a cobalt solution; a blue precipitate of impure hydrated oxide (Co2HO) falls. Add excess of ammonia; the precipitate is dissolved.

A similar precipitate is given by the fixed alkalies, *insoluble* in excess.

Third Analytical Reaction.—Add a fragment of nitrite of potassium (KNO_2) to two or three drops of a tolerably strong solution of a cobalt salt, and then excess of acetic acid; a yellow crystalline precipitate of double nitrite slowly separates. The liquid must not be boiled.

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The nitrite of potassium may be prepared by strongly heating a few grains of nitrate of potassium in a porcelain crucible. By this test cobalt in solution may be separated from nickel, otherwise not an easy task.

Fourth Analytical Reaction.—Make a borax bead by heating a fragment of the salt on the looped end of a platinum wire in the blowpipe-flame until a clear transparent globule is obtained. Place on the bead a minute portion of a cobalt compound, or touch it with a drop of solution. Again fuse the borax; a blue bead results.

This is a delicate test for cobalt. From what has previously been said, it will be seen that this experiment has also considerable synthetical interest.

Other reactions between a cobalt solution and different reagents may be performed, and various precipitates obtained; but these have no special analytical interest.

The hydrated salts of cobalt are light red, the anhydrous dark blue. Prove this by writing some words on paper with a solution of chloride of cobalt sufficiently dilute for the characters to be invisible when dry; hold the sheet before a fire or over a flame; the letters at once become visible, distinct, and of a blue colour. Breathe on the words, or set the sheet aside for a while; the characters are once more invisible owing to absorption of moisture, the salt becoming re-hydrated.

Solution of chloride of cobalt forms one of the so-called *sympathetic inks.*

NICKEL.

Symbol Ni. Atomic weight 58·8.

Nickel is, chemically, closely allied to cobalt, the ores of the two metals being commonly associated in nature. Indeed it is from *speiss*, an arsenio-sulphide of nickel obtained in the manufacture of smalt, a pigment of cobalt already mentioned, that most of the nickel met with in commerce is obtained. It is

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much used in the preparation of the white alloy known as German or nickel silver.

Like cobalt, nickel is doubtless sexivalent, but only exerts bivalent activity ($^{IV}Ni^{II}$) in its ordinary compounds. Its salts and their solutions are usually green. They are chiefly made, directly or indirectly, from the metal itself.

Analytical Reactions.

First Analytical Reaction.—Pass sulphuretted hydrogen through a solution of a salt of nickel (chloride $NiCl_2$, nitrate $Ni2NO_3$, sulphate $NiSO_4$, &c.); no decomposition occurs. Add ammonia; the sulphydrate of ammonium thus formed causes the precipitation of black sulphide of nickel (NiS) in a hydrated condition.

When sulphide of nickel is precipitated by the direct addition of the common yellow solution of sulphydrate of ammonium, which always contains sulphur, there is much difficulty in filtering the mixture, owing to the slight solubility of the sulphide of nickel in the reagent and the formation of some sulphate of nickel ($NiSO_4$), oxygen being absorbed from the air by the sulphide. This may be avoided by warming the mixture and using freshly made sulphydrate of ammonium, in which the sulphide of nickel is insoluble; or, where practicable, the salt of nickel may be precipitated from an ammoniacal solution by sulphuretted hydrogen.

Second Analytical Reaction.—Add ammonia drop by drop to a nickel solution; a pale-green precipitate of hydrated oxide of nickel (Ni2HO) falls. Add excess of ammonia; the precipitate redissolves.

A similar precipitate is given by the fixed alkalies, *insoluble* in excess.

Third Analytical Experiment.—Nitrite of potassium applied as directed for cobalt gives no reaction.

Fourth Analytical Reaction.—Nickel salts colour a borax bead, when hot, a reddish-yellow tint; the reaction is not very serviceable analytically.

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Other reactions between a nickel solution and various reagents give, in many cases, insoluble precipitates which, from their green colour, are occasionally useful in distinguishing nickel from allied elements.

CHROMIUM.

Symbol Cr. Atomic weight 52·5.

The chief ore of chromium is chrome ironstone, a mixture of the oxides of the metals (FeO, Cr_2O_3), occurring chiefly in the United States and Sweden. On fusing the powdered ore with carbonate of potassium and nitre, chromate of potassium (K_2CrO_4) is obtained; the mass, treated with acid, yields red or bichromate (K_2CrO_4, CrO_3); from this salt other chromates are prepared, and by reduction, as presently explained, the salts of chromium itself also. The yellow and orange chromates of lead are largely used as pigments.

Chromium stands in close chemical relation to iron, aluminium, and manganese. Its atom is sexivalent. Like iron and aluminium, it is pseudo-trivalent also, a condition explained under aluminium.

Reactions.

Chromium as *chromic acid*, or rather as *chromate*.—This is the state in which chromium will usually be met with by the student, the most common salt being the red chromate of potassium. In the analytical examination of solutions containing chromates, the chromium will, however, always come out in the state of green chromic oxide along with ferric compounds and alumina, the prior treatment by sulphuretted hydrogen reducing the chromic molecule to the lower state of oxidation, thus:—

$$Cr_2O_6 + 3H_2S = Cr_2O_3 + 3H_2O + S_3,$$

the actual reaction being

$$K_2CrO_4, CrO_3 + 8HCl + 3H_2S = Cr_2Cl_6 + 2KCl + 7H_2O + S_3.$$

Chromium having been found in a solution, its condition as chromate may be ascertained by applying to the original solution salts

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of barium, mercury, lead, and silver. (See the various paragraphs relating to those metals.)

$Ba2NO_3$	gives	yellow	$BaCrO_4$	with chromates.
$Hg_2 2NO_3$	„	red	Hg_2CrO_4	„
$AgNO_3$	„	red	Ag_2CrO_4	„
„	„	„	Ag_2CrO_4, CrO_3	with bichromates.
$Pb2C_2H_3O_2$	„	yellow	$PbCrO_4$	with both.

Nitrate of barium gives no precipitate with bichromates, bichromate of barium being soluble in water; the chromate of barium is insoluble in water or acetic acid, but soluble in hydrochloric or nitric acid. Mercurous nitrate does not wholly precipitate bichromates: mercuric nitrate or chloride only partially precipitates chromates, and does not precipitate bichromates. The mercurous chromate is insoluble, or nearly so, in diluted nitric acid. Acetate of lead precipitates chromates and bichromates, acetic acid being set free in the latter case. The silver chromates are soluble in acids and alkalies.

A delicate reaction for dry chromates will be found in the formation of *chlorochromic acid* (CrO_2Cl_2). A small portion of the chromate is placed in a test-tube with a fragment of dry chloride of sodium and a drop or two of oil of vitriol, and the mixture heated; red irritating fumes of chlorochromic acid are evolved, and condense in dark-red drops on the side of the tube.

Larger quantities of pure distilled chlorochromic acid are obtained by the same reaction, the operation being conducted in a retort, with thoroughly dry materials. It may be regarded as chromic anhydride in which an atom of oxygen is displaced by an equivalent quantity (two atoms) of chlorine. It is not used in medicine, but is of interest to the chemical student as being an illustration of a large class of similar bodies—*chloro-acidulous compounds.*

Passage of chromium from the acidulous to the basylous side of salts.—Through an acidified solution of red chromate of potassium pass sulphuretted hydrogen; sulphur is deposited, and a

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green salt of chromium remains in solution—chloride (Cr_2Cl_6) if hydrochloric acid be used, and sulphate ($Cr_2 3SO_4$) if sulphuric be the acid employed. Boil the liquid to expel excess of sulphuretted hydrogen, filter, and reserve the solution for subsequent experiments.

The reaction which occurs in this operation has just been given. Alcohol, sugar, or almost any substance which is tolerably liable to oxidation will answer as well as sulphuretted hydrogen. Sulphate of chromium ($Cr_2 3SO_4$), like sulphate of aluminium ($Al_2 3SO_4$), unites with alkaline sulphates to form *alums*, which resemble common alum both in crystalline form and, as far as we know, in internal structure: they are of a purple colour.

Analytical Reactions of Chromium Salts.

First Analytical Reaction.—To solution of a salt of chromium (chloride or sulphate, for example) add sulphydrate of ammonium; a bulky green precipitate of chromic oxide (Cr_2O_3), containing a large quantity of water (10 molecules, $10H_2O$), is precipitated.

$$Cr_2Cl_6 + 6AmHS + 3H_2O = Cr_2O_3 + 6AmCl + 6H_2S.$$

Second Analytical Reaction.—To solution of a chromium salt add ammonia; hydrated chromic oxide is precipitated, insoluble in excess.

Third Analytical Reaction.—To solution of a chromium salt add solution of potash or soda drop by drop; hydrated chromic oxide is precipitated. Add excess of the fixed alkali; the precipitate is dissolved. Well boil the solution; the chromic oxide is reprecipitated.

Ferric, chromic, and aluminic salts, chemically so alike, may be separated by this reaction. Hydrated ferric oxide is insoluble in solutions of the fixed alkalies, cold or hot; hydrated chromic oxide soluble in cold but not in hot; hydrated aluminic oxide in both. To a solution containing all three, therefore, add potash or soda, stir, and filter; the iron is thrown out: boil the filtrate, and filter; the chromium is thrown out: neutralize the filtrate by acid, and then add ammonia; the aluminium is thrown out.

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The three oxides are insoluble in ammonia, and may therefore be easily separated from the salts of the somewhat analogous metals zinc, cobalt, nickel, and manganese.

Fourth Analytical Reaction.—Add a salt of chromium (either of the above precipitates of chromic oxide or the dry residue of the evaporation of a few drops of a solution of a chromium salt) to a few grains of nitre and carbonate of sodium on platinum foil, and fuse the mixture in the blowpipe-flame; a yellow mass of chromate of potassium (K_2CrO_4) is formed. Dissolve the mass in water, add acetic acid to decompose excess of carbonate, and apply the reagents for chromates.

This is a delicate and useful reaction if carefully performed.

TIN.

Symbol Sn. Atomic weight 118.

The chief ore of tin is stannic oxide (SnO_2), occurring in veins under the name of *tinstone*, or in alluvial deposits as *stream tin*. The principal mines are those of Cornwall. The metal is obtained by reducing the roasted and washed ore by charcoal or anthracite coal at a high temperature, and is purified by slowly heating, when the pure tin, fusing first, is run off, a somewhat less fusible alloy of tin with small quantities of arsenic, copper, iron, lead, &c. remaining. The latter is known as *block tin*; the former heated till brittle and then hammered or let fall from a height splits into prismatic fragments resembling starch or basalt, and is termed *dropped* or *grain tin*. Good tin emits a crackling noise in bending, termed the cry of tin, caused by the friction of its crystalline particles on each other.

Tin is an important constituent of pewter, Britannia metal (teapots, &c.), solder, speculum-metal, bell-metal, gun-metal, and bronze. It is very ductile, and may be rolled into plates or leaves, known as *tin foil*, varying from $\frac{1}{250}$ to $\frac{1}{1000}$ of an inch in thickness. Common tin foil, however, usually contains a large proportion of lead. The reflecting surface of most *looking-glasses* is an amalgam of tin and mercury produced by carefully sliding a plate of glass over a sheet of tin foil on

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which mercury has been rubbed and then excess of mercury poured. Pins are made of brass wire on which tin is deposited. *Tin plate*, of which common utensils are made, is iron alloyed with tin by dipping the cleansed sheet into melted tin. *Tin tacks* are in reality tinned iron tacks, a tin nail would be too soft to drive into wood. Tin may be granulated by melting and triturating briskly in a hot mortar, or by shaking melted tin in a box on the inner sides of which chalk has been rubbed.

The chemical position of tin among the metals is close to that of arsenicum and antimony. Its atom is quadrivalent; but half its power is frequently latent, the atom then exhibiting bivalent affinities. The two classes of salts are termed stannic and stannous respectively. They are all made directly or indirectly from the metal itself.

Reactions having (*a*) Synthetical and (*b*) Analytical Interest.

(*a*) *Synthetical Reactions.*

First Synthetical Reaction.—Boil a fragment of tin with hydrochloric acid; hydrogen escapes and solution of stannous chloride ($SnCl_2$) is formed. It may be retained for future experiments.

By evaporation of this solution stannous chloride is obtained in crystals ($SnCl_2$, $2H_2O$). It is a powerful reducing agent, precipitating gold, silver, and mercury from their solutions, converting ferric and cupric into ferrous and cuprous salts, and deoxidizing arsenic, manganic, and chromic acids to their lower oxides. It absorbs oxygen from the air, and is decomposed when added to a large quantity of water. It is used as a mordant in dyeing and calico-printing.

Second Synthetical Reaction.—Through a portion of the solution of the stannous chloride of the previous reaction pass chlorine gas; solution of stannic chloride ($SnCl_4$) is formed. Or add hydrochloric acid to the stannous solution, boil, and slowly drop in nitric acid until no more fumes are evolved; again stannic chloride results. Reserve the solutions for subsequent experiments.

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Third Synthetical Reaction.—Boil a fragment of tin with nitric acid; white stannic oxide (SnO_2), in a hydrated state, is produced.

Hydrated stannic oxide is an acid body (H_2SnO_3). There are two varieties of it—that precipitated on adding a small quantity of an alkali to stannic chloride, and that prepared as above. They both yield soluble alkaline salts; but the former, termed *stannic acid*, is soluble in acids, while the latter, termed *metastannic acid* (from μετὰ, *meta*, beyond) (SnO_2), is insoluble. The metastannic acid of the foregoing reaction loses its water when strongly heated, and becomes of a buff colour; it is employed in polishing plate under the name of *putty powder*. *Stannate of sodium* (K_2SnO_3, $4H_2O$) is used as a mordant by dyers and calico-printers under the name of *tin prepare-liquor*.

(*b*) *Reactions having Analytical Interest.*

STANNOUS SALTS.

First Analytical Reaction.—Through a solution of a stannous salt (stannous chloride, for example) pass sulphuretted hydrogen; brown stannous sulphide (SnS), in a hydrated state, is precipitated. Pour off the supernatant liquid, add ammonia to the moist precipitate (to neutralize acid), and, lastly, yellow sulphydrate of ammonium; the precipitate is dissolved.

Aqueous solution of sulphydrate of ammonium becomes yellow when a day or two old, and then contains excess of sulphur, that element having become displaced by oxygen absorbed from the air: hence in the above reaction the stannous sulphide (SnS), in dissolving, becomes stannic sulphide (SnS_2); for the latter is precipitated on decomposing the alkaline liquid by an acid.

Second Analytical Reaction.—To solution of a stannous salt add solution of potash or soda; white hydrated stannous oxide falls (Sn2HO). Add excess of the alkali; the precipitate dissolves. Boil the solution; some of the oxide is reprecipitated in the black anhydrous condition.

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Ammonia gives a similar precipitate, insoluble in excess. The alkaline carbonates do the same, carbonic acid gas escaping.

STANNIC SALTS.

Third Analytical Reaction.—Through solution of a stannic salt (stannic chloride, for example) pass sulphuretted hydrogen; yellow stannic sulphide (SnS_2) is precipitated in a hydrated state. Pour off the supernatant liquid, and to the moist precipitate add ammonia (to neutralize acid), and then sulphydrate of ammonium; the precipitate dissolves.

In precipitating stannic sulphide the presence of too much hydrochloric acid must be avoided; the formation of the precipitate is also facilitated if the solution be warmed. Stannic sulphide, like the sulphides of arsenicum and antimony, dissolves in solutions of any alkaline sulphide, with formation of definite crystallizable salts.

Anhydrous stannic sulphide, prepared by sublimation, has a yellow or orange lustrous appearance, and is used by decorators as *bronzing powder*. It is sometimes termed *mosaic gold*.

Fourth Analytical Reaction.—To solution of a stannic salt add potash or soda; white stannic acid falls (H_2SnO_3). Add excess of the alkali; the precipitate dissolves. Boil the precipitate; no reprecipitation occurs—a fact enabling stannic to be distinguished from stannous salts.

Ammonia gives a similar precipitate, soluble, but not readily, in excess. The fixed-alkaline carbonates do the same, carbonic acid gas escaping; after a time the stannic oxide is again deposited, probably as stannate of the alkali-metal. Carbonate of ammonium and acid carbonates of alkali-metals give a precipitate of stannic acid insoluble in excess.

Antidotes.—In cases of poisoning by tin salts (dyers' tin-liquor &c.), solution of carbonate of ammonium should be given. White of egg is also said to form an insoluble compound with compounds of tin. Vomiting should be speedily induced, and the stomach-pump quickly applied.

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GOLD.

Symbol Au. Atomic weight 196·7.

Gold occurs in the free state in nature, occasionally in nodules or *nuggets*, but commonly in a finer state of division termed *gold dust*. Gold is separated from the sand, crushed quartz, or other earthy matter with which it may be associated, by agitation with water, when the gold, from its relatively greater specific gravity, falls to the bottom of the vessels first, the lighter mineral matter being allowed to run off with the water. From this rich sand the gold is dissolved out by mercury, the latter filtered and the amalgam distilled, when the mercury volatilizes and gold remains. The amalgamation may be much facilitated by the use of a small proportion of sodium, as described under silver.

Pure gold is too soft for general use as a circulating medium. *Gold coin* is an alloy of copper and gold, that of Great Britain containing 1 to 11, or $8\frac{1}{3}$ per cent., that of France, Germany, and the United States about 10 per cent. *Jewellers' gold* varies in quality, every 24 parts containing 18, 15, 12, 8, &c. parts of gold, the alloys being technically termed 18, 15, 12, 8, &c. *carat fine*. Articles made of the better qualities are usually stamped by authority. Trinkets of inferior intrinsic worth are commonly thinly coated with pure gold by electro-deposition or otherwise. *Gold leaf* is nearly pure gold passed between rollers till it is about $\frac{1}{800}$ of an inch in thickness and then hammered between sheets of animal membrane, termed gold-beater's skin and calf-skin vellum, till it is $\frac{1}{180000}$ or $\frac{1}{200000}$ of an inch in thickness. It may even be hammered till 280,000 leaves would be required to form a pile an inch thick.

In chemical position among the elements, gold is not far removed from mercury and silver. In analysis it comes out among the sulphides of the metals precipitated by sulphuretted hydrogen; and of those sulphides, it, like the sulphides of tin, antimony, and arsenicum, is soluble in sulphydrate of ammonium. Its atom is trivalent (Au‴); but in some compounds two-thirds of its power is latent, two of the bonds or affinities of the atom saturate each other, the third only being exerted in retaining another element within the molecule of the compound; in these cases gold is apparently univalent (″Au′).

Reactions.

Synthetical Reaction.—Place a fragment of gold in ten or

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twenty drops of aqua regia (a mixture of one part of nitric and three of hydrochloric acid), and set the test-tube aside in a warm place; solution of perchloride of gold or auric chloride ($AuCl_3$) results. When the metal is dissolved, evaporate nearly to dryness to remove most of the excess of acid, dilute with water, and retain the solution for subsequent experiments.

This reaction has analytical interest also; for in examining a substance suspected to be or to contain metallic gold, solution would have to be effected in the above way before reagents could be applied.

Analytical Reactions.

First Analytical Reaction.—Through a few drops of solution of an auric salt (the chloride, $AuCl_3$, is the only convenient one) pass sulphuretted hydrogen; black auric sulphide (Au_2S) is precipitated. Filter, wash, and add sulphydrate of ammonium; the precipitate dissolves.

Second Analytical Reaction.—To solution of a salt of gold add ferrous chloride or sulphate, and set the tube aside; metallic gold is precipitated, a ferric salt remaining in solution.

This is a convenient way of preparing pure gold, or *fine gold* as it is termed, or of working up the gold residues of laboratory operations. The precipitate, after boiling with hydrochloric acid, washing, and drying, may be obtained in a button by mixing with an equal weight of borax or bisulphate of potassium and fusing in a good furnace.

Third Analytical Reaction.—Add a few drops of dilute solutions of stannous and stannic chloride to a considerable quantity of distilled water; pour the liquid, a small quantity at a time, into a dilute solution of auric chloride ($AuCl_3$), well stirring; the mixture assumes a purple tint, and flocks of a precipitate, known as the *Purple of Cassius* (from the name of the discoverer, M. Cassius), are produced.

The same compound is formed on immersing a piece of tin foil

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in solution of auric chloride; it is said to be a mixture of auric, aurous, stannic, and stannous oxides. It is the colouring agent in the finer varieties of ruby glass.

PLATINUM.

Symbol Pt. Atomic weight 198.

Platinum, like gold, usually occurs in nature in the free state, the chief sources of supply being Mexico, Brazil, and Siberia. It is separated from the alluvial soil by washing.

The chief use of platinum is in the construction of foil, wire, crucibles, spatulas, capsules, evaporating-dishes, stills, &c. for the use of the chemical analyst or manufacturer. It is tolerably hard, fusible with very great difficulty, not dissolved by hydrochloric, nitric, or sulphuric acids, and only slightly affected by alkaline substances. It is attacked by aqua regia with production of perchloride of platinum ($PtCl_4$). It forms fusible alloys with lead and other metals; neither metallic substances, therefore, nor mixtures which may yield a metal, should be heated in platinum vessels. The chemical position of platinum among the elements is close to that of gold. Its atom is quadrivalent; but in some compounds half its power is latent, two of its four bonds or affinities saturate each other, the other two only exerting their power in retaining an atom or atoms of other elements within the molecule of the compound; in these cases the atom is apparently bivalent ("Pt").

Reactions.

Synthetical Reaction.—Place a fragment of platinum in a little aqua regia and set the vessel aside in a warm place; solution of perchloride of platinum ($PtCl_4$) results. Evaporate the solution to remove excess of acid, and complete the desiccation over a water-bath. Dissolve the residue in water and retain the solution for subsequent experiments, and as a reagent for the precipitation of salts of potassium and ammonium.

This reaction has analytical interest also; for in examining a substance suspected to be or to contain metallic platinum, solution would have to be effected in the above manner before reagents could be applied.

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Analytical Reactions.

First Analytical Reaction.—Through a few drops of a solution of a platinic salt ($PtCl_4$ is the only convenient one) to which an equal quantity of solution of chloride of sodium has been added, pass sulphuretted hydrogen; dark brown platinic sulphide (PtS_2) is precipitated. Filter, wash, and add sulphydrate of ammonium; the precipitate dissolves.

If chloride of sodium is not present in the above reaction, the precipitated sulphide contains platinous chloride, and detonates when heated.

Second Analytical Reaction.—Boil a few drops of solution of platinic chloride with a small quantity of alcohol; a black precipitate of finely divided metallic platinum falls.

It is important to bear this reaction in mind in subsequent quantitative experiments with platinum.

Platinum black is the name given to this precipitate. From the great extent of surface which its minute state of division enables it to present to the air, it possesses in a high degree a quality common to many substances, but largely possessed by platinum, namely that of condensing gases on its surface. In its ordinary state, after well washing and drying, it absorbs from the air and retains many times its bulk of oxygen. A drop of ether or alcohol placed on it is rapidly oxidized, the platinum becoming hot. This action may be prettily shown by pouring a few drops of ether into a beaker (one having portions of the top and sides broken off answers best), loosely covering the vessel with a card, and suspending within the beaker a platinum wire, one end being attached to the card by passing through its centre, the other terminating in a short coil or helix near the surface of the ether: on now warming the helix in a flame and then rapidly introducing it into the beaker, it will become red-hot and continue to glow so long as there is ether in the vessel. In this experiment real combustion goes on between the ether vapour and the concentrated oxygen of the air at the surface of the platinum, the products of the oxidation revealing themselves by their odour.

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Third Analytical Reaction.—To solution of perchloride of platinum add solution of chloride of ammonium; a yellow granular precipitate of double chloride of platinum and ammonium ($PtCl_4$, 2AmCl) falls. When slowly formed in dilute solutions, the precipitate is obtained in minute orange prisms.

Chloride of potassium (KCl) gives a similar precipitate ($PtCl_4$ 2KCl). Platinic chloride having been stated to be a test for potassium and ammonium salts, the student is prepared to find that potassium and sodium salts are tests for platinic salts. The double sodium compound ($PtCl_4 2NaCl$) is soluble in water.

Collect the precipitate, dry, and heat in a small crucible; it is decomposed, and metal, in the finely divided state of *spongy platinum*, remains.

$$3(PtCl_4 2NH_4Cl) = Pt_3 + 2NH_4Cl + 16HCl + 2N_2.$$

Heat decomposes the potassium salt into $Pt + 2KCl + Cl_4$, the chlorine escaping and the chloride of potassium remaining with the platinum.

In working up the platinum residues of laboratory operations, the mixture should be dried, burnt, boiled successively with hydrochloric acid, water, nitric acid, water, then dissolved in aqua regia, excess of acid removed by evaporation, chloride of ammonium added, the precipitate washed with water, dried, ignited, and the resulting spongy platinum retained or converted into perchloride for use as a reagent for alkali-metals. It is by this process that the native platinum is treated to free it from the rare metals palladium, rhodium, osmium, ruthenium, and iridium. The spongy platinum is converted into the massive condition by a refinement on the blacksmith's process of *welding* (German *wellen*, to join), or by fusing in a flame of pure oxygen and hydrogen gases—the oxyhydrogen blowpipe.

CADMIUM.

Symbol Cd. Atomic weight 112.

In most of its chemical relations cadmium resembles zinc. In nature it occurs chiefly as an occasional constituent of the ores of that metal. In distilling zinc containing cadmium, the latter,

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being the more volatile, passes over first. In analytical operations cadmium, unlike zinc, comes down among the metals precipitated by sulphuretted hydrogen; that is, its sulphide is insoluble in dilute hydrochloric acid, while sulphide of zinc is soluble.

Beyond the occasional employment of the sulphide as a pigment (*jaune brillant*), and the iodide in photography and medicine, cadmium and its salts are but little used. The atom of cadmium is bivalent (Cd″).

Reactions.

Synthetical Reaction.—Digest metallic cadmium in water in which a fragment of iodine is placed until the colour of the iodine disappears; solution of iodide of cadmium (*Cadmii Iodidum*, B. P.) (CdI_2) remains. Pearly crystals may be obtained on evaporating the solution.

This is the process alluded to in the British Pharmacopœia. The compound is used in medicine in the form of ointment, *Unguentum Cadmii Iodidi*, B. P.——The salt is also employed, with other iodides, in iodizing collodion for photographic purposes.

Analytical Reaction.—Through solution of a cadmium salt (CdI_2, $CdCl_2$, &c.) pass sulphuretted hydrogen; a yellow precipitate of sulphide of cadmium (CdS) falls, resembling in appearance arsenious, arsenic, and stannic sulphides. Add sulphydrate of ammonium; the precipitate, unlike the sulphides just mentioned, does not dissolve.

Before the blowpipe-flame, on charcoal, cadmium salts give a brown deposit of anhydrous oxide of cadmium (CdO).

BISMUTH.

Symbol Bi. Atomic weight 208.

Bismuth occurs in the metallic state in nature. It is freed from adherent quartz, &c. by simply heating, when the metal melts, runs off, and is collected in appropriate vessels. It is also met with in combination with other elements.

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Beyond the employment of some of its compounds in medicine bismuth is but little used. Melted bismuth expands considerably on solidifying, and hence is valuable in taking sharp impressions of dies. It is a constituent of some kinds of type-metal and of pewter-solder.

The position of bismuth among the metals is close to that of arsenicum and antimony. Its atom is quinquivalent (Bi^{V}); but in most compounds two-fifths of its power is latent, two of its five bonds or affinities saturate each other, the other three only exerting their power in retaining atoms of other elements within the molecule of the compound; in these cases the atom is apparently trivalent ($^{II}Bi^{III}$).

Reactions having (*a*) Synthetical and (*b*) Analytical Interest.

(*a*) *Reactions having Synthetical Interest.*

First Synthetical Reaction.—To a few drops of nitric acid and an equal quantity of water in a test-tube, add a little powdered bismuth, heating the mixture if necessary; nitric oxide (N_2O_2) escapes and solution of *nitrate of bismuth* ($Bi3NO_3$) results.

Bi_2	+	$8HNO_3$	=	$2(Bi3NO_3)$	+	N_2O_2	+	$4H_2O$
Bismuth.		Nitric acid.		Nitrate of bismuth.		Nitric oxide.		Water.

The solution evaporated gives crystals ($Bi3NO_3, 5H_2O$), any arsenicum which the bismuth might contain remaining in the mother-liquor. Native bismuth (*Bismuthum*, B. P.) commonly contains arsenicum, most of which is removed by roasting or by fusing with nitre (*Bismuthum Purificatum*, B. P.), or, finally, by converting the metal into subnitrate, as described in the next reaction, and reducing this with charcoal at a high temperature.

Second Synthetical Reaction.—Pour some of the above solution into a considerable quantity of water; decomposition occurs and subnitrate of bismuth ($BiNO_4$) in a hydrated state ($BiNO_4, H_2O$) (*Bismuthi Subnitras*, B. P.) is precipitated:—

$Bi3NO_3$	+	H_2O	=	$BiNO_3O$	+	$2HNO_3$
Nitrate of bismuth.		Water.		Oxynitrate of bismuth.		Nitric acid.

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Filter, and test the filtrate for bismuth by adding excess of carbonate of sodium; a precipitate shows that some bismuth remains in solution. The following equation, therefore, probably more nearly represents the decomposition:—

$$\underset{\text{Nitrate of bismuth.}}{5(Bi3NO_3)} + \underset{\text{Water.}}{8H_2O} = \underset{\text{Oxynitrate of bismuth.}}{4(BiNO_3O, H_2O)} + \underset{\text{Nitrate of bismuth in acid.}}{Bi3NO_3, 8HNO_3}$$

Decomposition of nitrate of bismuth by water is the process of the British Pharmacopœia for the preparation of subnitrate of bismuth for use in medicine. For this purpose the original metal must contain no arsenicum. In manufacturing the compound, therefore, before pouring the solution of nitrate into water, the liquid should be tested for arsenicum by one of the hydrogen tests; if that element be present, the solution must be evaporated and only the deposited crystals be used in the preparation of the subnitrate. For on pouring an arsenical solution of nitrate of bismuth into water, the arsenicum is not wholly removed in the supernatant liquid, unless the subnitrate be redissolved and reprecipitated several times, according to the amount of arsenicum present.

Subnitrate of bismuth is sometimes administered in the form of a lozenge (*Trochisci Bismuthi*, B. P.). It is used as a cosmetic under the name of *Pearl-white* (*Blanc de Perle*).

The student will notice that the formula for subnitrate of bismuth ($BiNO_4$) does not accord with that of other nitrates, the characteristic elements of which are NO_3. Analogy would seem to indicate, however, that the fourth atom of oxygen has different functions to the three in the NO_3; for on pouring solution of chloride of bismuth ($BiCl_3$) into water, oxychloride is produced (BiClO) (a white powder also used as a cosmetic, in enamels, and in some varieties of sealing-wax). The bromide ($BiBr_3$) and iodide (BiI_3) similarly yield oxybromide (BiBrO) and oxyiodide (BiIO). The subnitrate ($BiNO_4$) is, therefore, probably an analogous compound, an oxynitrate ($BiNO_3O$). The sulphate (Bi_23SO_4) also decomposes when placed in water, giving what may be termed an oxysulphate ($Bi_2SO_4O_2$).

Third Synthetical Reaction.—To solution of nitrate of bismuth add carbonate of ammonium; a white precipitate of hydrated oxycarbonate (Bi_2CO_5) (*Bismuthi Carbonas*, B. P.) falls.

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$$\underset{\text{Nitrate of bismuth.}}{2(Bi3NO_3)} + \underset{\text{Carbonate of ammonium.}}{3Am_2CO_3} = \underset{\text{Nitrate of ammonium.}}{6AmNO_3} + \underset{\text{Oxycarbonate of bismuth.}}{Bi_2CO_3O_2} + \underset{\text{Carbonic acid gas.}}{2CO_2}$$

This compound may be regarded as similar in constitution to those just described. In Bi_2CO_5 one scarcely recognizes the characteristic elements of carbonates; but considering the preparation to be an oxycarbonate ($Bi_2CO_3O_2$) its relations to carbonates and oxides are evident. These subsalts may all be viewed as normal bismuth salts in which an atom of oxygen replaces an equivalent proportion of other acidulous atoms or radicals:—

Chloride	$Bi3Cl$	Oxychloride .	$BiClO$
Bromide	$Bi3Br$	Oxybromide .	$BiBrO$
Iodide	$Bi3I$	Oxyiodide ..	$BiIO$
Nitrate.....	$Bi3NO_3$	Oxynitrate ..	$BiNO_3O$
Sulphate	Bi_23SO_4	Oxysulphate .	$Bi_2SO_4O_2$
Carbonate (unknown)	Bi_23CO_3	Oxycarbonate	$Bi_2CO_3O_2$

They may be viewed, in short, as salts in process of conversion to oxide; continue the substitution a little further, and each yields oxide of bismuth (Bi_2O_3). They have also been considered to be salts of the univalent radical bismuthyl (BiO).

Fourth Synthetical Reaction.—To solution of nitrate of bismuth add citric acid and then solution of ammonia until the precipitate at first formed is redissolved, and the liquid after shaking has a slight ammoniacal odour. The product contains citrate of bismuth dissolved in solution of citrate and nitrate of ammonium. Made with definite quantities of ingredients and an amount of bismuth salt equivalent to the three grains of oxide (Bi_2O_3) in a fluid drachm, the solution forms the *Liquor Bismuthi et Ammoniæ Citras*, B. P.

(*b*) *Reactions having Analytical Interest.*

First Analytical Reaction.—Through solution of a bismuth salt pass sulphuretted hydrogen; a black precipitate of sulphide of bismuth (Bi_2S_3) falls. Add ammonia (to neutralize acid) and then sulphydrate of ammonium; the precipitate, unlike As_2S_3 and Sb_2S_3, is insoluble.

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Second Analytical Reaction.—Concentrate almost any acid solution of a bismuth salt and pour into water; a white salt is precipitated.

This reaction is characteristic of bismuth salts; it has already been amply explained. The precipitate is distinguished from one formed by antimony under similar circumstances, by being insoluble in solution of tartaric acid.

The student is again advised to write out equations or diagrams representing each of the foregoing reactions, submitting them to a tutor or other authority for correction.

Bismuth is the last of the metals whose synthetical or analytical relations are of interest to the medical, pharmaceutical, or general student of chemistry. The position of the rarer among the common metals, and the influence which either has on the other during the manipulations of analysis, will now be considered. These objects will be best accomplished, and a more intimate acquaintance with all the metals be obtained, by analyzing solutions containing one or more metallic salts.

Of the following Tables, the first includes directions for the analysis of an aqueous or only slightly acid solution containing but one salt of any of the metals hitherto considered. Here the colour of the precipitate or precipitates afforded by a metal under given circumstances must be relied on to a considerable extent in attempting the detection of the various elements.

The second Table is intended as a chart for the analysis of solutions containing salts of more than one of the common and rare metals. It is simply a compilation from the foregoing reactions—an extension of the scheme for the analysis of salts of the ordinary metals. Hence it often may be altered or varied in arrangement to suit the requirements of the analyst.

The third is a mere outline of the preceding Tables. It gives the position of the metals in relation to each other, and will much aid the memory in recollecting that relation.

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APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS OR ONLY SLIGHTLY ACID SOLUTION OF ORDINARY SALTS OF ONE OF THE ELEMENTS HITHERTO CONSIDERED—THE COMMON AND RARER METALS.

Add hydrochloric acid.

Precipitate
Hg(ous) Pb Ag.
Collect, wash, add Am HO.
Hg, black ppt.
Pb, white ppt.
Ag, ppt. dissolved.
Sb and Bi may also be precipitated by HCL, but are dissolved on adding more HCL.

If HCl gave no precipitate the metal is still in the liquid; pass H_2S through the solution.

Precipitate
Cd Cu Hg(ic) Pb Bi As Sb Sn Au Pt.
Collect, wash, add AmHS.

Insoluble.		Soluble.	
Cd, yellow	black.	As(ous & ic)	yellow.
Cu	black.	Sn(ic)	yellow.
Hg(ic)	black.	Sb, orange	
Pb	black.	Sn(ous)	black.
Bi	black.	Au	black.
		Pt	black.

Apply special tests for each to the original solution. For these, see the previous pages.

If H_2S gave no precipitate add AmCl, AmHO, and AmHS.

Precipitate
Zn Mn Co Ni Al Fe Cr.
Zn, Al } white.
Cr, green.
Mn, skin-tint.
Ni, Co, e } black.
Test specially for each in original solution. See previous pages.

If AmHS gave no precipitate add Am_2CO_3.

Precipitate
Ba Sr Ca.
Collect, wash, dissolve in $HC_2H_3O_2$, add K_2CrO_4.

Ppt.	Sol.
Ba.	Sr Ca.

Add dil. H_2SO_4.

Ppt.	Sol.
Sr.	Ca.

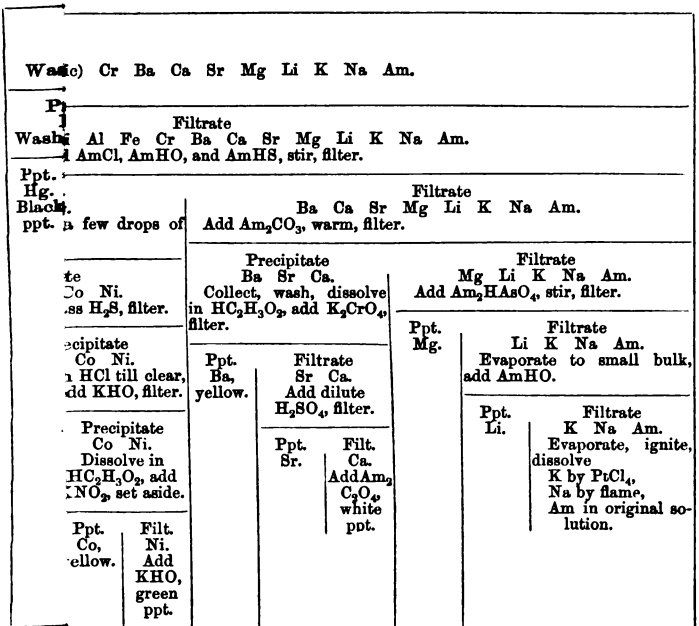
If Am_2CO_3 gave no precipitate, add Am_2HAsO_4.

Ppt.	
Mg.	If no precipitate, test original solution in flame on loop of Pt wire. Li, crimson. Na, yellow. K, violet. If neither, test original solution for Am.

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[To face p. 164.]

UTION OF ORDINARY SALTS OF ANY OF THE ELEMENTS



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OUTLINE OF THE PRECEDING TABLES.

HCl	H_2S	AmHS	Am_2CO_3	Am_2HAsO_4	
Hg (as mercurous salt)	Ca	Zn	Ba	Mg	K
Pb	Cu	Mn	Sr		Na
Ag	Hg (as mercuric salt)	Co	Ca		Am
	Pb	Ni			
	Bi	Al			
	As (as arsenious or arsenic salt)	Fe		Li	
	Sb	Cr			
	Sn (as stannous or stannic salt)				
	Au				
	Pt				

Insoluble in AmHS. Soluble in AmHS. Hydrates soluble in AmHO. Hydrates insol. in AmHO.

The student should practise the examination of aqueous solutions of salts of the above metals until he is able to analyze them with facility and accuracy.

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Memoranda relating to the preceding Tables.

General Memoranda.

These charts are constructed for the analysis of salts more or less soluble in water.——The student has still to learn how substances insoluble in water are to be brought into a state of solution; but, once dissolved, their analysis is effected by the same scheme as that just given. The second Table may therefore be regarded as fairly representing the method by which metallic constituents of chemical substances are separated from each other and recognized. The methods of isolation of the complementary constituent of the salt (the reactions of non-metals and acidulous radicals) will form the next object of practical study.

The group-tests adopted in the Tables are, obviously, hydrochloric acid, sulphuretted hydrogen, sulphydrate of ammonium, carbonate of ammonium, and arseniate of ammonium. If a group-test produces no precipitate, it is self-evident that there can be no member of the group present. At first, therefore, add only a small quantity of a group-test, and if it produces no effect add no more, for it is not advisable to overload a solution with useless reagents; substances expected to come down as precipitates are not unfrequently held in the liquid, not by the water or acid or alkali present, but by the strong aqueous solution of some group-reagent thoughtlessly added. Indeed experienced manipulators not unfrequently make preliminary trials with group-reagents on a few drops only of the liquid under examination; if a precipitate is produced, it is added to the bulk of the original liquid and the addition of the group-reagent continued; if a precipitate is not produced, the few drops are thrown away and the unnecessary addition of a group-reagent thus avoided altogether, an advantage fully making up for the extra trouble of making a preliminary trial. While shunning excess, however, care must be taken to avoid deficiency; a substance only partially removed from solution through the addition of an insufficient amount of a reagent will reappear where not expected, be consequently mistaken for something else, and cause much trouble; this will not occur if the appearance, odour, or reaction of the liquid on test-paper be duly observed. It is also a good plan, when a group-reagent has produced a precipitate and the latter has been filtered out, to add a little more of the reagent to the clear filtrate; if more precipitate is pro-

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duced, an insufficient amount of the group-test was introduced in the first instance; but the error is corrected by simply refiltering; if no precipitate occurs, the mind is satisfied and the way cleared for further operations.

Group-precipitates, or any precipitates still requiring examination, should, as a rule, be well washed before further testing; this is to remove the aqueous solution of other substances hanging about the precipitate (the mother-liquor as it is termed), so that subsequent reactions may take place fairly between the reagent used and the precipitate only. A precipitate is sometimes in so fine a state of division as to retard filtration by clogging the pores of the paper, or even to pass through the filter altogether; in these cases the mixture may be warmed or boiled, which usually causes aggregation of the particles of a precipitate, and hence facilitates filtration.

It is immaterial whether a solution be first divided into group-precipitates or each precipitate be examined as soon as produced; if the former method be adopted, confusion will be avoided by labelling or marking the funnels or papers holding the precipitate "the HCl ppt.," "the H_2S ppt.," and so on.

The colours and general appearance of the various sulphides, oxides, &c. precipitated should be borne in mind, as the absence of other bodies, as well as the presence of those thrown down, is often at once thus indicated. For example, if a precipitate by sulphydrate of ammonium is white, neither cobalt, nickel, nor iron can be present, and only small quantities of manganese and chromium.

Application of confirmatory tests should be frequent.

The student should record results of analyses neatly in his memorandum-book. The various reactions which occur in an analysis have already come before him in going through the tests for the individual metals or in other analytical operations, he need not, therefore, again draw out equations or diagrams. But he should think over the reactions; and if they are not perfectly clear to his mind, he should write them out again and again till thoroughly understood.

Special Memoranda.

The hydrochloric acid precipitate may at first include some antimony and bismuth as oxychlorides, readily dissolved, however, by excess of acid.——If either of these elements is present the washings of the precipitate will probably be milky; in that

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case add a few drops of hydrochloric acid, which will clear the liquid and make way for the application of the lead-test.

The sulphuretted hydrogen precipitate may be white, in which case it is nothing but sulphur; for, as already indicated, ferric salts are reduced to ferrous, and chromates to the lower salts of chromium by sulphuretted hydrogen, sulphur being deposited:—

$$2Fe_2Cl_6 + 2H_2S = 4FeCl_2 + 4HCl + S_2$$

$$4H_2CrO_4 + 6H_2S + 12HCl = 2Cr_2Cl_6 + 16H_2O + 3S_2.$$

The portion of the sulphuretted hydrogen precipitate dissolved by sulphydrate of ammonium may include a trace of copper, sulphide of copper being not altogether insoluble in sulphydrate of ammonium.——On adding hydrochloric acid to the sulphydrate of ammonium solution, a white precipitate of sulphur only may be precipitated, the sulphydrate of ammonium nearly always containing free sulphur.——Carbonate of ammonium does not readily dissolve small quantities of sulphide of arsenicum out of much sulphide of antimony; and, on the other hand, carbonate of ammonium takes into solution a small quantity of sulphide of antimony if much sulphide of arsenicum is present. The original solution should therefore always be examined by the hydrogen tests for arsenicum and antimony if any doubt exists concerning the presence or absence of either. Tin remains in the hydrogen-bottle in the metallic state, deposited as a black powder on the zinc used in the experiment. The contents of the bottle are turned out into a dish, ebullition continued until evolution of hydrogen ceases, and the zinc is taken up by the excess of sulphuric acid employed; any tin is then filtered out, washed, dissolved in a few drops of hydrochloric acid, and the liquid tested for tin by the usual reagents.

The portion of the sulphuretted hydrogen precipitate not dissolved by the sulphydrate of ammonium may leave a yellow semifused globule of sulphur on boiling with nitric acid. This globule may be black, not only from presence of mercuric sulphide, but also from enclosed particles of other sulphides protected by the sulphur from the action of the acid. It may also contain sulphate of lead, produced by the action of nitric acid on sulphide of lead. In cases of doubt the mass must be removed from the liquid, boiled with nitric acid till dissolved, the solution evaporated to remove excess of acid, and the residue examined; but usually it may be disregarded.——In testing for lead by sulphuric acid the liquid should be diluted and set aside

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for some time.——The cadmium carbonate may remain in solution with the copper, dissolved by the influence of alkaline salts. In that case acidify the liquid containing the two metals, pass sulphuretted hydrogen through it, wash the precipitate and digest in solution of cyanide of potassium; sulphide of copper is dissolved, the yellow sulphide of cadmium remains insoluble.

Mercury may also be isolated by digesting the sulphuretted hydrogen precipitate in sulphydrate of sodium instead of sulphydrate of ammonium. The sulphides of arsenicum, antimony, tin, and mercury are thus dissolved out. The mixture is then filtered, excess of hydrochloric acid added to it, and the precipitated sulphides collected on a filter, washed, and digested in sulphydrate of ammonium; sulphide of mercury remains insoluble, while the sulphides of arsenicum, antimony, and tin are dissolved. By this method copper also appears in its right place only, sulphide of copper being quite insoluble in sulphydrate of sodium. The other metals are then separated in the usual way.

The sulphydrate-of-ammonium precipitate may, if the original solution was acid, contain Phosphates, Oxalates, Silicates, and Borates of the alkaline earths. These will subsequently come out with the iron and, being white, give the iron precipitate a light-coloured appearance; their examination must be conducted separately, by a method described subsequently in connexion with the treatment of substances insoluble in water.——Precipitates containing aluminium, iron, and chromium often carry down some manganese, which subsequently comes out with the iron. This manganese may be detected by washing the ferric hydrate to remove all trace of chlorides, boiling with nitric acid, adding puce-coloured oxide of lead and setting the vessel aside; permanganic acid is formed, recognized in the clear liquid by its purple tint.——The precipitate containing iron, aluminium, and chromium may also be treated by a somewhat different method, as follows:—wash, dry, fuse with nitrate and hydrate of sodium, boil the residue with water; the iron remains insoluble as oxide: the aluminium may be precipitated as hydrate by adding excess of acid to the alkaline filtrate and then excess of ammonia: the chromium may be recognized by adding excess of acetic acid to the alkaline liquid and then acetate of lead. By this process the oxide of chromium is oxidized, chromate of potassium being formed, the oxides of iron and aluminium remaining unaltered. ——If much cobalt or nickel be present in the sulphydrate-of-ammonium precipitate, the greater part may remain undissolved by the hydrochloric acid. Collect any residue, therefore, wash,

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test a portion for cobalt on a borax bead in the blowpipe-flame (=blue colour); dissolve the remainder in a few drops of hydrochloric with one or two of nitric acid, and if cobalt is not present, test at once for nickel by solution of potash or soda (=green precipitate); if cobalt is present, evaporate the acid solution nearly to dryness, add acetic acid and then nitrite of potassium, set aside; and when the yellow cobalt precipitate has separated, filter, and then add potash or soda for nickel.

The carbonate-of-ammonium precipitate may not contain the whole of the barium, strontium, and calcium in the mixture unless free ammonia is present; for the carbonates of those metals are soluble in water charged with carbonic acid. If, therefore, the liquid is not distinctly ammoniacal, solution of ammonia should be added.——Neither carbonate nor hydrate of ammonium wholly precipitate magnesian salts; and as a partial precipitation is undesirable, a solvent, in the form of an alkaline salt (chloride of ammonium), if not already present, must be added.

The search for lithium may usually be omitted. Should a precipitate, supposed to be due to lithium, be obtained, it must be tested in a flame (=scarlet tint), as a little magnesium not unfrequently shows itself under similar circumstances. If present only in minute proportions, the lithium may also remain with the alkalies; it can then only be detected by physical analysis (by a prism) of the light emitted from a tinged flame; by, in short, an instrument termed a spectroscope. Such a method of examination is termed spectrum analysis, a subject of much interest and of no great difficulty, but scarcely within the range of Pharmaceutical Chemistry.

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ACIDS.

The radicals which have up to this point mainly occupied the attention of the student are (admitting ammonium) metals; and they have been almost exclusively studied not in the free state, but in the condition in which they exist in salts. Moreover these metals have been treated as if they formed the more important constituent, the stronger half, the foundation or base, of salts. Attention has been continuously directed to the metallic or *basylous* side of salts. There is still one more basylous radical worthy of a passing notice, though it usually plays only a subordinate part in reactions; and this radical, differing from the others that have been studied, is, so far as we know at present, a non-metal—Hydrogen. Unlike the salts of the metals, too, the salts of hydrogen are never, in medicine or the arts generally, used for the sake of their hydrogen, but always for the other half of the salt, the *acidulous* side. And it is not for their basylous radical that these hydrogen salts are now commended to the notice of the student *, but in order that he may study, under the most favourable circumstances, those acidulous groupings which he has been continually meeting in operations on salts, but which, to him, were for the time of secondary importance. He may now treat them as the primary objects of attention; and there is no better way of doing so than in operating on their compounds with hydrogen, the relatively inferior importance of which element, as compared with potassium, iron, &c., will

* It must not be forgotten that the commonest salt of any radical whatsoever is a salt of hydrogen, the oxide of hydrogen (H_2O), *water*. In the reactions already performed, the value of this compound has been constantly recognized, both for its hydrogen and for its oxygen, but most of all as the vehicle or medium by which nearly all other atoms are enabled to come into that contact with each other without which their existence would be almost useless; for some atoms are like some animals, out of water they are as inactive as fishes. It is true that both fishes and salts have usually to be removed from water to be utilized by man; but before they can be assimilated, either as food or as medicine, they must again seek the agency of water.

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serve to give the desired prominence to the acidulous bodies in question.

These salts of hydrogen are the common, sharp, sour bodies termed acids (from the Latin root *acies*, an edge). The following Table includes the formulæ and names of the most important. A few of those mentioned are unstable or somewhat rare; in such cases a common metallic salt containing the acidulous radical may be used for reactions in the place of the hydrogen salt:—

HCl	hydrochloric acid.
HBr	hydrobromic acid.
HI	hydriodic acid.
HCN (HCy)	hydrocyanic acid.
HNO_3	nitric acid.
$HClO_3$	chloric acid.
HBO_2	boracic acid.
$HC_2H_3O_2$	acetic acid *.
H_2S	hydrosulphuric acid †.
H_2SO_3	sulphurous acid.
H_2SO_4	sulphuric acid.
H_2CO_3?	carbonic acid.
$H_2C_2O_4$	oxalic acid.
$H_2C_4H_4O_6$	tartaric acid.
$H_3C_6H_5O_7$	citric acid.
H_3PO_4	phosphoric acid.

The student will at once notice a prominent point of difference between the basylous radicals he has met with up to the present time and the acidulous groupings now brought before him. The former are nearly all elements, ammonium only being a compound; the latter are mostly compounds, chlorine, bromine, iodine, and sulphur being the only elements. This difference will not, how-

* The hydrogen on the acidulous side must not be confounded with the basylous hydrogen in all these hydrogen salts or acids; the two perform entirely different functions. Hydrogen in the acidulous portion is like the hydrogen in the basylous radical ammonium, it has combined with other atoms, to form a group which plays more or less the part of an elementary radical, and to which a single symbol is not unfrequently applied (Am; Cy, $\overline{A}$, $\overline{O}$, $\overline{T}$, $\overline{C}$, &c.). Cobalt, chromium, iron, platinum, &c. resemble hydrogen in this respect in often uniting with other atoms to form definite acidulous radicals in which the usual basylous character of the metals has for the time disappeared.

† Synonyms:—sulphydric acid and sulphuretted hydrogen.

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ever, be so apparent when the chemistry of alcohols, ethers, and such bodies has been mastered, for they are all salts of *compound* basylous radicals.

The above acids contain the only acidulous groupings that commonly present themselves in analysis, or in pharmaceutical operations. There are, however, several other acids (such as hypochloric, nitrous, hypophosphorous, valerianic, benzoic, gallic, tannic, uric, hyposulphurous, hydroferrocyanic, hydroferridcyanic, &c.) with which the student should be more or less familiar; reactions concerning these will therefore be described. Arsenious, arsenic, stannic, manganic, and chromic acids have already been treated of in connexion with the metals they contain; in practical analysis they always become sufficiently altered to come out among the metals.

A glance at the foregoing Table is sufficient to show the quantivalence of the acidulous radicals, if so they may be called. The first eight are clearly univalent; then follow six bivalent, leaving two trivalent.

These all combine with equivalent amounts of basylous radicals to form various salts; hence they may be termed monobasylous, dibasylous, and tribasylous radicals. The acids themselves are often spoken of as monobasic, dibasic, and tribasic respectively, or monobasic and polybasic.

The practical study of the acidulous side of salts will occupy far less time than the basylous. Salts will then be briefly examined as a whole.

One word of caution. It is only for purposes of convenience in the division of chemistry for systematic study that salts may be considered to contain basylous and acidulous radicals, or separate sides, so to speak; for we possess no absolute knowledge of the internal arrangement of the atoms (admitting that there are such things) in the molecule of a salt. A salt is probably a whole, having no such sides as those mentioned.

HYDROCHLORIC ACID.

Formula HCl. Molecular weight* 36·5.

The acidulous radical of hydrochloric acid and of other chlorides is the element chlorine (Cl). It occurs in nature chiefly as chloride of sodium (NaCl), either solid, under the name of *rock-salt*,

* The weight of a molecule is the sum of the weights of its atoms.

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mines of which are not unfrequently met with, or in solution in the water of all seas. Common table-salt is more or less pure chloride of sodium in minute crystals. Chlorine, like hydrogen, is univalent (Cl'); its atomic weight is 35·5. For the method by which it is prepared, and its properties, see page 12.

Reactions.

First Synthetical Reaction.—To two or three fragments of chloride of sodium add a few drops of strong sulphuric acid; colourless and invisible gaseous hydrochloric acid is evolved, sulphate of sodium remaining. Adapt to the mouth of the test-tube, by a perforated cork, a piece of glass tubing bent twice at right angles, and convey the gas into another test-tube containing a few drops of water; solution of hydrochloric acid results.

$2NaCl$	$+$	H_2SO_4	$=$	$2HCl$	$+$	Na_2SO_4
Chloride of sodium.		Sulphuric acid.		Hydrochloric acid.		Sulphate of sodium.

The product of this operation is the liquid commonly termed hydrochloric acid. When of certain given strengths it forms *Acidum Hydrochloricum*, B. P., and *Acidum Hydrochloricum Dilutum*, B. P. The process is also that of the Pharmacopœia, larger vessels being employed, and the gas being freed from any trace of sulphuric acid by washing. Other chlorides yield hydrochloric acid when heated with sulphuric acid; but chloride of sodium is always used because cheap and common. The acid is a by-product in the manufacture of carbonate of sodium (p. 205).

Invisible gaseous hydrochloric acid forms visible greyish-white fumes on coming into contact with air. This is due to combination with the moisture of the air. The intense greediness of hydrochloric gas and water for each other is strikingly demonstrated on opening a test-tube full of the gas under water; the latter rushes into and instantly fills the tube. If the water is tinged with blue litmus, the acid character of the gas is prettily shown at the same time. The test-tube, which should be perfectly dry, may be filled from the delivery-tube direct, for the gas is somewhat heavier than, and therefore readily displaces, air. The mouth may be closed by the thumb of the operator.

The process, as described in the British Pharmacopœia, includes the use of more sulphuric acid than is theoretically necessary;

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hence some acid sulphate of sodium remains with the normal sulphate of sodium in the generating vessel. A hot solution of this residue, carefully neutralized by carbonate of sodium, filtered and set aside, yields normal sulphate (*Sodæ Sulphas*, B. P.) only.

$$\underset{\text{Acid sulphate of sodium.}}{2NaHSO_4} + \underset{\text{Carbonate of sodium.}}{Na_2CO_3} = \underset{\text{Sulphate of sodium.}}{2Na_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Second Synthetical Reaction.—To a few drops of hydrochloric acid (that is, the common aqueous solution of the gas) add a few grains of black oxide of manganese, and warm the mixture; chlorine, the acidulous radical of all chlorides, is evolved, and may be recognized by its peculiar odour, or irritating effects on the nose and air-passages.

$$4HCl + MnO_2 = Cl_2 + 2H_2O + MnCl_2.$$

This is the process of the British Pharmacopœia for the production of chlorine-water (*Liquor Chlori*, B. P.), the gas being first washed and then passed into water.

To obtain the chlorine from other chlorides, sulphuric acid, as well as black oxide of manganese, must be added. Hydrochloric acid is first formed (*vide* page 174). The action described in the above equation then goes on, except that half instead of the whole of the oxygen of the black oxide is available for the removal of the hydrogen from the chlorine of the hydrochloric acid, the other half being taken up by the hydrogen of the sulphuric acid. Thus, supposing common salt to be the chloride used, the following equations may represent the supposed steps of the process:—

$$\begin{aligned} 2NaCl + H_2SO_4 &= Na_2SO_4 + 2HCl \\ MnO_2 + H_2SO_4 &= MnSO_4 + H_2O + O \\ 2HCl + O \quad &= H_2O \quad + Cl_2; \end{aligned}$$

or the whole may be included in one equation:—

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

This reaction may have occasional analytical interest, a very small quantity of combined chlorine being recognized by its means. But the following reaction is nearly always applicable for the detection of this element, and leaves nothing to be desired in point of delicacy:—

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Analytical Reaction.

To a drop of hydrochloric acid, or to a dilute solution of any other chloride, add solution of nitrate of silver; a white curdy precipitate falls. Pour off most of the supernatant liquid, add nitric acid, and boil; the precipitate does not dissolve. Pour off the acid, and add ammonia; the precipitate quickly dissolves. Neutralize the solution by an acid, chloride of silver is once more precipitated.

The formation of this white precipitate, its appearance, insolubility in boiling nitric acid, solubility in ammonia, and reprecipitation by an acid, form abundant evidence of the presence of chlorine. Its occurrence as a chloride of a metal is determined by testing for the metal with the appropriate reagents; its occurrence as hydrochloric acid is considered to be indicated by the odour, if strong, and the sour taste, if weak, of the liquid, and the action of the liquid on blue litmus paper, which, like other acids, it reddens.

If hydrochloric acid be present in excessive quantity it will, in addition to the above reactions, give rise to strong effervescence on the addition of a carbonate, a chloride being formed. In cases of poisoning by strong hydrochloric acid, a solution of carbonate of sodium (common washing soda) or a mixture of magnesia and water may be administered as antidotes.

HYDROBROMIC ACID.

Formula HBr. Molecular weight 81.

The acidulous radical of hydrobromic acid and other bromides is the element bromine, Br (*Bromum*, B. P.). It occurs in nature chiefly as bromide of magnesium in sea-water. It may be liberated from its compounds just as chlorine, to which it bears strong analogies—that is, by heating with black oxide of manganese and sulphuric acid. It is a dark-red volatile liquid, emitting an odour more irritating, if possible, than chlorine.

The atom of bromine, like that of chlorine, is univalent (Br'); its atomic weight is 80. The bromide of hydrogen, hydrobromic acid, is made by decomposing bromide of phosphorus by water—$PBr_5 + 4H_2O = 5HB + H_3PO_4$. Bromide of potassium (KBr) is occasionally employed in pharmacy, and is the salt, therefore, which

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may be used in studying the reactions of this acidulous radical. The officinal method of making the salt has been alluded to under the salts of potassium (page 35). Other bromides are seldom used; they may be prepared in the same way as, and closely resemble, the corresponding chlorides or iodides. Bromide of ammonium (AmBr) (*Ammonii Bromidum*, B. P.) may be made by saturating hydrobromic acid with ammonia: $HBr + AmHO = AmBr + H_2O$. Bromine is slightly soluble in water: *Solution of Bromine*, B. P., is such an aqueous solution.

Analytical Reactions.

First Analytical Reaction.—To a few drops of solution of a bromide (KBr, *e. g.*) add solution of nitrate of silver; a yellowish-white precipitate of bromide of silver (AgBr) falls. Treat the precipitate successively with nitric acid and ammonia, as described for the chloride of silver; it is insoluble in, or only sparingly dissolved by, the ammonia.

Second Analytical Reaction.—To solution of a bromide add a drop or two of chlorine-water, or a bubble or two of chlorine gas; then add a few drops of chloroform or ether, shake the mixture, and set the test-tube aside; the chlorine, from the greater strength of its affinities, liberates the bromine, which is dissolved by the chloroform or ether, the solution falling to the bottom of the tube in the case of the heavy chloroform, or rising to the top in the case of the light ether. Either solution has a distinct yellow or reddish-yellow or red colour, according to the amount of bromine present.

This reaction serves for the isolation of bromine when mixed with many other substances. Excess of chlorine must be avoided, as colourless chloride of bromine is then formed. Iodides give a somewhat similar result; the absence of iodine must therefore be insured by a process given in the next section. The above solution in chloroform or ether may be removed from the tube by drawing up into a pipette (small pipe, a narrow glass tube, usually having a bulb or expanded portion in the centre) the bromine fixed by the addition of a drop of solution of potash or soda,

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the chloroform or ether evaporated off, and the residue tested as described in the next reaction.

The above operation is frequently employed for synthetical purposes.

Third Analytical Reaction.—Liberate bromine from a bromide by the cautious addition of chlorine or chlorine-water, then add a few drops of cold decoction of starch; a yellow combination of bromine and starch, commonly termed "bromide of starch," is formed.

Decoction of starch is made by rubbing down two or three grains of starch with some drops of cold water, then adding more water and boiling the mixture.

The above reaction may be varied by liberating the bromine by a little black oxide of manganese and a drop of sulphuric acid, the upper part of the inside of the test-tube being smeared over with some thick decoction of starch or thin starch-paste.

HYDRIODIC ACID.

Formula HI. Molecular weight 128.

The acidulous radical of hydriodic acid and other iodides is the element iodine (I). It occurs in nature chiefly as iodide of sodium, and of magnesium in sea-water. Seaweeds, sponges, and other marine plants, which derive much of their nourishment from sea-water, store up the iodides in their tissues, and it is from the ashes of these plants that our supplies of iodine (*Iodum*, B. P.) are obtained. Iodine is liberated from iodides, as bromine from bromides, or chlorine from chlorides—namely, by the action of black oxide of manganese and sulphuric acid. Iodine is a crystalline purplish-black substance; its vapour, readily seen on heating a fragment in a test-tube, is dark violet. Its vapours are irritating to the lungs; but a trace may be inhaled with safety (*Vapor Iodi*, B. P.).

The atom of iodine, like those of bromine and chlorine, is univalent (I′); its relative weight is 127. The iodide of hydrogen, hydriodic acid, is rarely employed, and is therefore seldom met with; but the iodide of potassium (KI) is largely used in medi-

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cine, and hence is the most convenient iodide on which to experiment in studying the reactions of this acidulous radical. Solid iodine itself might be taken for the purpose; but its use and action in that state have already been alluded to in describing the iodides of potassium, cadmium, and mercury; its analytical reactions in the combined condition are those which may now occupy attention.

Iodine is slightly soluble in water (iodine-water), and readily soluble in an aqueous solution of iodide of potassium (see *Liquor Iodi*, B. P., and *Unguentum Iodi*, B. P.). It is more soluble in spirit, or in a spirituous solution of iodide of potassium (*Tinctura Iodi*, B. P.). It apparently combines with sulphur (*Sulphuris Iodum*, B.P., and *Unguentum Sulphuris Iodidi*); but the compound is ill-defined and unstable.

Analytical Reactions.

First Analytical Reaction.—To a few drops of an aqueous solution of an iodide (KI, &c.) add solution of nitrate of silver; a yellowish-white precipitate of iodide of silver (AgI) falls. Treat the precipitate with nitric acid, it is not dissolved; add ammonia, it is insoluble, or only sparingly dissolved.

This reaction is useful in separating iodine from most other acidulous radicals, but does not distinguish iodine from bromine.

Second Analytical Reaction.—Liberate iodine from an iodide by the cautious addition of chlorine, then add cold decoction of starch; a deep blue combination of iodine and starch, commonly termed "iodide of starch," is formed.

Starch is highly sensitive to the action of iodine; this reaction is consequently very delicate and characteristic. Excess of chlorine must be avoided, or colourless chloride of iodine will be produced. Nitrous acid, or a nitrite acidulated with sulphuric acid, may be used instead of chlorine. The reaction is not observed in hot liquids.

Third Analytical Reaction.—To a neutral aqueous solution of an iodide add a solution containing one part of sulphate of copper

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to two parts of green sulphate of iron; a dirty-white precipitate of cuprous iodide (Cu_2I_2) falls.

$$2KI + 2CuSO_4 + 2FeSO_4 = Cu_2I_2 + K_2SO_4 + Fe_23SO_4.$$

Chlorides and bromides are not affected in this way; the reaction is useful, therefore, in removing iodine from a solution in which bromides have to be sought. The total removal of iodine by this process is insured by supplementing the addition of the cupric and ferric sulphates by a few drops of ammonia, any acid which might be keeping cuprous iodide in solution being thereby neutralized, ferric or ferrous oxide, precipitated at the same time, not affecting the reaction. Chloride of the rare metal palladium performs a similar useful office in removing iodine, but not bromine or chlorine, from solutions.

Fourth Analytical Reaction.—Iodides have been shown to be useful in testing for mercuric salts (see the Mercury reactions, page 117); a mercuric salt (corrosive sublimate, for example) may, therefore, be used in testing for iodides, a scarlet precipitate of mercuric iodide (HgI_2) being produced.

This reaction may be employed where large quantities of an iodide are present; but its usefulness in analysis is much impaired by the fact that the precipitate is soluble in excess of the dissolved iodide, or in excess of the mercuric reagent. Its colour and insolubility in water distinguish it from mercuric chloride, bromide, and cyanide, which are white soluble salts.

Fifth Analytical Reaction.—Iodides have also (see the Lead reactions, page 124) been shown to be useful in testing for lead salts; similarly a lead salt (acetate, for example) may be used in testing for iodides, a yellow precipitate of iodide of lead (PbI_2), soluble in hot water and crystallizing in yellow scales on cooling, being produced.

Chloride, bromide, and cyanide of lead are white; hence the above reaction may be occasionally useful in distinguishing iodine from the allied radicals. But iodide of lead is slightly soluble in cold water; hence small quantities of iodine cannot be detected by this reaction.

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HYDROCYANIC ACID.

Formula HNC or HCy. Molecular weight 27.

The acidulous radical of hydrocyanic acid and other cyanides is a compound body, cyanogen (Cy). It is so named from κύανος, *kuanos*, blue, and γεννάω, *gennao*, I generate, in allusion to its prominent chemical character of forming, with iron, the different varieties of Prussian blue. It was from Prussian blue that Scheele in 1782 first obtained what we now, from our knowledge of its composition, term hydrocyanic acid, but which he called Prussic acid. Cyanogen was isolated by Gay-Lussac in 1814, and was the first compound radical distinctly proved to exist.

Cyanogen does not occur in nature, and is only formed from its elements under certain circumstances. It is found in small quantities among the gases of iron-furnaces, and is produced to a slight extent in distilling coals for gas. It is obtained abundantly by strongly heating animal refuse containing nitrogen, such as the scrapings of horns, hoofs, hides, &c., with carbonate of potassium and waste iron. The cyanogen thus produced unites with the potassium and iron to form what is known as the yellow prussiate of potash (*Potassæ Prussias Flava*, B. P.), or ferrocyanide of potassium ($K'_4Fe''Cy'_6$). From this salt all other cyanides are directly or indirectly prepared. Cyanide of potassium (KCy), which is the most common, is procured by fusing ferrocyanide of potassium with carbonate of potassium in a crucible; carbonic acid gas (CO_2) is evolved, iron (Fe) is set free, and cyanate of potassium (KCyO), a body that will be subsequently noticed, is formed at the same time:—

$$K_4FeCy_6 + K_2CO_3 = 5KCy + KCyO + Fe + CO_2.$$

Cyanogen, like chlorine, bromine, and iodine, is univalent (Cy'). It may be isolated by simply heating mercuric cyanide ($HgCy_2$) or cyanide of silver (AgCy). It is a colourless gas, burning, when ignited, with a beautiful peach-blossom-coloured flame.

Reactions.

Synthetical Reaction.—Dissolve two or three grains of ferrocyanide of potassium in water in a test-tube, add a few drops of sulphuric acid and boil the mixture, conveying the evolved gas by a bent glass tube (adapted to the test-tube by a cork) into

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another test-tube containing a little water; the product is a dilute solution of hydrocyanic acid. Made in larger quantities and of a certain definite strength (2 per cent.), this solution is the *Acidum Hydrocyanicum Dilutum*, B. P. The process is also that of the Pharmacopœia.

$$2K_4FeCy_6 + 6H_2SO_4 = Fe''K_2FeCy_6 + 6KHSO_4 + 6HCy.$$

The residue of this reaction is acid sulphate of potassium ($KHSO_4$), which remains in solution, and ferrocyanide of potassium and iron ($Fe''K_2FeCy_6$), an insoluble powder sometimes termed Everitt's yellow salt, from the name of the chemist who first made out the nature of the reaction. The latter compound becomes bluish green during the reaction, owing to absorption of oxygen. Pure anhydrous hydrocyanic acid is a colourless, highly volatile, intensely poisonous liquid, solidifying when cooled to a low temperature. It may be made by passing sulphuretted hydrogen over mercuric cyanide.

A few drops of diluted hydrocyanic acid so placed that its vapour may be inhaled, forms the *Vapor Acidi Hydrocyanici*, B. P., or Inhalation of Hydrocyanic Acid.

Analytical Reactions.

First Analytical Reaction.—To a few drops of the hydrocyanic acid solution produced in the above reaction, or to any solution of a cyanide, add solution of nitrate of silver; a white precipitate of cyanide of silver (AgCy) falls. Add nitric acid to the liquid; the precipitate does not dissolve: add ammonia; it is insoluble, or only sparingly soluble.

Cyanogen in an insoluble cyanide, such as cyanide of silver itself, is readily recognized on heating the substance in a short piece of glass tubing closed at one end like a test-tube and drawn out at the other end, so as to have but a small opening; on applying a flame, the escaping cyanogen ignites and burns with a characteristic peach-blossom-tint.

Second Analytical Reaction.—To solution of hydrocyanic acid, or a soluble cyanide, add a few drops of solution of a ferrous

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salt and a drop or two of solution of a ferric salt; to the mixture add potash or soda, and then hydrochloric acid; a precipitate of Prussian blue remains. The decompositions may be traced in the following equations:—

$$\begin{aligned} HCy &+ KHO = KCy &+ H_2O \\ 2KCy &+ FeSO_4 = FeCy_2 &+ K_2SO_4 \\ 4KCy &+ FeCy_2 = K_4FeCy_6 \text{ or } K_4Fcy \\ 3K_4Fcy &+ 2Fe_2Cl_6 = 12KCl &+ Fe_4Fcy_3 \end{aligned}$$

The test depends on the conversion of the cyanogen into ferrocyanogen by the iron of a ferrous salt, and the combination of the ferrocyanogen, so produced, with the iron of a ferric salt. Hence a mixture of green sulphate of iron, solution of perchloride of iron, and either magnesia or carbonate of sodium, is the recognized antidote in cases of poisoning by hydrocyanic acid or cyanide of potassium. From the rapidity of the action of these poisons, however, there is seldom time to prepare an antidote. Emetics, the stomach-pump, the application of a stream of cold water to the spine, and the above antidote, form the usual treatment.

Third Analytical Reaction.—To solution of any alkaline cyanide, or to hydrocyanic acid and ammonia, add common yellow sulphydrate of ammonium, and evaporate the liquid nearly or quite to dryness in a small dish, occasionally adding ammonia till the excess of sulphydrate of ammonium is decomposed; acidify the liquid with hydrochloric acid, and then add a drop of solution of a ferric salt; a blood-red solution of sulphocyanate of iron will be formed.

This is a very delicate reaction. The free sulphur in the yellow sulphide of ammonium unites with the alkaline cyanide and forms sulphocyanate ($2AmCy + S_2 = 2AmCyS$), the ammonia combines with excess of free sulphur and forms, among other salts, sulphydrate of ammonium, the whole of which is removed by the ebullition. If the liquid has not been evaporated far enough, sulphydrate of ammonium may still be present, and give black sulphide of iron on the addition of the ferric salt.

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NITRIC ACID.

Formula HNO_3. Molecular weight 63.

The group of elements represented by the formula NO_3 is that characteristic of nitric acid and all other nitrates; hence it is expedient to regard these elements as forming an acidulous radical, which may be termed *the nitric radical*. Like the hypothetical basylous radical ammonium (NH_4), this supposed acidulous radical (NO_3) has not been isolated. Possibly it is liberated when chlorine is brought into contact with nitrate of silver; but if so, its decomposition into white crystalline nitric anhydride (N_2O_5) and oxygen (O) is too rapid to admit of its identification.

The nitrogen and oxygen of the air combine and ultimately form nitric acid whenever a current of electricity (as in the occurrence of lightning) passes; hence nitrates are commonly met with in waters, soils, and the juices of plants. Nitric acid and other nitrates are obtained from nitrates of potassium and sodium, and these from the surface soil of tropical countries. Nitrate of potassium or prismatic nitre (from the form of its crystals) is chiefly produced in India. The natives simply scrape the surface of waste grounds, mud heaps, banks, and other spots where a slight incrustation indicates the presence of appreciable quantities of nitre, mix the scrapings with wood-ashes (carbonate of potassium to decompose the nitrate of calcium always present), digest the mixture in water, and evaporate the liquor. The impure product is purified by careful recrystallizations. Besides its use in medicine, it is employed in very large quantities in the manufacture of gunpowder. Nitrate of sodium occurs in more distinct incrustations on the surface of the ground in Peru, Bolivia, and Chili, more especially in the district of Atacama; it is distinguished as Chili saltpetre or (from the form of its crystals) cubic nitre, and is chiefly used as a manure and as a source of nitric acid, its tendency to absorb moisture unfitting it for use in gunpowder. In many parts of Europe nitrate of potassium is made artificially by exposing heaps of animal manure, refuse, ashes, and soil to the action of the air and the heat of the sun: in the course of a year or two the nitrogen of the animal matter becomes oxidized to nitrates, and the latter are removed by washing. The word *nitre* is the English equivalent of the Greek νίτρον (*nitron*), a name applied to certain natural deposits of *natron* (carbonate of sodium), for which nitrate of potassium seems at first to have been mistaken. *Saltpetre* is simply *sal*

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petræ, salt of the rock, in allusion to the natural origin of nitrate of potassium. *Sal prunella* (from *sal*, a salt, and *pruna*, a live coal) is nitrate of potassium melted over a fire and cast into cakes or bullets.

The nitric radical is univalent (NO_3').

Memorandum.—It is here necessary again to caution the reader against regarding salts as invariably possessing a known constitution, or supposing that they always possess two or more sides, or contain definite radicals. The erroneous conception which, of all others, is most likely to be imperceptibly formed is that of considering salts as binary bodies. For, first, the names of salts are necessarily binary. A student hears the names "sulphate of iron," "sulphate of copper," and simultaneously receives the impression that each salt has two sides, copper or iron occupying one and something indicated by the words "sulphate of" the other. The words "vitriol," green or blue, "nitre," &c. would perhaps implant unitary ideas in his mind; but it is simply impossible to give such names to all salts as will convey the impression that each salt is a whole, and therefore unitary. The name "sulphate of potash" produces binary impressions; and the less incorrect name, "sulphate of potassium," is in this respect no better.

Secondly, it is impracticable to study salts as a whole. Teachers are unanimous in the opinion that students should first master the reactions characteristic of the metals in salts, and then the residues which, with those metals, make up the salts, or *vice versâ*. It is not only impracticable, but impossible, to study salts as a whole; binary ideas concerning them are, therefore, almost inevitably imbibed. We come to regard a salt as a body which splits up in one direction only, look upon nitre, for instance, and all other nitrates, as containing NO_3 and a metal; whereas KNO_3 may be split up into KNO_2 and O; or into K_2O, N_2, and O_5; or may contain K_2O and N_2O_5. Under these circumstances perhaps the best plan is to make a virtue of a necessity, and regard salts as binary bodies containing a basylous and an acidulous radical, but not to give the acidulous radical any very definite name unless it has been isolated or is well known to exist. Thus in nitre let the group of elements which, with potassium, makes up the whole salt be termed the nitric radical. Similarly let the acidulous residues of other salts of metals be termed respectively chloric, boracic, acetic, sulphurous, sulphuric, carbonic, oxalic, tartaric, phosphoric, citric, &c. radicals. In short, let these compound radicals be regarded as groupings common to

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many salts, and which may usually be transferred without any apparent breaking or splitting; at the same time we must be prepared to find that occasionally a salt splits up in other directions. Whenever there is good reason to believe that the acidulous grouping is not itself a radical, but only contains a radical, the attention of the student will be drawn to the matter. In this way perhaps erroneous impressions will gain least hold on the mind, and a way be left open for the easy entrance of new truths, should the real constitution of salts be discovered.

Reactions.

Synthetical Reaction.—To a fragment of nitrate of potassium in a test-tube add a drop or two of sulphuric acid, and warm; nitric acid (HNO_3) is evolved in vapour. The fumes may be condensed by a bent tube fitted to the test-tube, not by a cork as for hydrochloric acid, because the nitric vapours would strongly act on it, but by plaster of Paris, a paste of which sets hard in a few minutes, and is unaffected by the acid.

On the somewhat larger scale of the Pharmacopœia, nitric acid may be prepared by heating, in a stoppered or plain retort, a mixture of equal weights of nitrate of potassium and sulphuric acid; the acid distils over, and acid sulphate of potassium remains behind:—

KNO_3	+	H_2SO_4	=	HNO_3	+	$KHSO_4$
Nitrate of potassium.		Sulphuric acid.		Nitric acid.		Acid sulphate of potassium.

Half the quantity of sulphuric acid may be taken; but in that case neutral sulphate of potassium (K_2SO_4) is produced, which, from its hard, slightly soluble character, is removed with difficulty from the retort. On the large scale the less proportion is used; but instead of retorts iron cylinders are employed, from which the residual salt is removed by chisels. Moreover the cheaper sodium salt is the nitrate from which manufacturers usually prepare nitric acid.

Pure nitric acid (HNO_3) is a colourless liquid, somewhat difficult of preparation; its specific gravity is 1·52. The strongest acid met with in commerce has a sp. gr. of 1·5, and contains 93

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per cent. of real nitric acid (HNO_3); it fumes disagreeably, is unstable, and, except as an escharotic, is seldom used. The British Pharmacopœia contains two acids:—*Acidum Nitricum*, prepared as above, of sp. gr. 1·42, and containing 70 per cent. of real acid (HNO_3); and another, *Acidum Nitricum Dilutum*, sp. gr. 1·101, containing 17½ per cent. Either of the stronger liquids, although containing water, is usually simply termed "nitric acid."

Three fluid-ounces of nitric acid (B. P.), four of hydrochloric acid (B. P.), and twenty-five of water, form the *Acidum Nitro-hydrochloricum Dilutum* of the British Pharmacopœia. The acids must be mixed some time before dilution to ensure mutual decomposition and full development of the chief active product, chlorine:—

$$\underset{\text{Nitric acid.}}{2HNO_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Chloronitric gas.}}{N_2O_2Cl_4} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Chlorine.}}{Cl_2}$$

In the later stages of the reaction, the decomposition expressed in the following equation also probably occurs:—

$$\underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Hydrochloric acid.}}{3HCl} = \underset{\text{Chloronitrous gas.}}{NOCl} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{Cl_2}$$

Analytical Reactions.

First Analytical Reaction.—To nitric acid or solution of any nitrate add sulphuric acid, and then copper turnings, and warm; nitric oxide gas (N_2O_2) is evolved, which at once unites with the oxygen in the tube, giving *red fumes* of peroxide of nitrogen (N_2O_4).

$$2HNO_3 + 3H_2SO_4 + Cu_3 = N_2O_2 + 3CuSO_4 + 4H_2O;$$
$$N_2O_2 + O_2 = N_2O_4.$$

Performed on a larger scale, this reaction becomes of synthetical interest, being the process for the preparation of nitric oxide gas.

Small amounts of a nitrate may be overlooked by this test, the colour of the red fumes not being very intense.

Second Analytical Reaction.—To solution of a nitrate, even if

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very dilute, add three or four crystals of sulphate of iron, shake gently for a minute in order that some of the sulphate may become dissolved, and then pour eight or ten drops of strong sulphuric acid down the side of the test-tube, so that it may form a layer at the bottom of the vessel; a reddish-purple or black coloration will appear between the acid and the supernatant liquid.

This is a very delicate test for the presence of nitrates. The black colour is due to a solution, or perhaps combination, of nitric oxide with a portion of the ferrous salt. The nitric oxide is liberated from the nitrate by the reducing action of the hydrogen of the sulphuric acid, the sulphuric radical of which is absorbed by the ferrous sulphate, the latter salt becoming ferric sulphate.

$$2HNO_3 + 3H_2SO_4 + 6FeSO_4 = 4H_2O + 3(Fe_23SO_4) + N_2O_2.$$

The process of *oxidation* is one frequently employed in experimental chemistry; and nitrates, from their richness in oxygen, but more especially because always at hand, are the oxidizers usually selected for the purpose. In the operation they generally split up in one way, namely into oxide of their basylous radical, nitric oxide gas, and available oxygen. Thus hydrogen nitrate (nitric acid) yields oxide of hydrogen (water) and the other bodies mentioned, as shown in the following equation:—

$$4HNO_3 = 2H_2O + 2N_2O_2 + 3O_2.$$

When nitrates, other than nitric acid, are used for the purpose of oxidation, a stronger acid, generally sulphuric, is commonly added in order that nitric acid may be formed; the hydrogen nitrate splitting up more readily than other nitrates.

Third Analytical Reaction.—Direct the blowpipe-flame on to charcoal until a spot is red-hot; now place on the spot a fragment of a nitrate; deflagration ensues.

This reaction does not distinguish nitrates from chlorates. It is insufficient for the recognition of very small quantities of either class of salts, especially when they are mixed with other substances.

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The presence of the nitric radical in a solution having been proved by the above reactions, its occurrence as the nitrate of a metal is demonstrated by the neutral, or nearly neutral, deportment of the liquid with test-paper and the detection of the metal—its occurrence as nitric acid by the sourness of the liquid to the taste, and the effervescence produced on the addition of a carbonate. In cases of poisoning by strong nitric acid, solution of carbonate of sodium (common washing soda), a mixture of magnesia and water, &c. may be administered as antidotes.

CHLORIC ACID.

Formula $HClO_3$. Molecular weight 84·5.

The group of elements represented by the formula ClO_3 is that characteristic of chloric acid and all other chlorates; hence it is expedient to regard it as being an acidulous radical, which may be termed the chloric radical. Like the nitric radical, it has not been isolated. Chloric anhydride also (Cl_2O_5), unlike nitric anhydride, has not yet been obtained in the free condition.

Chlorates are artificial salts. They are formed when chlorine and certain metallic hydrates come into contact, the mass being subsequently boiled with water, thus (M=metal):—

$$3Cl_2 + 6MHO = MClO_3 + 5MCl + 3H_2O.$$

Mixed hydrates yield a chlorate of one metal and chloride of the other, a point of considerable importance in making the chlorate used in medicine (chlorate of potassium), as otherwise five-sixths of the potassium would be wasted as chloride; whereas from a proper mixture of hydrate of potassium and the inexpensive hydrate of calcium (slaked lime), the potassium all comes out as chlorate,—chloride of calcium, a valueless salt, being the by-product:—

$6Cl_2$	+ $2KHO$	+ $5CaH_2O_2$	= $2KClO_3$	+ $5CaCl_2$	+ $6H_2O$
Chlorine.	Hydrate of potassium.	Hydrate of calcium.	Chlorate of potassium.	Chloride of calcium.	Water.

This is the process of the Pharmacopœia for *Potassæ Chloras*,—carbonate of potassium and a little more lime, for the conversion of the carbonate into hydrate, being used instead of hydrate, previously made.

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$$\underset{\text{Chlorine.}}{6Cl_2} + \underset{\text{Carbonate of potassium.}}{K_2CO_3} + \underset{\text{Hydrate of calcium.}}{6CaH_2O_2} = \underset{\text{Chlorate of potassium.}}{2KClO_3} + \underset{\text{Carbonate of calcium.}}{CaCO_3} + \underset{\text{Chloride of calcium.}}{5CaCl_2} + \underset{\text{Water.}}{6H_2O}$$

The salt can also be made from chloride of potassium. Chlorate of potassium is readily soluble in water, and is usually administered medicinally in aqueous solution, sometimes also in lozenges (*Trochisci Potassæ Chloratis*, B. P.).

Chlorate of potassium, when heated, yields chloride of potassium and oxygen, and is the salt commonly employed in the preparation of the gas for experimental purposes. But if the action be arrested when one-third of the oxygen has escaped, the residual salt is found to contain perchlorate of potassium ($KClO_4$):—

$$2KClO_3 = KClO_4 + KCl + O_2.$$

Chloric acid ($HClO_3$) may be isolated, but is unstable, quickly decomposing into chlorine, oxygen, and perchloric acid; some other chlorate must therefore be used in studying the reactions of the chloric radical. Perchloric acid ($HClO_4$) may be obtained by distilling perchlorate of potassium with sulphuric acid; it is quite stable, and is occasionally administered in medicine.

The chloric radical is univalent (ClO_3').

Reactions.

First Analytical Reaction.—To solution of a chlorate (*e. g.* chlorate of potassium) add solution of nitrate of silver; no precipitate falls, showing that the chlorine must be performing different functions to those it possesses in chlorides. Evaporate the solution to dryness, and place the residue in a small dry test-tube; or at once drop a fragment of a chlorate into a test-tube and heat strongly; oxygen is evolved, and may be recognized by its power of reinflaming an incandescent match inserted in the tube. Boil the residue with water, and again add solution of nitrate of silver; a white precipitate falls, having all the characters of chloride of silver, as described under hydrochloric acid.

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This is a trustworthy test, and, omitting the recognition of the oxygen, may be applied in the detection of small quantities of chlorates.

Second Analytical Reaction.—To a fragment of a chlorate add two or three drops of strong sulphuric acid; an explosive gas (Cl_2O_4) is evolved, having a peculiar odour somewhat like chlorine, but deeper in colour than that element.

$$3KClO_3 + H_2SO_4 = Cl_2O_4 + KClO_4 + K_2SO_4 + H_2O.$$

Warm the upper part of the test-tube to 150° F. or 200° F., or introduce a hot wire; a sharp explosion ensues, due to decomposition of the gas, peroxide of chlorine, into its elements.

Third Analytical Reaction.—Heat a small fragment of a chlorate with hydrochloric acid; a yellowish-green explosive gas, termed *euchlorine*, is evolved. Its colour is deeper than that of chlorine, hence the name (from εὖ, *eu*, well, and χλωρὸς, *chloros*, green). In odour it resembles chlorine, and is probably a mixture of that element with one of the oxides of chlorine.

Fourth Analytical Reaction.—Direct the blowpipe-flame on to charcoal until a spot is red-hot, and then place on the spot a fragment of a chlorate; deflagration ensues as with nitrates.

BORACIC ACID.

Formula HBO_2. Molecular weight 44.

Boracic acid exists in the jets of steam (*fumerolles* or *suffioni*) that issue from the earth in some districts of Tuscany. It collects in the water of the *lagoni* (lagoons or little lakes) formed at the orifice of the steam-channel. Neutralized by carbonate of sodium it gives common borax ($2NaBO_2, B_2O_3, 10H_2O$), a salt somewhat similar in constitution to the red chromate of potassium and other similar abnormal salts. Borax is also found native, particularly in Thibet. Fused borax readily dissolves metallic oxides, as will have been already noticed in testing for cobalt, &c. Hence, besides its use in medicine (*Borax;*

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Mel Boracis, B. P., and *Glycerinum Boracis*, B. P.), it is employed as a flux in refining and other metallurgic and ceramic operations.

The boracic radical is univalent (BO_2'); it has not been isolated. The element boron, like carbon, occurs in the amorphous, graphitoidal, and crystalline condition. It is a trivalent element (B'''), yielding definite salts, such as the chloride (BCl_3) &c. Its atomic weight is 11.

Reactions.

Synthetical Reaction.—To a hot solution of a crystal of borax add a few drops of sulphuric acid and set the tube aside; on cooling, crystalline scales of boracic acid (HBO_2, H_2O) are deposited.

When fused, these crystals lose water and yield boracic anhydride (B_2O_3).

Analytical Reactions.

First Analytical Reaction.—Dip a piece of turmeric paper (paper soaked in tincture of turmeric tubers and dried) into a solution of boracic acid; it is coloured brown-red, as by alkalies.

The usual way of applying this test is as follows:—Add to the borate a few drops of hydrochloric acid, immerse half of a slip of turmeric paper in the liquid, then remove the hydrochloric acid by drying the paper over a flame. Concentrated hydrochloric acid and ferric chloride produce a somewhat similar effect.

Second Analytical Reaction.—To a fragment of a borate (borax, for example) in a small dish or watch-glass add a drop of sulphuric acid and then a little alcohol, warm the mixture and set light to the spirit; the resulting flame will be tinged of a greenish colour at its edges by the volatilized boracic acid.

The liquid should be well stirred while burning. Salts of copper and some metallic chlorides produce a somewhat similar colour.

Other Analytical Reactions.—In solutions of normal borates

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($NaBO_3$ &c.) barium salts give a white precipitate of barium borate ($Ba2BO_3$) soluble in acids and alkaline salts. Nitrate of silver gives borate of silver ($AgBO_3$), soluble in nitric acid and in ammonia. Chloride of calcium, if the solution is not too dilute, gives white borate of calcium.

ACETIC ACID.

Formula $HC_2H_3O_2$, or $H\bar{A}$. Molecular weight 60.

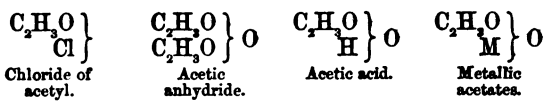
Acetic acid is said to occur naturally in certain plant-juices and animal fluids in minute proportions, but otherwise is an artificial product. Much is furnished by the destructive distillation of wood, hence the term *pyroligneous acid* for the crude product, a hybrid word from *πῦρ, pūr*, fire, and *lignum*, wood. In Germany and France large quantities are made by the spontaneous oxidation of the alcohol in inferior wines, hence the *white-* and *red-wine vinegar* (*vinegar*, from the French *vin*, wine, and *aigre*, sour). In England also the domestic form of acetic acid (vinegar) has a similar origin: infusion of malt is fermented; and the resulting oxidation of its sugar, instead of being arrested when the product is an alcoholic liquid, a sort of beer, is allowed to go on to the next stage, acetic acid; it usually contains from 3 to 6 per cent. of acetic acid ($HC_2H_3O_2$). The officinal vinegar (*Acetum*, B. P.) contains nearly 5½ (5·4) per cent. The so-called vinegar of Cantharides (*Acetum Cantharidis*, B. P.) is a solution of the active principle of cantharides in very strong acetic acid, not in vinegar. The vinegar of squills (*Acetum Scillæ*, B. P.) is also a solution of the active principle of squills in diluted acetic acid, not in true vinegar. In the Pharmacopœia, vinegar, except its use for its own sake, is only employed in the preparation of *Emplastrum Cerati Saponis*.

The group of elements represented by the formula $C_2H_3O_2$ is that characteristic of acetic acid and other acetates, and may, for convenience of study, be assumed to be an acidulous univalent radical. It has not been isolated, unless indeed a compound of similar composition, resulting from the action of peroxide of barium on acetic anhydride, is the radical in question.

$C_2H_3O_2$, the characteristic grouping in acetates, is frequently considered to contain, rather than to be, a radical—the radical C_2H_3O, termed *acetyl*. Acetates may be made to yield a body

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having the composition C_2H_3OCl, which is regarded as chloride of acetyl; from this may be obtained acetic anhydride ($C_4H_6O_3$), which by absorbing water becomes acetic acid.



The relation of acetic acid to alcohol will be evident from the following equation representing the formation of the acid:—

$$\underset{\text{Alcohol.}}{C_2H_6O} + O_2 = \underset{\text{Acetic acid.}}{C_2H_4O_2} + H_2O$$

Reactions.

Synthetical Reaction.—To a few grains of acetate of sodium in a test-tube add a little water and some sulphuric acid, and heat the mixture; acetic acid is evolved, and may be condensed by a bent tube adapted to the test-tube by a cork in the usual way.

This is the process by which acetate of sodium or calcium (the neutralized products of the distillation of wood) are made to yield acetic acid on the large scale. As with nitric and hydrochloric acids, the loose term "acetic acid" is that usually applied to aqueous solutions of acetic acid. The *Acidum Aceticum*, B. P., contains nearly 33 per cent. of real acid—that is, of $HC_2H_3O_2$; for it contains only 28 per cent. of acetic anhydride ($C_4H_6O_3$). *Acidum Aceticum Dilutum*, B. P., contains about $4\frac{1}{4}$ per cent. of $HC_2H_3O_2$. Glacial acetic acid ($HC_2H_3O_2$) contains no water. It solidifies to a crystalline mass at temperatures below 63° F., hence the appellation *glacial* (from *glacies*, ice). Good commercial glacial acetic acid (*Acidum Aceticum Glaciale*, B. P.) does not contain more than 1 per cent. of water; it solidifies at 34°, and again liquefies at 48°.

The following equation is expressive of the above reaction:—

$$\underset{\text{Acetate of sodium.}}{2NaC_2H_3O_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Acetic acid.}}{2HC_2H_3O_2} + \underset{\text{Sulphate of sodium.}}{Na_2SO_4}$$

or, assuming the existence of acetyl (C_2H_3O) in acetic acid, and a corresponding radical sulphuryl (SO_2) in sulphuric acid,

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$$2\left.\begin{matrix}C_2H_3O\\Na\end{matrix}\right\}O + \left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 = 2\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + \left.\begin{matrix}SO_2\\Na_2\end{matrix}\right\}O_2;$$

or, thirdly, on the assumption that salts contain the oxide of a basylous radical united with the anhydride of an acid, the old view under which such names as acetate of soda were formed,

$$Na_2O, C_4H_6O_3 + H_2O, SO_3 = Na_2O, SO_3 + H_2O, C_4H_6O_3.$$

Which of these three equations, or, more broadly, which of the three views of the constitution of salts illustrated by the equations, is correct, it is impossible to say. Whether it is $C_2H_2O_2$, C_2H_3O, or $C_4H_6O_3$ which migrates from one acetic compound to another, whether it is SO_4, SO_2, SO_3 which migrates from one sulphuric compound to another, and so on with other acidulous groupings, cannot at present be determined. There are strong objections to each view, and probably neither is right. Either the given radicals cannot be isolated; or application of the forces of heat, light, and electricity do not confirm views arrived at by the results of operations with the chemical force; or a salt comes to be regarded as having so large a number of constituent parts that the view, however true, breaks down in practice from the sheer inability of the mind to grasp the complicated analogies involved.

Yet for the purposes of description, study, and conversation some system must be adopted. Let the first, then, be generally taken, over-reliance on it being checked by general instead of special names for the hypothetical radicals, and other systems be used in certain cases. (See also p. 185.)

Acetic acid often contains sulphurous acid. The method by which this impurity is detected will be described hereafter.

Analytical Reactions.

First Analytical Reaction.—To an acetate add sulphuric acid and heat the mixture; acetic acid, recognized by its odour, is evolved.

Iodine, sulphurous acid, and other substances of powerful odour mask that of acetic acid; they must be removed, therefore, usually by precipitation or oxidation, before applying this test.

It will be noticed that this reaction is identical with the pre-

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vious one; it has synthetical or analytical interest, according to the object and method of its performance.

Second Analytical Reaction.—Repeat the above action, a few drops of spirit of wine being added to the mixture before applying heat; acetic ether (acetate of ethyl, $C_2H_5C_2H_3O_2$), also of characteristic odour, is evolved.

The basylous radical ethyl (C_2H_5) will be referred to subsequently.

Third Analytical Reaction.—Heat a fragment of a dry acetate in a test-tube, and again notice the odour of the gaseous products of the decomposition; among them is *acetone* (C_3H_6O), the smell of which is characteristic. Carbonate of the metal remains in the test-tube.

Fourth Analytical Reaction.—To a solution of an acetate, made neutral by the addition of acid or alkali, as the case may be, add a few drops of neutral solution of perchloride of iron; a deep-red liquid results, owing to the formation of ferric acetate ($Fe_26C_2H_3O_2$).

Note.—The student will notice that the formation of characteristic precipitates, the usual method of removing radicals from solution for recognition, is not carried out in the qualitative analysis of acetates. This is because all acetates are soluble. Acetate of silver ($AgC_2H_3O_2$) and mercurous acetate ($Hg_22C_2H_3O_2$) are only sparingly soluble in cold water, but the fact can seldom be utilized in analysis. Hence peculiarities of colour and odour, the next best characters on which to rely, are adopted as means by which acetates may be detected. Acetates, like other organic compounds, char when heated to a high temperature.

HYDROSULPHURIC ACID.

Formula H_2S. Molecular weight 34.

The acidulous radical of *hydrosulphuric acid, sulphydric acid,* or *sulphuretted hydrogen* and other sulphides, is the element sulphur (S). It occurs in nature in combination with metals, as

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already stated in describing the ores of some of the metals, and also in the free state. Most of the sulphur used in medicine is imported from Sicily, where it occurs chiefly associated with blue clay. It is purified by fusion, sublimation, or distillation. Melted and poured into moulds, it constitutes a crystalline mass termed *roll sulphur*. If distilled and the vapour carried into large chambers, so that it may be rapidly condensed, the crystals are so minute as to give the sulphur a pulverulent character; this is *sublimed sulphur* (*Sulphur Sublimatum*, B. P.), or *flowers of sulphur*. The third common form, *milk of sulphur*, will be noticed subsequently. Sulphur also occurs in nature in combination as a constituent of animal and vegetable tissues, as sulphurous acid gas (SO_2) in volcanic vapours, and as sulphuretted hydrogen in some waters, as those of Harrogate.

Sulphur (S″) being the first acidulous radical of bivalent activity met with up to the present time, it is desirable to here draw attention to a new class of salts to which such a radical may obviously give rise. These are acid salts, which are intermediate between normal salts and acids. Univalent radicals with an atom of hydrogen give an acid, and with an atom of other basylous radicals an ordinary or normal salt. But bivalent radicals, from the fact that they give with two atoms of hydrogen an acid, and with two atoms of univalent metals, &c. a normal salt, may obviously give intermediate bodies containing one atom of hydrogen and one atom of metal; these are appropriately termed acid salts: they are neither normal acids nor normal salts, but salt acids, or rather acid salts. Whether or not these salts give an acid reaction with blue litmus paper depends on the strength of the respective radicals. Usually they do redden the test-paper, but sometimes not; thus the acid sulphide or sulphydrate of potassium (KHS), of sodium (NaHS), or ammonium (AmHS) has alkaline properties*.

Reactions.

First Synthetical Reaction.—The preparation of sulphuretted

* Some chemists regard these sulphydrates as compounds of basylous radicals with HS, a univalent grouping termed hydrosulphyl (persulphide of hydrogen), just as hydrates are similarly viewed as compounds of the univalent radical hydroxyl (HO) (peroxide of hydrogen),—H_2S becoming HHS or HHs (hydrosulphylide of hydrogen), and H_2O becoming HHO or HHo (hydroxylide of hydrogen).

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hydrogen. This operation was described on page 47, and probably has been performed by the student many times.

Second Synthetical Reaction.—Prepare the variety of the radical of sulphides known as *Precipitated Sulphur* (*Sulphur Præcipitatum*, B. P.) by boiling a few grains of flowers of sulphur with an equal bulk of slaked lime and some water in a test-tube, filtering, and adding to a portion of the filtrate dilute hydrochloric acid; sulphur is precipitated, and may be collected on a filter, washed, and dried.

This is the process of the Pharmacopœia. Polysulphide of calcium and hyposulphite of calcium are formed:—

$$\underset{\text{Hydrate of calcium.}}{3CaH_2O_2} + \underset{\text{Sulphur.}}{6S_2} = \underset{\text{Polysulphide of calcium.}}{2CaS_5} + \underset{\text{Hyposulphite of calcium.}}{CaS_2O_3} + \underset{\text{Water.}}{3H_2O}$$

On adding the acid both salts are decomposed and sulphur separates:—

$$\underset{\text{Polysulphide of calcium.}}{2CaS_5} + \underset{\text{Hyposulphite of calcium.}}{CaS_2O_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Chloride of calcium.}}{3CaCl_2} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Sulphur.}}{6S_2}$$

Polysulphide of calcium alone would yield sulphuretted hydrogen as well as sulphur on the addition of acid. Hyposulphite of calcium alone would yield sulphurous acid gas as well as sulphur. If these gases are formed in the above operation, they at once react and give sulphur and water:—

$$4H_2S + 2SO_2 = 3S_2 + 4H_2O.$$

To another portion of the filtrate add sulphuric acid; the precipitate is in this case largely contaminated with sulphate of calcium:—

$$\underset{\text{Polysulphide of calcium.}}{2CaS_5} + \underset{\text{Hyposulphite of calcium.}}{CaS_2O_3} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} = \underset{\text{Sulphate of calcium.}}{3CaSO_4} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Sulphur.}}{6S_2}$$

Place a little of each of these moist specimens of precipitated sulphur with a drop of the supernatant liquid on a strip of glass, cover each spot with a piece of thin glass, and examine the precipitates under the microscope; the pure sulphur will be found

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to consist of minute grains or globules, the impure to contain comparatively large tabular crystals (sulphate of calcium).

By far the larger proportion of precipitated sulphur met with in commerce is still (1867) adulterated with sulphate of calcium, most specimens containing less than half their weight of sulphur. Moreover this fraud has been so persistently practised that many persons have become sufficiently accustomed to the satiny appearance of the impure article to regard the pure article with suspicion, sometimes refusing to purchase it.

To ascertain the amount of sulphate of calcium in an impure specimen of precipitated sulphur, place a weighed quantity in a tared crucible and heat till no more vapours are evolved. The weight of the residue, with one-fourth thereof added, is the amount of crystalline sulphate of calcium ($CaSO_4, 2H_2O$) present in the original quantity of impure sulphur.

Analytical Reactions.

To a sulphide add a few drops of hydrochloric acid; sulphuretted hydrogen will probably be evolved, well known by its odour. If the sulphide is not acted upon by the acid, or if free sulphur be under examination, mix a minute portion with a fragment of solid caustic potash or soda, and fuse on a silver coin or spoon. When cold place a drop of dilute hydrochloric acid on the spot, sulphuretted hydrogen is evolved, and a black stain, due to sulphide of silver (Ag_2S) left on the coin.

Other sulphur reactions may be adopted as tests, but the above are sufficient for all ordinary purposes.

SULPHUROUS ACID.

Formula H_2SO_3. Formula of sulphurous acid gas or sulphurous anhydride, commonly termed sulphurous acid, SO_2.

When sulphur is burnt in the air it combines with oxygen and forms sulphurous acid gas (SO_2), more correctly termed sulphurous anhydride, or commonly, but erroneously, sulphurous acid. If this gas becomes moist or is passed into water, heat is evolved and true sulphurous acid (H_2SO_3) formed. The latter body may

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be obtained in crystals; but it is very unstable, and hence the properties of the sulphurous radical must be studied under the form of some other sulphite; sulphite of calcium ($CaSO_3$), or sulphite of sodium (Na_2SO_3), may be used for the purpose.

The radical of the sulphites is bivalent (SO_3''), and hence forms acid sulphites, such as acid sulphite of potassium ($KHSO_3$) and normal sulphites, such as sulphite of sodium (Na_2SO_3).

The sulphites are so named from the usual rule, that salts corresponding with acids whose names end in *ous* have a name ending in *ite*. They are generally made by passing sulphurous acid gas over moist oxides or carbonates.

Synthetical Reaction.—To a few drops of sulphuric acid, in a test-tube, add a piece of charcoal and apply heat; sulphurous acid gas is evolved, and may be conveyed by a bent tube into a small quantity of cold water in another test-tube. The product is the *Acidum Sulphurosum*, B. P. It contains, if saturated, nearly 12 (11·79) per cent. of sulphurous acid (H_2SO_3), or about 9 (9·2) per cent. of the gas (SO_2). The process is also that described in the Pharmacopœia, except that the gas is purified by passing through a small wash-bottle before final collection.

If in this process the water were replaced by solutions of metallic oxides or carbonates, sulphites of the various metals would be formed.

$$\underset{\text{Sulphuric acid.}}{4H_2SO_4} + \underset{\substack{\text{Carbon}\\\text{(charcoal).}}}{C_2} = \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{2CO_2} + \underset{\text{Water.}}{4H_2O} + \underset{\substack{\text{Sulphurous}\\\text{acid gas.}}}{4SO_2}$$

$$\underset{\substack{\text{Sulphurous}\\\text{acid gas.}}}{SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sulphurous}\\\text{acid.}}}{H_2SO_3}$$

Analytical Reactions.

First Analytical Reaction.—To a sulphite add a drop or two of dilute hydrochloric acid; sulphurous acid gas escapes, known by its odour.

This odour is the same as that evolved on burning lucifer matches that have been tipped with sulphur. It is due, pro-

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bably not to the gas (SO_2), but to sulphurous acid (H_2SO_3) formed by the union of sulphurous acid gas with either the moisture of the air or that on the surface of the mucous membrane of the nose.

Second Analytical Reaction.—To a sulphite add a little water, a fragment or two of zinc, and then hydrochloric acid; sulphuretted hydrogen will be evolved, known by its odour or by its action on a piece of paper placed like a cap on the mouth of the test-tube, and moistened with a drop of solution of acetate of lead, black sulphide of lead being formed. Sulphurous acid may be detected in acetic acid by this test.

$$H_2SO_3 + H_6 = H_2S + 3H_2O.$$

Other Analytical Reactions.

To solutions of neutral sulphites add nitrate or chloride of barium, chloride of calcium, or nitrate of silver; in each case white sulphites of the various metals are precipitated. The barium sulphite is soluble in weak hydrochloric acid; but if a drop or two of chlorine-water is first added, barium sulphate is formed, which is insoluble in acids. The other precipitates are also soluble in acids. The silver sulphite is decomposed on boiling, sulphuric acid being formed, and metallic silver set free.

SULPHURIC ACID.

Formula H_2SO_4. Molecular weight 98.

Sulphates occur in nature; but the common and highly important hydrogen sulphate, sulphuric acid, is made artificially. Sulphur itself, or sometimes the sulphur in iron pyrites, is first converted into sulphurous acid gas by burning in air, and this gas, by moisture and oxygen, into sulphuric acid ($SO_2+H_2O+O=H_2SO_4$). The oxygen necessary to oxidize the sulphurous acid is obtained from the air, but not directly, the agency of nitric oxide (N_2O_2) being employed—this gas becoming nitric peroxide (N_2O_4) by action of the air, and the nitric peroxide again becoming nitric oxide by the action of the sulphurous acid gas, and so on. A

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small quantity of nitric peroxide will in this way act as carrier of oxygen from the air to very large quantities of sulphurous acid.

The nitric peroxide is in the first instance obtained from nitrate of potassium or sodium by the action of a small quantity of the sulphuric acid of a previous operation. Sulphuric acid may be obtained by other processes, as by distilling the sulphate of iron resulting from the natural oxidation of iron pyrites by air; but it is seldom so made at the present day. The following equations represent the various steps in the usual process:—

$$\underset{\text{Nitrate of sodium.}}{2NaNO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sulphate of sodium}}{Na_2SO_4} + \underset{\text{Nitric acid.}}{2HNO_3}$$

$$\underset{\text{Sulphur.}}{S_2} + \underset{\text{Oxygen.}}{2O_2} = \underset{\text{Sulphurous acid gas.}}{2SO_2}$$

$$\underset{\text{Sulphurous acid gas.}}{SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphurous acid.}}{H_2SO_3}$$

$$\underset{\text{Sulphurous acid.}}{3H_2SO_3} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Sulphuric acid.}}{3H_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Nitric oxide.}}{N_2O_2}$$

$$\underset{\text{Nitric oxide.}}{N_2O_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Nitric peroxide.}}{N_2O_4}$$

$$\underset{\text{Nitric peroxide.}}{N_2O_4} + \underset{\text{Sulphurous acid.}}{2H_2SO_3} = \underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Nitric oxide.}}{N_2O_2}$$

On the large scale the sulphurous acid gas is produced by burning sulphur in furnaces; it is carried, together with the nitric vapours, by flues into leaden chambers, where jets of steam supply the necessary moisture; the steam also, condensing, prevents other reactions. Sulphuric acid may be freed from any trace of nitrous compounds by heating with a half per cent. of sulphate of ammonium, water and nitrogen being produced (Pelouze).

The sulphuric radical being bivalent (SO_4''), acid as well as normal sulphates may exist. Acid sulphate of potassium ($KHSO_4$) is an illustration of the former, sulphate of sodium (Na_2SO_4) of the latter; *double sulphates* may also exist, such as $KMgSO_4$. Sulphates generally contain water of crystallization.

Pure sulphuric acid (H_2SO_4) is of specific gravity 1·848. The best "oil of vitriol" of commerce is of specific gravity 1·843, and

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contains 96·8 per cent. of real acid (H_2SO_4). This is the *Acidum Sulphuricum*, B. P. The *Acidum Sulphuricum Dilutum*, B. P., contains about 12½ (12·42) per cent. of acid (H_2SO_4); and the *Acidum Sulphuricum Aromaticum*, B. P., a dilute acid in which is dissolved the soluble aromatic parts of cinnamon and ginger, contains nearly 13½ (13·36) per cent. of acid (H_2SO_4). There are some definite compounds of sulphuric acid with water; the first (H_2SO_4, H_2O) may be obtained in crystals.

Sulphuric anhydride (S_2O_6) is a white silky crystalline solid, having no acid properties. It is made by distilling sulphuric acid with phosphoric anhydride ($2H_2SO_4 - 2H_2O = S_2O_6$). It appears to unite with sulphuric acid and some other normal sulphates to form compounds ($R_2SO_4SO_3$) resembling in constitution red chromate of potassium or borax. The fuming sulphuric acid (H_2SO_4, SO_3), made at Nordhausen in Saxony, seems to be such a body.

Sulphuric acid is a most valuable compound to all chemists. It is the key by which hundreds of chemical salts are unlocked, and their contents utilized. To describe its uses would be to write a work on chemistry.

Analytical Reactions.

First Analytical Reaction.—To solution of a sulphate add nitric acid, and then solution of a barium salt; a white precipitate of sulphate of barium ($BaSO_4$) falls. Boil the mixture, the precipitate does not dissolve.

This reaction is as highly characteristic of sulphates, as it has been stated to be of barium salts (*vide* page 53). The only error likely to be made in its application is that of overlooking the fact that nitrate and chloride of barium are less soluble in strong acid than in water. On adding the barium salt to the acid liquid, therefore, a white precipitate may be obtained, which is simply the nitrate or chloride of barium. The appearance of such a precipitate differs considerably from that of the barium sulphate; hence a careful student will not be misled. Should any doubt remain, water should be added, which will dissolve the nitrate or chloride, but not affect the sulphate.

Second Analytical Reaction.—Mix a fragment of an insoluble sulphate ($BaSO_4$ *e.g.*) with carbonate of potassium or of sodium,

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or, better, with both carbonates, and fuse the mixture in a small crucible. Digest the residue when cold, in water, and filter; the filtrate may be tested for the sulphuric radical.

This is a convenient method of qualitatively analyzing insoluble sulphates, such as those of barium and lead.

Third Analytical Reaction.—Mix a fragment of an insoluble sulphate with a little alkaline carbonate on a piece of charcoal, taking care that some of the charcoal-dust is included in the mixture. Heat the little heap in the blowpipe-flame until it fuses, and, when cold, add a drop of acid; sulphuretted hydrogen is evolved, recognized by its odour.

This is another process for the recognition of insoluble sulphates. Other compounds of sulphur, and sulphur itself, give a similar result. It is therefore rather a test for sulphur and its compounds than sulphates only; but the absence of the other compounds can generally, if necessary, be previously determined.

The presence of the sulphuric radical in a solution having been proved by the above reactions, its occurrence as the normal sulphate of a metal is demonstrated by the neutral, or nearly neutral, deportment of the liquid with test-paper, and the detection of the metal; its occurrence as sulphuric acid by the sourness of the liquid to the taste, and the effervescence produced on the addition of a carbonate. In cases of poisoning by strong nitric acid, solution of carbonate of sodium (common washing-soda), magnesia and water, &c. may be administered as antidotes.

CARBONIC ACID.

Formula H_2CO_3. Formula of carbonic acid gas, commonly termed carbonic acid, CO_2.

Carbonates (compounds containing the grouping CO_3) are very common in nature, the calcium carbonate ($CaCO_3$) being widely distributed as chalk, limestone, or marble. The hydrogen carbonate, true carbonic acid, is not known, unless, indeed, carbonic acid gas assumes that condition on dissolving in water. Such a solution changes the colour of blue litmus paper, and the gas does not; this may be because only the true acid (H_2CO_3) affects the litmus, or because the gas (CO_2) cannot come into real

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contact with the litmus without a medium. From the commonest natural carbonate, carbonate of calcium, are derived the carbonic constituents of the one most frequently used in medicine, carbonate of sodium. Carbonate of sodium is prepared from the chief natural salt, the chloride. After the chloride has been converted into sulphate (salt-cake) by sulphuric acid,

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$

the sulphate is roasted with limestone and small coal, by which carbonate of sodium and an oxysulphide of calcium are formed:—

$$5Na_2SO_4 + C_{20} + 7CaCO_3 = 5Na_2CO_3 + 5CaS,2CaO + 20CO + 2CO_2.$$

Carbonic oxide gas and some carbonic acid gas escape; and carbonate of sodium (soda-ash) is dissolved out of the residual mass (black ash) by water, the oxysulphide of calcium remaining insoluble. The reaction is rendered more intelligible by regarding it as occurring in two stages:—1st, the reduction of the sulphate of sodium to sulphide by the carbon of the coal,

$$Na_2SO_4 + C_4 = Na_2S + 4CO;$$

2nd, the reaction of the sulphide of sodium and carbonate of calcium, thus—

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS;$$

and, 3rd, the combination of sulphide of calcium with lime from the chalk,

$$5CaS + 2CaCO_3 = 5CaS,2CaO + 2CO_2.$$

Carbonic acid gas is a product of the combustion of all carbonaceous matters. It is constantly exhaled by animals and inhaled by plants, its intermediate storehouse being the atmosphere, which contains about 4 parts in 10,000. A larger proportion than that just mentioned gives to air depressing effects, 4 or 5 per cent. rendering the atmosphere poisonous when taken into the blood from the lungs. Carbonic acid may, however, be taken into the stomach with beneficial sedative effects; hence, probably, much of the value of such effervescing liquids as soda-water, lemonade, and solutions of the various granulated preparations and effervescing powders. The gas liquefies on being compressed, and the liquid solidifies on being cooled.

Reactions.

Synthetical and Analytical Reactions.—To a fragment of marble

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in a test-tube add water and then hydrochloric acid; carbonic acid gas (CO_2) is evolved, and may be conveyed into water &c. by the usual delivery-tube.

This is the process of the British Pharmacopœia, and the one usually adopted for experimental purposes. Passed into carbonate of sodium, the gas gives *Sodæ Bicarbonas*, B. P., and into carbonate of potassium, *Potassæ Bicarbonas*, B. P. On the large scale the gas is prepared from chalk and sulphuric acid, frequent stirring promoting its escape.

Pass the gas into lime-water, and a white precipitate of carbonate of calcium ($CaCO_3$) occurs. Solution of subacetate of lead may be used instead of, and is perhaps even a more delicate test than, lime-water.

The evolution of a gas on adding an acid to a salt, warming the mixture if necessary, the gas being inodorous and giving a white precipitate with lime-water, is sufficient evidence of the presence of a carbonate.

Blow air from the lungs through a glass tube into lime-water; the presence of carbonic acid gas is at once indicated.

The passage of a considerable quantity of normal air through lime-water produces a similar effect. A bottle containing lime-water soon becomes coated with carbonate of calcium from absorption of carbonic acid gas.

Fill a dry test-tube with the gas, by passing the delivery-tube of the above apparatus to the bottom of the test-tube. Being rather more than once and a half as heavy as the air (1·5203), it will displace the latter. Prove the presence of the gas by pouring it slowly, as if a visible liquid, into another test-tube containing lime-water; the characteristic cloudiness and precipitate is obtained on gently shaking the lime-water.

Pass carbonic acid gas through lime-water until the precipitate at first formed is dissolved. The resulting liquid is a solution of carbonate of calcium in carbonic acid water. Boil the solution;

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carbonic acid gas escapes, and the carbonate is again precipitated.

This experiment will serve to show how chalk is kept in solution in ordinary well-waters, giving the property of "hardness," and how the *fur* or stone-like deposit in tea-kettles and boilers is formed. It should be here stated that sulphate of calcium produces the same result, and that these, with the sulphate and carbonate of magnesium, constitute the hardening constituents of well-waters; a curd (oleate of calcium or magnesium) being formed whenever soap is used with such waters.

OXALIC ACID.

Formula $H_2C_2O_4, 2H_2O$ or $H_2\overline{O}, 2Aq$. Molecular weight 126.

Oxalates occur in nature in the juices of some plants, as wood-sorrel, rhubarb, the common dock, and certain lichens; but the hydrogen oxalate (oxalic acid) and other oxalates are all made artificially. Many organic substances yield oxalic acid when boiled with nitric acid, and an alkaline oxalate when roasted with a mixture of the hydrates of potassium or sodium. On the small scale, a mixture of nitric acid and loaf-sugar yields the acid in the purest form, the two being boiled together for some time. On the large scale, sawdust is roasted with alkalies, resulting oxalate of sodium decomposed by lime with formation of oxalate of calcium, the latter digested with sulphuric acid, and the liberated oxalic acid purified by recrystallization. The elements represented by the formula C_2O_4 are those characteristic of oxalates. They form a bivalent grouping; hence normal oxalates ($R'_2C_2O_4$) and acid oxalates ($R'HC_2O_4$) exist. *Salt of sorrel* is a crystalline compound of oxalic acid with acid potassium oxalate (KHC_2O_4, $H_2C_2O_4$), the crystals containing two molecules of water of crystallization.

Analytical Reactions.

First Analytical Reaction.—To solution of an oxalate (oxalate of ammonium, B. P., for instance) add solution of chloride of calcium; a white precipitate falls. Add to the precipitate excess of acetic acid; it is insoluble. Add hydrochloric acid; the precipitate is dissolved.

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The formation of a white precipitate on adding a calcium or barium salt, insoluble in acetic but soluble in hydrochloric or nitric acid, is usually sufficient proof of the presence of an oxalate. The action of the liquid on litmus paper &c. would indicate that the oxalate is that of hydrogen, oxalic acid. In cases of poisoning by oxalic acid or an alkaline oxalate (salt of sorrel &c.), chalk and water may be administered as a chemical antidote, emetics and the stomach-pump being used as soon as possible.

Second Analytical Reaction.—Heat a fragment of a metallic oxalate in a test-tube; decomposition occurs, carbonic oxide (CO) is liberated, and a carbonate of the metal remains. Add water and then an acid to the residue; effervescence occurs.

This is a ready test for insoluble oxalates, and is trustworthy if, on heating the substance, no charring occurs. Organic salts of metals decompose when heated, and leave a residue of carbonate, but, except in the case of oxalates, the residue is always accompanied by much charcoal.

Other Analytical Reactions.—Nitrate of silver gives, with oxalates, white oxalate of silver ($Ag_2C_2O_4$).——Dry oxalates are decomposed when heated with strong sulphuric acid, carbonic oxide and carbonic acid gases escaping. If much of the substance be operated on, the gas may be washed with an alkali, the carbonic acid be thus removed, and the carbonic oxide be ignited; it will be found to burn with a characteristic bluish flame.

Oxalates, when mixed with water, black oxide of manganese (free from carbonates), and sulphuric acid, yield carbonic acid gas, which may be tested by lime-water in the usual manner.—— Insoluble oxalates, such as those of calcium and magnesium, may be decomposed by ebullition with solution of carbonate of sodium; after filtration the oxalic radical will be found in the clear liquid as soluble oxalate of sodium.

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TARTARIC ACID.

Formula $H_2C_4H_4O_6$, or $H_2\overline{T}$. Molecular weight 150.

Tartrates exist in the juice of many fruits; but it is from that of the grape that our supplies are usually obtained. Grape-juice contains much acid tartrate of potassium, which is gradually deposited when the juice is fermented, as in making wine; for acid tartrate of potassium, not very soluble in aqueous liquids, is still less so in spirituous, and hence crystallizes out as the sugar of the grape-juice is gradually converted into alcohol. It is found with tartrate of calcium lining the vessels in which wine is kept; and it is from this crude tartar, alluded to under potassium (pp. 27 and 33), that tartaric acid and other tartrates are prepared.

The elements represented by the formula $C_4H_4O_6$ are those characteristic of tartrates. They form a bivalent grouping; hence normal tartrates ($R'_2\overline{T}$) and acid tartrates ($R'H\overline{T}$) exist. The only officinal tartrate not apparently included in these general formulæ is tartar-emetic (*Antimonium Tartaratum*, B. P.), which is sometimes regarded as the double tartrate of potassium and a hypothetical radical, antimonyl (SbO), thus, $KSbOC_4H_4O_6$. Possibly, however, it is but an oxytartrate of antimony, with normal tartrate of potassium. For there are several oxycompounds of antimony analogous to the oxycompounds of bismuth that have been described, normal salts only partially decomposed by water into oxides; and many of these oxycompounds readily unite with normal salts of other basylous radicals. Tartar-emetic would thus be oxytartrate of antimony with tartrate of potassium ($Sb_2\overline{T}O_2, K_2\overline{T}$). Tartaric acid (*Acidum Tartaricum*, B. P.) is obtained, according to the British Pharmacopœia, by boiling cream of tartar (*Potassæ Tartras Acida*, B. P.) with chalk, filtering, and adding chloride of calcium to the filtrate; the two portions of tartrate of calcium thus consecutively formed are together treated with sulphuric acid, and the resulting solution of tartaric acid evaporated till crystals form:—

$$\underset{\text{Acid tartrate of potassium.}}{2KH\overline{T}} + \underset{\text{Carbonate of calcium.}}{CaCO_3} = \underset{\text{Tartrate of calcium.}}{Ca\overline{T}} + \underset{\text{Tartrate of potassium.}}{K_2\overline{T}} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

$$\underset{\text{Tartrate of potassium.}}{K_2\overline{T}} + \underset{\text{Chloride of calcium.}}{CaCl_2} = \underset{\text{Tartrate of calcium.}}{Ca\overline{T}} + \underset{\text{Chloride of potassium.}}{2KCl}$$

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$$\underset{\text{Tartrate of calcium.}}{CaT} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sulphate of calcium.}}{CaSO_4} + \underset{\text{Tartaric acid.}}{H_2T}$$

Reactions.

Synthetical Reactions.—To a small quantity of a strong solution of carbonate of potassium add acid tartrate of potassium so long as effervescence occurs; the resulting liquid is solution of normal tartrate of potassium (*Potassæ Tartras*, B. P.) (K_2T), crystals of which may be obtained on evaporation.

This is a common method of converting an acid salt of a bivalent acidulous radical into a normal salt. The carbonate added need not be a carbonate of the same, but may be of a different metal; compounds like Rochelle salt ($KNaT$) are then obtained. Thus:—

To a strong solution of carbonate of sodium add acid tartrate of potassium until effervescence ceases; the resulting liquid is solution of tartrate of potassium and sodium. This is the officinal process (*Soda Tartarata*, B. P.) ($KNaT$, $4H_2O$).

Analytical Reactions.

First Analytical Reaction.—To solution of tartaric acid, or any tartrate carefully made neutral by solution of soda, add solution of chloride of calcium; a white precipitate, tartrate of calcium, falls. Collect the precipitate on a filter, wash, place a small quantity in a test-tube, and add solution of potash; on stirring the mixture the precipitate dissolves. Heat the solution; the tartrate of calcium is again precipitated.

The solubility of tartrate of calcium in cold potash solution enables the analyst to distinguish between tartrates and citrates, otherwise a difficult matter. Citrate of calcium is not soluble in the alkali. The absence of much ammoniacal salt must be ensured in both cases, the precipitates being soluble in such liquids.

Second Analytical Reaction.—Acidulate a solution of a tartrate with acetic acid, add acetate of potassium, and well stir the mixture; a crystalline precipitate of acid tartrate of potassium slowly

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separates. The precipitate being insoluble in alcohol, the addition of a little spirit of wine renders the test more delicate.

This reaction is not applicable in testing for very small quantities of tartrates, the acid tartrate of potassium being not altogether insoluble.

Third Analytical Reaction.—To a neutral solution of a tartrate add solution of nitrate of silver; a white precipitate of tartrate of silver, $Ag_2C_4H_4O_6$, falls. Boil the mixture; it turns black, owing to the reduction of the salt to metallic silver.

Other Reactions.—Tartrates heated with strong sulphuric acid char immediately.——Tartaric acid and the soluble tartrates prevent the precipitation of ferric and other oxides by alkalies, soluble double tartrates being formed, which on evaporation yield liquids that do not crystallize, but, spread on sheets of glass, dry up to thin transparent plates or scales. The potassio-tartrate of iron (*Ferrum Tartaratum*, B. P.) is a preparation of this kind. ——Tartrates decompose when heated, carbonates being formed and carbon set free, the gaseous products having a peculiar, more or less characteristic odour, resembling that of burnt sugar.

CITRIC ACID.

Formula $H_3C_6H_5O_7$, H_2O or $H_3\bar{C}iAq$.

Molecular weight 210.

Citric acid exists in the juice of many of our common garden fruits; but it is from the lemon or lime that the acid of commerce is usually obtained. The British Pharmacopœia directs that the hot lemon-juice be saturated by chalk, the resulting citrate of calcium collected on a filter, washed with hot water till the liquor passes from it colourless, then mixed with cold water, decomposed by diluted sulphuric acid, and the filtered solution evaporated to the crystallizing point.

$$\underset{\text{Citric acid (impure).}}{2H_3C_6H_5O_7} + \underset{\text{Carbonate of calcium.}}{3CaCO_3} = \underset{\text{Citrate of calcium.}}{Ca_32C_6H_5O_7} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Carbonic acid gas.}}{3CO_2}$$

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$$\underset{\text{Citrate of calcium.}}{Ca_3 2C_6H_5O_7} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} = \underset{\text{Citric acid (pure).}}{2H_3C_6H_5O_7} + \underset{\text{Sulphate of calcium.}}{3CaSO_4}$$

The elements represented by the formula $C_6H_5O_7$ are those characteristic of citrates. They form a trivalent grouping; hence three classes of salts may exist—one, two, or three atoms of the basylous hydrogen in the acid, $H_3C_6H_5O_7$, being displaced by equivalent proportions of other basylous radicals. Citric acid itself is the only citric compound of much direct importance to the pharmaceutist.

Analytical Reactions.

First Analytical Reaction.—To solution of citric acid, or any citrate carefully neutralized by alkali, add solution of chloride of calcium; a white precipitate, citrate of calcium ($Ca_3\bar{Ci}_2$), falls. Treat the precipitate for tartrate of calcium; it is *not* dissolved by the potash.

A mixture of citrates and tartrates can be separated by this reaction. They are precipitated as calcium salts, and the washed precipitate mixed with solution of potash, diluted and filtered; the filtrate contains the tartrate, which is shown to be present by reprecipitation on boiling. The precipitate still on the filter is washed, dissolved in solution of chloride of ammonium, and the solution boiled; the citrate of calcium is reprecipitated. The presence of much sugar interferes with this reaction.

Second Analytical Reaction.—To a neutral solution of a citrate add solution of nitrate of silver; a white precipitate of citrate of silver ($Ag_3\bar{Ci}$) falls. Boil the mixture; the precipitate does not turn black as tartrate of silver does.

Other Analytical Reactions.—Citric acid forms no precipitate corresponding with the acid tartrate of potassium.——Lime-water gives no precipitate with citric acid or citrates, unless the solution is boiled; it usually precipitates tartrates in the cold. ——Citrates, when heated with strong sulphuric acid, do not char immediately.——Citric acid and citrates prevent the pre-

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cipitation of oxide of iron by alkalies, soluble double compounds being formed. The *Ferri et Ammoniæ Citras*, B. P., is a preparation of this kind.——Citrates decompose when heated, carbonates being formed and carbon set free: the odour of the gaseous products is not so characteristic as that of tartrates.

PHOSPHORIC ACID.

Formula H_3PO_4. Molecular weight 98.

The source of the ordinary phosphates and of phosphorus itself (*Phosphorus*, B. P.) is the tricalcic phosphate (Ca_32PO_4). It is the chief constituent of the bones of animals, being derived from the plants on which they feed, plants again obtaining it from the soil. Phosphorus is obtained from bones by the following processes:—The bones are burnt to remove all traces of animal matter. The resulting *bone-earth* is treated with sulphuric acid, by which an acid phosphate (CaH_42PO_4), often called *superphosphate of lime*, is produced:—

$$Ca_32PO_4 + 2H_2SO_4 = CaH_42PO_4 + 2CaSO_4.$$

The acid phosphate is mixed with charcoal and strongly heated in a retort, when it splits up into tricalcic phosphate and phosphoric acid—

$$3CaH_42PO_4 = Ca_32PO_4 + 4H_3PO_4,$$

the phosphoric acid being reduced by the charcoal to phosphorus and hydrogen, and carbonic oxide gas liberated:—

$$H_3PO_4 + C_4 = P + H_3 + 4CO.$$

The chief use of phosphorus in pharmacy is in the formation of a dilute solution of phosphoric acid. Phosphorus is boiled with nitric acid until dissolved, the operation being conducted in a retort in order that any nitric acid which would otherwise be lost may be condensed and again poured on to the phosphorus. A flask, in the neck of which a funnel is inserted and a second funnel inverted so that its mouth rests within the mouth of the first, is even more efficient and convenient for this operation than a retort. The solution evaporated to a low bulk to remove nitrous compounds, and rediluted so as to contain nearly 14 (13·8) per cent. of acid (H_3PO_4), constitutes the *Acidum Phosphoricum*

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Dilutum, B. P. If the necessary appliances are at hand, the student should make four or five ounces of this preparation.

$$\underset{\text{Phosphorus.}}{P_6} + \underset{\text{Nitric acid.}}{10HNO_3} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Phosphoric acid.}}{6H_3PO_4} + \underset{\text{Nitric oxide.}}{5N_2O_2}$$

Some phosphorous acid (H_2PHO_2) is also formed in the first stages of the reaction.

The elements represented by the formula PO_4 are those characteristic of phosphates. The grouping is trivalent; hence there may exist trimetallic or normal phosphates (M'_3PO_4), dimetallic acid phosphates (M'_2HPO_4), monometallic acid phosphates ($M'H_2PO_4$), and lastly, trihydric phosphate (H_3PO_4), common phosphoric acid, itself. These are the ordinary phosphates met with in nature or used in pharmacy; the rarer phosphates and metaphosphates will be mentioned subsequently.

Analytical Reactions.

First Analytical Reaction.—To an aqueous solution of a phosphate (*e. g.* Na_2HPO_4) add solution of sulphate of magnesium with which chloride of ammonium and ammonia has been mixed; a white crystalline precipitate of ammonio-magnesian phosphate falls ($MgAmPO_4$).

Chloride of ammonium is added to prevent the precipitation of hydrate of magnesium. Arseniates, from their close analogy to phosphates, give a similar precipitate with the magnesian reagent.

Second Analytical Reaction.—To an aqueous solution of a phosphate add solution of nitrate of silver; light-yellow phosphate of silver (Ag_3PO_4) is precipitated. To a portion of the precipitate add ammonia; it dissolves. To another portion add nitric acid; it dissolves.

A phosphate may be distinguished from an arseniate by this reaction, arseniate of silver being of a chocolate colour.

Third Analytical Reaction.—To a solution (in a few drops of acid) of a phosphate insoluble in water (*e. g.* Ca_32PO_4) add an

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alkaline acetate (that is, a mixture of soda or ammonia with excess of acetic acid), and then a drop or two of solution of perchloride of iron; yellowish-white ferric phosphate ($Fe_2 2PO_4$) is precipitated.

Too much of the ferric chloride must not be added, or ferric acetate will be produced, in which ferric phosphate is to some extent soluble.

To remove the whole of the phosphoric radical from solution, add ferric chloride so long as a precipitate is produced, and then boil the mixture; ferric phosphate and ferric subacetate is precipitated.

To obtain confirmatory evidence of the presence of phosphate in this precipitate and to separate the phosphoric radical as a pure unmixed phosphate, collect the precipitate on a filter, wash, drop some solution of ammonia on it, then sulphide of ammonium, and finally wash with water; black ferrous sulphide remains on the filter, while phosphate of ammonium is found in the filtrate. To the filtrate add a mixture of solutions of sulphate of magnesium and chloride of ammonium, and well stir; ammonio-magnesian phosphate is precipitated.

The above reaction is useful in the analysis of bone-earth, other earthy phosphates, phosphate of iron, &c. which are insoluble in water. Only arseniates give similar appearances; but the acid solution of these may be decomposed by sulphuretted hydrogen (H_2S), especially after agitation with sulphurous acid and subsequent ebullition.

Other Analytical Reactions.—Solutions of barium and calcium salts give, with aqueous solutions of phosphates, white precipitates of the respective phosphates $BaHPO_4$, or $Ba_3 2PO_4$, and $CaHPO_4$, or $Ca_3 2PO_4$, all of which are soluble in acetic and the stronger acids.

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The foregoing acids contain the only acidulous radicals that are commonly met with in analysis or in ordinary pharmaceutical operations. There are, however, many others which occasionally present themselves, and of which the student should have some knowledge; the chief of these will now be shortly noticed. They are arranged in alphabetical order to facilitate reference.

Benzoic Acid ($HC_7H_5O_2$).—Slowly heat a fragment of benzoin in a test-tube; benzoic acid (*Acidum Benzoicum*, B. P.) rises in vapour and condenses in small white crystalline plates on the cool sides of the tube. Or boil the benzoin with one-fourth its weight of lime, filter, concentrate, decompose the benzoate of calcium by hydrochloric acid, collect the precipitated benzoic acid, press between paper, dry, and sublime in a tube or other vessel.

$2HC_7H_5O_2$	+	$Ca2HO$	=	$Ca2C_7H_5O_2$	+	$2H_2O$
Benzoic acid (impure).		Hydrate of calcium.		Benzoate of calcium.		Water.

$Ca2C_7H_5O_2$	+	$2HCl$	=	$CaCl_2$	+	$2HC_7H_5O_2$
Benzoate of calcium.		Hydrochloric acid.		Chloride of calcium.		Benzoic acid (pure).

There is always associated with the product a minute quantity of a volatile oil of agreeable odour.

To a little benzoic acid add a few drops of solution of ammonia; it readily dissolves, forming benzoate of ammonium (*Ammoniæ Benzoas*, B. P.) ($AmC_7H_5O_2$).

$HC_7H_5O_2$	+	$AmHO$	=	$AmC_7H_5O_2$	+	H_2O
Benzoic acid.		Ammonia.		Benzoate of ammonium.		Water.

On evaporation, crystals of an acid benzoate (or, ammonia being added, a normal benzoate) of ammonium are deposited.

The following are the *tests* for benzoic acid:—To a portion of the above solution of benzoate of ammonium add a drop or two of sulphuric or hydrochloric acid; a white crystalline precipitate of benzoic acid separates. To another portion, carefully made

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neutral, add a drop or two of neutral solution of perchloride of iron; reddish ferric benzoate separates. Benzoic acid is distinguished from an allied body, cinnamic acid (occurring in Balsam of Tolu &c.), by not yielding hydride of benzoyl (C_7H_5OH) (oil of bitter almonds) when distilled with chromic acid—that is, with a mixture of red chromate of potassium and sulphuric acid.

Cyanic Acid (HCyO).—The valuable reducing-power of cyanide of potassium (KCy) (or ferrocyanide) (K_4Fcy) on metallic oxides &c. is due to the avidity with which it forms cyanate (KCyO). Fuse a few grains of cyanide of potassium in a small porcelain crucible and add powdered oxide of lead; a globule of metallic lead is at once set free, excess of the oxide converting the whole of the cyanide of potassium into cyanate of potassium. Cyanate of potassium (KCNO) treated with sulphate of ammonium yields cyanate of ammonium (NH_4CNO); and solution of cyanate of ammonium, when simply heated, changes to artificial *urea* (CH_4N_2O), the most important constituent of urine and the chief form in which the nitrogen of food is eliminated from the animal system.

Formic Acid ($HCHO_2$).—The red ant (*Formica rufa*) and several other insects, when irritated, eject a strongly acid, acrid liquid, having a composition expressed by the above formula, and which has appropriately received the name of formic acid; it is also contained in the leaves of the stinging-nettle. It may be artificially prepared by heating equal weights of oxalic acid and glycerin to a temperature of from 212° to 220° for fifteen hours. The glycerin has, apparently, no chemical action, but, for some unknown reason, induces decomposition of the oxalic acid at a lower temperature than would otherwise be necessary; at a higher temperature the formic acid itself is decomposed. On distilling the mixture with water the formic acid slowly passes over. The dilute acid may be concentrated by neutralizing with carbonate of lead, filtering, evaporating to a small bulk, collect-

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ing the deposited crystalline formiate of lead, drying, decomposing in a current of sulphuretted hydrogen, and separating the resulting syrupy acid, or distilling the formiate of lead with strong sulphuric acid.

$$\underset{\text{Oxalic acid.}}{H_2C_2O_4} = \underset{\text{Formic acid.}}{HCHO_2} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

It may be instructively but not economically prepared by the oxidation of methylic alcohol (wood-spirit), just as acetic acid and valerianic acid are obtained from ethylic alcohol and amylic alcohol respectively.

$$\underset{\text{Wood-spirit.}}{CH_3HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Formic acid.}}{HCHO_2} + \underset{\text{Water.}}{H_2O}$$

Formic acid does not char when heated alone or with sulphuric acid, but splits up into carbonic oxide gas and water. It is recognized by this property and by its reducing action on salts of gold, platinum, mercury, and silver. It is solid below 32°.

Gallic Acid.—See *Tannic Acid.*

Hydroferrocyanic Acid ($H_4Fe''Cy_6$, or H_4Fcy'''').—The ferrocyanide of most interest is that of potassium, the yellow prussiate of potash (*Potassæ Prussias Flava*, B. P.) (K_4Fcy), the formation of which was alluded to in connexion with hydrocyanic acid (see page 181). It cannot be regarded as simply a double salt of cyanide of potassium with cyanide of iron ($FeCy_2$, $4KCy$), its chemical properties being entirely different from either of those substances; moreover, unlike cyanide of potassium, it is not poisonous. Most of its reactions point to the conclusion that its iron and cyanogen are intimately united to form a definite quadrivalent radical appropriately termed *ferrocyanogen* ($FeCy_6$, or Fcy).

Many of the ferrocyanides are insoluble, and are therefore precipitated when solution of ferrocyanide of potassium is added to the various salts. Those of iron and copper being of characteristic colour, are adopted as tests of the presence of the metals or,

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of the ferrocyanogen, as the case may be. To solution of ferrocyanide of potassium add a ferric salt; ferrocyanide of iron (Fe_4Fcy_3) (Prussian blue) is precipitated. To another portion add solution of a copper salt; reddish-brown ferrocyanide of copper (Cu_2Fcy) is precipitated. The ferrocyanogen in ferrocyanide of potassium is broken up when the salt is heated with sulphuric acid, carbonic oxide being evolved if the acid is strong, and hydrocyanic acid if weak:—

$$K_4FeC_6N_6 + 6H_2O + 6H_2SO_4 = 2K_2SO_4 + FeSO_4 + 3((NH_4)_2SO_4) + 6CO.$$

$$2K_4FeCy_6 + 6H_2SO_4 = FeK_2FeCy_6 + 6KHSO_4 + 6HCy.$$

Hydroferridcyanic Acid ($H_6Fe'''_2Cy_{12}$, or $H^I_6Fdcy^{VI}$).—Pass chlorine gas through a few drops of solution of ferrocyanide of potassium until the liquid ceases to give a blue precipitate when a minute portion is taken out on the end of a glass rod and brought into contact with a drop of a dilute solution of a ferric salt; it now contains ferridcyanide of potassium ($K_6Fe'''_2Cy_{12}$, or $K^I_6Fdcy^{VI}$), *red prussiate of potash* (B. P.), as it is termed, from the colour of its crystals:—

$$2K'_4Fe''Cy'_6 + Cl'_2 = 2K'Cl' + K'_6Fe'''_2Cy'_{12}.$$

The removal of two atoms of potassium from the ferrocyanide is the only change of composition that occurs; but the ferrocyanogen is altered in quality, its iron passing from the ferrous to the ferric condition, from bivalent to trivalent activity, a condition in which it no longer precipitates ferric salts, but, on the other hand, gives a dark-blue precipitate with ferrous salts. To a portion of the solution add solution of ferrous sulphate; a precipitate falls. This precipitate is ferridcyanide of iron (Turnbull's blue), $Fe''_3Fe'''_2Cy'_{12}$, or $Fe^{II}_3Fdcy^{VI}$.

$$K_6Fdcy + 3FeSO_4 = Fe_3Fdcy + 3K_2SO_4.$$

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It will be noticed that this change in the condition of the iron keeps up the balance of the atomic values of the various parts of the radicals or of the salts; the equivalential, or rather quanti-valential, equilibrium is maintained.

Hydrofluoric Acid (HF).—Molecular weight 20. The chief use of hydrofluoric acid is in etching on glass. The operation, performed on the small scale, also constitutes the best test for fluorine, the elementary radical of all fluorides. Warm any odd piece of window-glass having an inch or two of surface until a piece of beeswax rubbed on one side yields a thin oily film. When cool make a cross, letter, or other mark on the glass by pressing a pointed piece of wood, a penknife, file, &c. through the wax. Place two or three grains of powdered fluor spar, the commonest natural fluoride, in a small porcelain crucible, add a drop or two of sulphuric acid, cover the crucible with the prepared glass, wax side downwards, and gently warm the bottom of the crucible in such a way as not to melt the wax. After a few minutes remove the glass, wash the waxed side by pouring water over it, scrape off most of the wax, then warm the glass, and wipe off the remainder; the marks made through the wax will be found to be permanently etched on the glass; the acid has eaten into or *etched* (from the German *ätzen*, to corrode) the glass.

In the above operation the fluoride of calcium and sulphuric acid yield hydrofluoric acid, thus:—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The hydrofluoric acid gas and the silica of the glass then yield gaseous fluoride of silicon (SiF_4), which escapes, and water, thus:—

$$4HF + SiO_2 = 2H_2O + SiF_4.$$

The silica being removed from the glass leaves furrows or etched portions.

In the experiment just described, the liberated hydrofluoric

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acid also attacks the siliceous glazing of the porcelain crucible; so that in important cases, where search is made for very small quantities of fluorine, vessels of platinum or lead must be employed. The aqueous solution of hydrofluoric acid used by etchers, and commonly termed simply hydrofluoric acid, or fluoric acid, is prepared in leaden stills and receivers, and kept in leaden or gutta-percha bottles. Except these materials, as well as platinum and fluor-spar, hydrofluoric acid rapidly attacks any substance of which bottles, basins, &c. are usually made. It quickly cauterizes the skin, producing a painful slow-healing sore.

The atom of fluorine, like that of chlorine, bromine, or iodine, is univalent (Fl′). The student will notice the great analogy existing between these radicals, extending to their compounds. Fluorine is said to be a colourless gas; but, from the avidity with which it combines with all elements (except oxygen), it is so difficult of isolation as to preclude satisfactory study of its physical properties.

Hypochlorous Acid (HClO).—Place a few grains of red oxide of mercury in a test-tube, half-fill the tube with chlorine-water and well shake the mixture; the resulting liquid is a solution of hypochlorous acid, mercuric oxychloride remaining undissolved:—

$$2HgO + Cl_4 + H_2O = 2HClO + HgO, HgCl_2.$$

By the double decomposition of hypochlorous acid and oxides, hydrates, &c., other hypochlorites are formed:—

$$HClO + NaHO = NaClO + H_2O.$$

The direct action of chlorine on metallic hydrates is supposed to give a mixture of chloride and hypochlorite, as described in connexion with the synthetical reactions of Sodium (p. 41, *Liquor Sodæ Chloratæ*, B. P.) and Calcium (p. 58, *Calx chlorata*, B. P.).

$$Cl_2 + 2NaHO = NaCl, NaClO + H_2O$$
$$Cl_4 + 2CaH_2O_2 = CaCl_2, Ca2ClO + 2H_2O.$$

But the presence of chlorides cannot be directly demonstrated in these bodies; so that their constitution is yet to be ascertained.

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The action of acids on them results in the evolution of chlorine; hence the great value of the calcium compound (chlorinated lime, or chloride of lime) in bleaching-operations:—

$$CaCl_2, Ca2ClO + 2H_2SO_4 = Cl_4 + 2CaSO_4 + 2H_2O.$$

The solubility of hypochlorites in water, their peculiar odour, greatly intensified on the addition of acid, and their bleaching-powers (see the above sodium and calcium reactions) are the characters on which to rely in searching for hypochlorites.

Hypophosphorous Acid (H_3PO_2, or HPH_2O_2).—Boil together, in a fume-chamber, a grain or two of phosphorus, a few grains of slaked lime, and about a quarter of an ounce of water until phosphoretted hydrogen, a spontaneously inflammable, badly-smelling gas ceases to be evolved. The mixture, filtered, yields solution of hypophosphite of calcium ($Ca2PH_2O_2$).

$$P_8 + 6H_2O + 3CaH_2O_2 = 3(Ca2PH_2O_2) + 2PH_3.$$

The solution, when concentrated by evaporation, has been known to explode, probably from formation of phosphoretted hydrogen. This may be prevented, it is said, by evaporating at a low temperature, especially towards the close of the operation; or by adding alcohol, which decomposes any traces of liquid phosphoretted hydrogen (PH_2) or solid phosphoretted hydrogen (P_2H) which possibly may be present, and to which it is conceivable explosion may be due.

Hypophosphite of calcium may be obtained in crystals; but the solution is usually at once evaporated to dryness, a white pulverulent salt being obtained. Other hypophosphites may be obtained in the same way from other hydrates, or by double decomposition of the calcium salt and carbonates &c. Hypophosphorous acid, the hydrogen hypophosphite, may be prepared by decomposing the calcium salt by oxalic acid; hypophosphite of quinine by dissolving the alkaloid in hypophosphorous acid, or by decomposing sulphate of quinine by hypophosphite of barium. The hypophosphites are often used in medicine in the form of syrups. The term hypophosphite is in allusion to the smaller amount (*ὑπό*, *upo*, under or deficiency) of oxygen in these compounds than in the phosphites (R_3PO_3), a class of salts having

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again less oxygen in their molecules than exists in those of the phosphates (R_3PO_4).

To a portion of the above solution of hypophosphite of calcium add solution of chloride of barium, chloride of calcium, or acetate of lead; in neither case is a precipitate obtained, whereas soluble phosphates and phosphites yield white precipitates of baric, calcic, or plumbic phosphate or phosphite. To other portions add solutions of nitrate of silver and mercuric chloride; the respective metals are precipitated as by phosphites. To another small portion add zinc and dilute sulphuric acid; hydrogen and phosphoretted hydrogen are evolved as from phosphites. To another portion add sufficient oxalic acid to remove the calcium; filter; to the solution of hypophosphorous acid add solution of sulphate of copper and slowly warm the mixture; solid hydride of copper is precipitated; increase the heat to the boiling-point; hydrogen is evolved and metallic copper set free. Dry hypophosphites when heated split up into pyrophosphates, phosphoretted hydrogen, and water.

$$2(Ca2PH_2O_2) = Ca_2P_2O_7 + 2PH_3 + H_2O.$$

Hyposulphurous Acid ($H_2S_2O_3$). — The only hyposulphite of much interest in pharmacy is the sodium salt (Hyposulphite of Soda, B. P.) ($Na_2S_2O_3, 5H_2O$). Heat together in a test-tube, or set aside in a warm place, a mixture of solution of sulphite of sodium (Na_2SO_3), and a little powdered sulphur; combination slowly takes place, and hyposulphite of sodium is formed. The solution, filtered from excess of sulphur, readily yields crystals. In the British Pharmacopœia hyposulphite of sodium is given as a reagent for the quantitative estimation of free iodine in volumetric analysis. To a few drops of iodine-water add cold mucilage of starch; a deep-blue colour (starch-iodide) is produced. To a portion of the aqueous solution of iodine add solution of hyposulphite of sodium until the liquid ceases to give a

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blue colour with the starch. This reaction is sufficiently definite and delicate to admit of application for quantitative purposes. It depends on the combination of the iodine with half of the sodium in two molecules of the hyposulphite, the hyposulphurous radicals of the two molecules apparently coalescing to form a new radical, the tetrathionic (from *τέτρας, tetras,* four, and *θεῖον, theion,* sulphur),—tetrathionate and iodide of sodium being formed.

The sodium hyposulphite is largely used in photography to dissolve chloride, bromide, or iodide of silver off plates which have been exposed in the camera. Prepare a little chloride of silver by adding a chloride (chloride of sodium) to a few drops of solution of nitrate of silver. Collect the precipitated chloride on a filter, wash, and add a few drops of solution of hyposulphite of sodium; the silver-salt is dissolved, solution of double hyposulphite of sodium and silver being formed. The solution of this double hyposulphite has a remarkably sweet taste, sweeter than syrup. The double hyposulphite of sodium and gold is employed for giving a pleasant tint to photographic prints.

To solution of a hyposulphite add a few drops of dilute sulphuric or other acid; hyposulphurous acid is set free, but at once begins to decompose into sulphurous acid, recognized by its odour, and free sulphur ($2H_2S_2O_3 = 2H_2SO_3 + S_2$). This reaction constitutes the best test for hyposulphites. Another good test of a soluble simple hyposulphite is its power of dissolving chloride of silver with production of a sweet solution.

Lactic Acid ($H_2C_3H_4O_3$).—When milk turns sour its sugar has become converted into an acid appropriately termed lactic (*lac, lactis*). Other saccharine and amylaceous substances also by fermentation yield lactic acid. Neither the hydrogen lactate (lactic acid) nor other lactates are much used in medicine.

Lactate of calcium and lactic acid may be prepared as follows:—Mix together eight parts of sugar, one of common cheese,

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three of chalk, and fifty of water, and set aside in a warm place (about 80° F.) for two or three weeks; a mass of small crystals of lactate of calcium results. Remove these, recrystallize from hot water, decompose by sulphuric acid, avoiding excess, digest in alcohol, filter off the sulphate of calcium, evaporate the clear solution to a syrup; this residue is lactic acid.

No single reaction of lactic acid is sufficiently distinctive to form a test. The crystalline form of the lactate of calcium, as seen by the microscope, is characteristic. The production of this salt, and the isolation of the syrupy acid itself, are the only means, short of quantitative analysis, on which reliance can be placed.

A variety of lactic acid has been obtained from the juice of flesh; it is termed *sarcolactic* acid (from σὰρξ, gen. σαρκὸς, flesh).

MALIC ACID ($H_3C_4H_3O_5$) (from *malum*, an apple).—The juice of unripe apples, gooseberries, currants, rhubarb stalks, &c. contains malic acid and malate of potassium. When isolated it occurs in deliquescent prismatic crystals. Its aqueous solution is not precipitated by lime-water; but on evaporation a crystalline malate of calcium ($CaHC_4H_3O_5$) is deposited, soluble in boiling water. Malate of calcium being soluble in water, the aqueous solution of malic acid is not precipitated by chloride of calcium; but on adding spirit of wine to this solution a white precipitate falls, owing to the insolubility of the calcium malate in alcohol. Malates are precipitated by lead-salts; on warming the malate of lead with dilute acid it dissolves, separating out in acicular crystals on cooling.

METAPHOSPHORIC ACID (HPO_3).—Prepare phosphoric anhydride (P_2O_5) by burning a small piece of phosphorus in a porcelain crucible placed on a plate and covered by an inverted test-glass, tumbler, half-pint measure-glass, or some such vessel. After waiting a few minutes for the phosphoric anhydride to fall, pour

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a little water on the plate and filter the liquid; the product is solution of metaphosphoric acid (from μετὰ, *meta*, a preposition denoting change).

$$P_2O_5 + H_2O = 2HPO_3.$$

To solution of metaphosphoric acid or other metaphosphate add solution of nitrate of silver; a white precipitate ($AgPO_3$) is obtained. This reaction sufficiently distinguishes metaphosphates from the ordinary phosphates or orthophosphates (from ὀρθὸς, *orthos*, straight), as the common phosphates may, for distinction, be termed (which give, it will be remembered, a *yellow* precipitate with nitrate of silver). Another variety of phosphates shortly to be considered, the pyrophosphates, also give a white precipitate with nitrate of silver. To the solution of metaphosphoric acid obtained as above or by the action of acetic acid on a metaphosphate, add an aqueous solution of white of egg; coagulation of the albumen ensues. Neither orthophosphoric nor pyrophosphoric acid coagulates albumen. Boil the aqueous solution of metaphosphoric acid for some time; on testing the solution the acid will be found to have been converted into orthophosphoric acid:—

$$HPO_3 + H_2O = H_3PO_4.$$

The ordinary medicinal phosphoric acid is made from phosphorus and nitric acid, the liquid being evaporated to a syrupy consistence to remove the last traces of nitric acid. It may contain pyrophosphoric and metaphosphoric acids, if the heat employed be high enough to remove the elements of water:—

$$H_3PO_4 - H_2O = HPO_3.$$

On redilution the metaphosphoric acid only slowly reabsorbs water. If, therefore, on testing, metaphosphoric be found to be present, the solution should be boiled until conversion to orthophosphoric acid has occurred.

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Nitrous Acid (HNO_2).—Strongly heat a fragment of nitrate of potassium or of sodium on a piece of platinum-foil; oxygen is evolved and nitrite of potassium remains. Dissolve the residne in water, add a few drops of dilute sulphuric acid, then a little weak solution of iodide of potassium, and, lastly, some mucilage of starch; the deep-blue compound of iodine and starch is at once produced. Repeat this experiment, using nitrate instead of nitrite; no blue colour is produced.

This liberation of iodine by nitrites and not by nitrates is a reaction of considerable value in searching for nitrites in ordinary drinking waters, the occurrence of such salts being held to indicate the presence of animal matter in a state of oxidation or decay.——The liquid commonly termed in pharmacy nitrous acid is simply nitric acid impure from the presence of nitrous acid. ——The only nitrite used in medicine is a nitrite of an organic basylous radical, ethyl; nitrite of ethyl ($C_2H_5NO_2$), or nitrous ether, is the chief constituent of "*sweet spirit of nitre*" (*Spiritus Ætheris Nitrosi*, B. P.).

Phosphorous Acid (H_3PO_3, or H_2PHO_3).—It is necessary to notice this compound in order that the student may have brought before him the three acids of phosphorus, namely, phosphoric acid (H_3PO_4), phosphorous acid (H_2PHO_3), and hypophosphorous acid (HPH_2O_2): it will be noticed that in composition they differ from each other simply in the proportion of oxygen, the molecules containing four, three, and two atoms respectively. In constitution they differ by the hypothetical phosphoric radical or grouping being trivalent, the phosphorous bivalent, and the hypophosphorous univalent. These three acids and corresponding salts must not be confounded with pyrophosphoric and metaphosphoric acids and salts: the former are acids of phosphorus; the latter, varieties of phosphoric acid; the former, in composition, differ from each other in the proportion of oxygen they contain; the latter, by the elements of water:—

Acids of phosphorus.	*Varieties of phosphoric acid.*
H_3PO_4 phosphoric acid.	H_3PO_4 (ortho)phosphoric acid.
H_2PHO_3 phosphorous acid.	$H_4P_2O_7$ pyrophosphoric acid.
HPH_2O_2 hypophosphorous acid.	HPO_3 metaphosphoric acid.

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When hypophosphorous acid is exposed to the air, oxygen is absorbed and phosphorous acid results; by prolonged exposure more oxygen is absorbed and phosphoric acid is obtained. When phosphoric acid, or rather, for distinction, orthophosphoric acid is heated, every two molecules yield the elements of a molecule of water, and pyrophosphoric acid results; by prolonged exposure to heat more water is evolved, and metaphosphoric acid is obtained. These differences of composition will be further evident if the several formulæ of the hydrogen salts be written empirically, nearly all being doubled in order to render them comparable with the formula of pyrophosphoric acid, thus:—

$H_6P_2O_4$ hypophosphorous acid.
$H_6P_2O_6$ phosphorous acid.
$H_6P_2O_8$ phosphoric acid, or orthophosphoric acid.
$H_4P_2O_7$ pyrophosphoric acid.
$H_2P_2O_6$ metaphosphoric acid.

Or thus:—

Phosphoric acid
$H_6P_2O_8$.

Phosphorous acid $H_6P_2O_6$. $H_4P_2O_7$ pyrophosphoric acid.

$H_6P_2O_4$
hypophosphorous acid.

$H_2P_2O_6$
metaphosphoric acid.

From the central compound, phosphoric acid, the acids of phosphorus differ by regularly diminishing proportions of the element oxygen, the varieties of phosphoric acid by regularly diminishing proportions of the elements of water.

Prepare phosphorous acid by exposing a moist stick of phosphorus to the air; a thin stream of heavy white vapour falls, which is the acid in question. The best method of collection is to place the stick in an old test-tube having a hole in the bottom, to support this tube by a funnel or otherwise, the neck of the funnel being supported in a bottle, test-glass, or tube, at the bottom of which is a little water. Having collected some phosphorous acid in this way, apply the various tests already alluded to under *Hypophosphorous Acid*. The means by which the varieties of

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phosphoric acid are distinguished have been given under *Metaphosphoric Acid.*

Pyrogallic Acid.—See *Tannic Acid.*

Pyrophosphoric Acid ($H_4P_2O_7$).—Heat ordinary phosphate of sodium ($Na_2HPO_4, 12H_2O$) in a crucible; water of crystallization is first evolved, and dry phosphate (Na_2HPO_4) remains. Continue the heat to redness; two molecules of the salt yield one molecule of water, and a salt having new properties is obtained:—

$$2Na_2HPO_4 - H_2O = Na_4P_2O_7.$$

It is termed pyrophosphate of sodium in allusion to its origin (πῦρ, *pur*, fire). Other pyrophosphates are produced in a similar way, or by double decomposition and precipitation, or by neutralizing pyrophosphoric acid by an oxide, hydrate, or carbonate. Possibly the pyrophosphates are only compounds of orthophosphates with metaphosphates:—

$$Na_4P_2O_7 = Na_3PO_4, NaPO_3.$$

To solution of a pyrophosphate add solution of nitrate of silver; white pyrophosphate of silver ($Ag_4P_2O_7$) falls as a dense white powder, differing much in appearance from the white gelatinous metaphosphate of silver or the yellow orthophosphate. To pyrophosphoric acid, or to a pyrophosphate mixed with acetic acid, add an aqueous solution of albumen (white of egg); no precipitate occurs. Metaphosphoric acid, it will be remembered, gives a white precipitate with albumen.

Silicic Acid (H_4SiO_4).—Silicates of various kinds are among the commonest of minerals. The ordinary *sandstones* are chiefly calcium silicates; *meerschaum* is an acid silicate of magnesium; the various *clays* are aluminium silicates; *sand, flint, quartz, agate, chalcedony, opal,* &c. are silicic anhydride or *silica* (SiO_2). Artificial silicates are familiar under the forms of *glass* and *earth-*

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enware. Common English window-glass is usually silicate of calcium, sodium, and aluminium; French glass, silicate of calcium and sodium; Bohemian, chiefly silicate of potassium and calcium; English flint- or crystal-glass for ornamental, table, and optical purposes, is mainly silicate of potassium and lead. Earthenware is mostly silicate of aluminium (clay), with more or less of silicate of calcium, sodium, and potassium, and, in the commoner forms, iron. The various kinds of *porcelain* (China, Sèvres, Meissen, Berlin, English), *Wedgwood-ware, stoneware,* &c. are varieties of earthenware. *Crucibles, bricks, tiles,* &c. are clay-silicates. *Mortar* is essentially silicate of calcium. *Portland, Roman,* and other hydraulic *cements* are silicates of calcium with more or less silicate of aluminium.

Mix together a few grains of powdered flint or sand with about five or six times its weight of carbonate of sodium and an equal quantity of carbonate of potassium, and fuse a little of the mixture on platinum foil in the blowpipe-flame; the product is a kind of *soluble glass.* Boil the foil in water for a few minutes, filter; to a portion add excess of hydrochloric acid, evaporate the solution to dryness, and again boil the residue in water and acid; silica (SiO_2) remains as a light, flaky, insoluble powder.

The foregoing operation constitutes the *test* for silicates. By fusion with alkali the silicate is decomposed, and a soluble alkaline silicate formed. On addition of acid, silicic acid (H_4SiO_4) is set free, but remains in solution if sufficient water is present. The heat subsequently applied eliminates water and reduces the silicic acid to silica (SiO_2), which is insoluble in water or acid. By the addition of hydrochloric acid to soluble glass, and removal of the resulting alkaline chloride and excess of hydrochloric acid by dialysis (a process to be subsequently described), a pure aqueous solution of silicic acid may be obtained; it readily changes into a gelatinous mass of silicic acid. Possibly some of the natural crystallized varieties of silica may have been obtained from the silica contained in such an aqueous solution, nearly all waters yielding a small quantity of silica when treated as above described.

Sulphocyanic Acid (HCyS).—Boil together sulphur and solution of cyanide of potassium; solution of sulphocyanate of potas-

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sium (KCyS) is formed. Filter, and to a small portion of the solution add a ferric salt (Fe_2Cl_6); a deep blood-red solution of ferric sulphocyanate is formed. This is the best test of the presence of a sulphocyanate, and therefore, indirectly, of the presence of hydrocyanic acid or cyanogen. To solution of a sulphocyanate add solution of mercuric nitrate; mercuric sulphocyanate is precipitated as a white powder.

It is this powder, washed and made up into little cones, that forms the toy termed Pharoah's serpent. It readily burns when ignited, the chief product being a light solid matter (mellon (C_9N_{13}) and melam ($C_3H_6N_6$)), which issues from the cone in a snake-like coil of extraordinary length. The other products are mercuric sulphide (of which part remains in the snake and part volatilized), nitrogen, sulphurous and carbonic acid gases, and vapour of metallic mercury.

The sulphocyanic radical (CyS) is often termed sulphocyanogen (Scy), and its compounds regarded as sulphocyanides.

TANNIC ACID OR TANNIN ($C_{27}H_{22}O_{17}$).—This is a common astringent constituent of plants, but is contained in largest quantity in galls (excrescences on the oak formed by the puncture and deposited ova of an insect). Mix a small quantity of powdered galls with sufficient water to make it damp, place it in a test-tube with enough ether to form a thin paste, set aside for twenty-four hours, add more ether (washed ether, containing water and a little alcohol), filter through a small piece of calico, set aside till clear, pour off the solution, evaporate spontaneously on a plate, and dry the residue over a water-bath; scales of tannic acid result. This is the officinal process (*Acidum Tannicum*, B. P.).

To an aqueous solution of tannic acid add aqueous solution of gelatin; a flocculent compound of the two substances is precipitated. This is a good test of the presence of tannic acid.

This reaction also serves to explain the chemical principle involved in *tanning*—the operation of converting skin into leather.

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In that process the skin is soaked in infusion of oak-bark, the tannic acid of which uniting with the gelatinous tissues of the skin yields a compound very well represented by the above precipitate. Other infusions and extracts besides that of oak-bark are largely used by tanners; but they appear to act too quickly, and give a harsh, hard, less durable leather. The tannic acid of these preparations is probably slightly different from that of oak-bark.

Tannic acid is very soluble in water, and in this form is usually administered in medicine. Its officinal preparations are *Glycerinum Acidi Tannici*, *Suppositoria Acidi Tannici*, and *Trochisci Acidi Tannici*.

To an aqueous solution of tannic acid add a neutral solution of a ferric salt; dark bluish-black tannate of iron is slowly precipitated. This is an excellent test for the presence of tannic acid in vegetable infusions. The precipitate is the basis of nearly all black writing-ink. Ferrous salts give only a slight reaction with tannic acid.

To an aqueous solution of tannic acid add solution of tartar-emetic; tannate of antimony is precipitated. This reaction and that with gelatin are useful in the quantitative estimation of the amount of tannic acid in various substances.

Tannic acid is a glucoside; that is, like several other substances, it yields glucose (grape-sugar) when boiled with dilute sulphuric or hydrochloric acid, the other product being gallic acid:—

$$C_{27}H_{22}O_{17} + 4H_2O = C_6H_{12}O_6 + 3H_3C_7H_3O_5.$$

Gallic acid ($H_3C_7H_3O_5$, H_2O) occurs in small quantity in oak-galls and other vegetable substances, but is always prepared from tannic acid. Powdered galls are moistened with water and set aside in a warm place, fermentation occurs, and impure gallic acid is deposited. It is purified by solution in hot water and treatment with animal charcoal, which absorbs colouring-matter. On cooling, most of the acid separates in the form of slender acicular crystals.

The nature of the action by which gallic acid is thus produced

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is probably similar to that of the action of dilute acids on tannic acid. During the process oxygen is absorbed and carbonic acid gas evolved, the sugar being thus broken up or perhaps prevented from being formed.

To an aqueous solution of gallic acid add a neutral solution of a ferric salt; a bluish-black precipitate of gallate of iron falls similar in appearance to tannate of iron. Ferrous salts also are blackened by gallic acid. To more of the solution add an aqueous solution of gelatin; no precipitate occurs. By the latter test gallic is distinguished from tannic acid.

Pyrogallic acid ($C_6H_6O_3$).—This substance sublimes in light feathery crystals when gallic acid is heated. To an aqueous solution add a neutral solution of a ferric salt; a red colour is produced. To another portion add a ferrous salt; a deep-blue colour results.

To three separate small quantities of milk of lime in test-tubes add, respectively, tannic, gallic, and pyrogallic acids; the first slowly turns brown, the second more rapidly, while the pyrogallic mixture at once assumes a beautiful purplish-red colour changing to brown. These reactions are highly characteristic. They are accompanied by absorption of oxygen from the air. A mixture of pyrogallic acid and solution of potash absorbs oxygen with such rapidity and completeness that a strong solution of each passed up successively by a pipette into a graduated tube, containing air or other gas, form an excellent means of estimating free oxygen. The student may roughly practise this method by pouring a small quantity of each solution into a phial, immediately and firmly closing its mouth with a cork, thoroughly shaking the mixture and then removing the cork under water; the water rushes in and occupies about one-fifth of the previous volume of air, indicating that the atmosphere contains one-fifth of its bulk of oxygen. The small amount of carbonic acid gas present in the air is also absorbed by the alkaline liquid; in delicate experiments this should be removed by the alkali before the addition of pyrogallic acid.

URIC ACID ($H_2C_5H_2N_4O_3$).—Acidulate a few ounces of human urine with nitric acid, and set aside for twenty-four hours; a few minute crystals of uric acid will be found adhering to the

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sides and bottom of the vessel and floating on the surface of the liquid. Remove some of the floating particles by a slip of glass, and examine by a powerful lens or microscope; the chief portion will be found to be in yellowish semitransparent crystals, more or less square, two of the sides of which are even, and two very jagged; but other forms are common. Collect more of the deposit, place in a watch-glass or small white evaporating-dish, remove adherent moisture by a piece of blotting- or filter-paper, add a drop of concentrated nitric acid, and evaporate to dryness; the residue will be red. When the dish is cold, add a drop of solution of ammonia; a purplish-crimson colour results. The colour is deepened on the addition of a drop of solution of potash.

Uric acid and urates of sodium, potassium, calcium, and ammonium are common constituents of animal excretions. Human urine contains about one part of urate (usually urate of sodium) in 1000. When more than this is present the urate is often deposited as a sediment in the excreted urine, either at once, or after standing a short time. The acid or the urate is also occasionally deposited before leaving the bladder, and, slowly accumulating there, forms a common variety of urinary calculus. The urates are not definitely crystalline; but when treated with a drop of solution of potash, and then a drop or two of acetic acid, jagged microscopic crystals of uric acid are usually formed. All urates yield the crimson colour when treated as above described. This colour is a definite substance, *murexid* ($C_8H_8N_6O_6$) (from the *murex*, a shell-fish of similar tint); and the test is known as *the murexid test.* The formation of murexid is due to the action of ammonia on *alloxan* ($C_4H_4N_2O_5$, $3H_2O$) and other white crystalline products of the oxidation of uric acid by nitric acid. Murexid is a good dye; it may be prepared from *guano* (the excrement of sea-fowl), which contains a large quantity of urates of ammonium. The excrement of the serpent is almost pure ammonium urate.

Uric acid and the urates will be again alluded to in connexion with the subject of morbid urine.

Valerianic Acid or Valeric Acid ($HC_5H_9O_2$).—Heat in a test-tube a few drops of amylic alcohol (fousel oil) with a little dilute

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sulphuric acid and a grain or two of red chromate of potassium; valerianic acid of characteristic valerian-like odour is evolved. Or heat any valerianate with dilute sulphuric acid; double decomposition occurs, and valerianic acid is set free.

Valerianic acid occurs naturally in valerian-root, but is usually prepared artificially from amylic alcohol, to which it bears the same relation as acetic acid does to common alcohol:—

$$C_2H_5HO + O_2 = HC_2H_3O_2 + H_2O$$
$$C_5H_{11}HO + O_2 = HC_5H_9O_2 + H_2O.$$

Valerianate of Sodium ($NaC_5H_9O_2$) (*Sodæ Valerianas*, B. P.) is prepared by distilling the mixture of amylic alcohol, sulphuric acid, and red chromate of potassium.

$$2(K_2CrO_4, CrO_3) + 8H_2SO_4 = 2(Cr_2 3SO_4) + 2K_2SO_4 + 8H_2O + 3O_2$$

Red chromate of potassium. | Sulphuric acid. | Sulphate of chromium. | Sulphate of potassium. | Water. | Oxygen.

$$C_5H_{11}HO + O_2 = HC_5H_9O_2 + H_2O$$

Amylic alcohol. | Oxygen. | Valerianic acid. | Water.

$$2C_5H_{11}HO + O_2 = C_5H_{11}C_5H_9O_2 + 2H_2O$$

Amylic alcohol. | Oxygen. | Valerianate of amyl. | Water.

The distillate is saturated with soda, which not only yields valerianate of sodium with the free valerianic acid, but decomposes the valerianate of amyl produced at the same time, more valerinate of sodium being formed, according to the following equations:—

$$HC_5H_9O_2 + NaHO = NaC_5H_9O_2 + H_2O$$

Valerianic acid. | Soda. | Valerianate of sodium. | Water.

$$C_5H_{11}C_5H_9O_2 + NaHO = NaC_5H_9O_2 + C_5H_{11}HO$$

Valerianate of amyl. | Soda. | Valerianate of sodium. | Amylic alcohol.

Or $$Ay\overline{V} + NaHO = Na\overline{V} + AyHO.$$

Other valerianates.—Valerianate of zinc (*Zinci Valerianas*, B. P.), ferric valerianate, &c. may be made by double decomposition of valerianate of sodium with the sulphate or other salt of the metal the valerianate of which is desired, the new valerianate precipitating or crystallizing out.

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DETECTION OF THE ACIDULOUS RADICALS OF SALTS SOLUBLE IN WATER.

In analyzing salts soluble in water, search must first be made for any basylous radicals by the appropriate methods. Certain metals having been thus detected, a little reflection on the character of their salts will at once indicate what acidulous radicals may be, and what cannot be, present. Thus, for instance, if the substance under examination is freely soluble in water, and lead is found, only the nitric and acetic radicals need be sought, none other of the lead-salts than nitrate or acetate being freely soluble in water. Moreover the salt is more likely to be acetate than nitrate of lead, for two reasons: the former is more soluble than the latter, and is by far the commoner salt of the two. Medical and pharmaceutical students have probably, in dispensing, already learnt much concerning the solubility of salts, and whether a salt is rarely employed or in common use. And although but little dependence can be placed on the chances of a salt being present or absent according to its rarity, still the point may have its proper weight. If, in a mixture of salts, ammonium, potassium, and magnesium have been found associated with the sulphuric, nitric, and hydrochloric radicals, and we are asked how we suppose these bodies may exist in the mixture, it is far more in accordance with common sense to suggest that sal-ammoniac, nitre, and epsom salts were originally mixed together than to suppose any other possible combination: a tutor's aim in preparing mixtures of salts for analysis is to instruct, not puzzle, his pupils. Such appeals to experience regarding the solubility, rarity, &c. of salts cannot be made by any one not previously acquainted, or insufficiently acquainted, with the characters of salts; in such cases the relation of a salt to water and acids can be ascertained by referring to the following Table of the solubility or insolubility of salts in water and acids.

The opposite course to the above (namely, to ascertain what acidulous radicals are present in a mixture, and then to appeal to experience to tell what basylous radicals may be and what cannot be present) is impracticable; for acidulous radicals cannot be separated out, one after the other, from one and the same quantity of substance by a similar treatment to that already given for basylous radicals. Indeed such a sifting of acidulous

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radicals could scarcely be accomplished at all, or only by a vast deal of labour.

Even when the basylous radicals have been detected, the acidulous radicals which may be present must be sought for singly, the only additional aid which can be brought in being the action of sulphuric acid, a barium salt, a calcium salt, nitrate of silver, and ferric chloride on *separate* small portions of the solution under examination.

Commence the analysis of an aqueous solution of a salt or salts, the basylous radicals in which are known, by writing out a list of the acidulous radicals which may be, or, if more convenient, of those which cannot be present. To this end consult the following Table (p. 238) of the solubility of salts in water. Look for the name of the metal of the salt in the vertical column; the letters S and I indicate which salts are soluble and which insoluble in water, an asterisk attached to the S meaning that the salt is slightly soluble. The acidulous part of the name is given in the top line of the Table. All the names are in alphabetical order, for facility of reference.

Some of the salts marked as insoluble in water are soluble in aqueous solutions of soluble salts, a few forming soluble double salts. To characterize salts as soluble, slightly soluble, or insoluble, only roughly indicates their relation to water: on the one hand, very few salts are absolutely insoluble in water; on the other, there is a limit to the solubility of every salt.

If only one, two, or perhaps three given acidulous radicals can be in the liquid, test directly for it or them according to the reactions given in the previous pages. If several may be present, pour small portions of the solution, rendered neutral if necessary by ammonia, into five test-tubes, and add respectively sulphuric acid, nitrate or chloride of barium, chloride of calcium, nitrate of silver, and ferric chloride; then consult the Table on page 239, in order to correctly interpret the effects these reagents may have produced.

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TABLE OF THE SOLUBILITY OR INSOLUBILITY OF SALTS IN WATER.

	Acetate.	Arseniate.	Arsenite.	Carbonate.	Chloride.	Citrate.	Chromate.	Cyanide.	Hydrate.	Iodide.	Nitrate.	Oxalate.	Oxide.	Phosphate.	Sulphate.	Sulphite.	Tartrate.
Aluminium	S	I	I	I	S	S*	I	?	I	?	S	I	I	I	S	I	S
Ammonium	S	S	S	S	S	S	S	S	S	S	S	S	?	S	S	S	S
Antimony	S	I	I	I	S	S	I	?	I	I	S	S*	I	I	S	I	I
Barium	S	I	I	I	S	S*	I	I	S	S	S	I	S	I	S	I	I
Bismuth	S	I	?	I	S	S*	?	?	I	I	S	I	I	I	S	I	S
Cadmium	S	?	?	?	S	S*	?	?	I	S	S	I	I	I	S	I	S*
Calcium	S	I	I	I	S	S*	I	S	S*	S	S	I	S*	I	S*	S*	S*
Chromium	S	I	?	I	S	S	I	I	I	S	S	S	I	I	S	I	S
Cobalt	S	I	I	I	S	S	?	I	I	S	S	I	I	I	S	S	S
Copper	S	I	I	I	S	S	S	I	I	I	S	I	I	I	S	I	S*
Ferric	S	I	I	?	S	S	S	?	I	S	S	S*	I	I	S	I	S
Ferrous	S	I	I	I	S	S	S	I	I	S	S	S*	I	I	S	I	S
Gold	?	I	?	?	S	?	?	I	I	S	S	?	I	I	S	I	?
Lead	S	I	I	I	S*	S*	?	I	I	S*	S	?	I	I	?	I	?
Magnesium	S	I	I	I	S	S	S	?	I	S	S	I	I	I	S	S	S
Manganese	S	I	?	I	S	I	S	I	I	S	S	I	I	I	S	S*	S
Mercuric	S	I	I	I	S	?	S*	I	I	S	S	I	I	I	S	I	I
Mercurous	S*	I	I	I	I	I	I	?	?	I	S	I	I	I	S*	?	I
Nickel	S	I	I	I	S	S	I	I	I	S	S	I	I	I	S	S*	S*
Platinum	?	I	?	?	S	?	?	?	I	S*	S	?	I	?	I	?	?
Potassium	S	S	S	S	S	S	S	S	S	S	S	S	S	I	S	S	S
Silver	S*	I	I	I	I	I	I	I	S	I	S	I	I	I	I	I	I
Sodium	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Stannic	S	?	I	?	S	?	I	?	I	S	S	S	I	S	S	?	?
Stannous	S	I	I	?	S	?	I	?	S	S	S	I	I	I	S	I	S
Strontium	S	I	I	I	S	I	I	S	S	S	S	I	S	I	I	I	S*
Zinc	S	I	?	I	S	S*	S	I	I	S	S	I	I	I	S	S*	S*

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TABLE TO AID IN THE DETECTION OF CHLORIDES, BROMIDES, IODIDES, CYANIDES, NITRATES, CHLORATES, BORATES, ACETATES, SULPHIDES, SULPHITES, SULPHATES, CARBONATES, OXALATES, TARTRATES, PHOSPHATES, AND CITRATES IN A NEUTRAL AQUEOUS SOLUTION.

Sulphuric acid decomposes	Chloride of Barium precipitates	Chloride of Calcium precipitates	Nitrate of Silver precipitates	Ferric Chloride precipitates	Not precipitated.
Sulphides, Sulphites, Carbonates, with effervescence—hydrosulphuric, sulphurous, and carbonic acid gases, known by their odour, &c. being evolved. Cyanides, with production of the odour of hydrocyanic acid. Acetates, with production of the odour of acetic acid when the solution is warmed.	Borates. Sulphites. Sulphates. Carbonates. Oxalates. Tartrates. Phosphates. Citrates. Of these white barium precipitates, the sulphate is the only one insoluble in hydrochloric acid; the tartrate and citrate char when heated on platinum foil; the sulphite and carbonate are decomposed with effervescence by acids.	Borates. Oxalates. Sulphites. Tartrates. Sulphates. Phosphates. Carbonates. Citrates. Of these white calcium precipitates, the sulphate only is soluble in much water; the borate, tartrate, and citrate are soluble in solution of chloride of ammonium; all are soluble in acetic acid except oxalate and some sulphate; all are soluble in hydrochloric acid, much sulphate excepted; the dry tartrate and citrate char when heated; the sulphite and carbonate effervesce with acids.	Chlorides, white. Bromides, white. Iodides, yellow. Cyanides, white. Borates, white. Sulphides, black. Sulphites, white. Carbonates, white. Oxalates, white. Tartrates, white. Phosphates, yellow. Citrates, white. Of these silver precipitates, the chloride, bromide, iodide, cyanide, and sulphide are insoluble in dilute nitric acid; the rest soluble.	Borates, yellowish. Sulphides, black. Carbonates, reddish. Oxalates, yellow. Phosphates, yel.-white. Gives red colour with Acetates, if neutral.	Nitrates. Chlorates. Apply special tests.

The student should practise the examination of aqueous solutions of salts until he is able to detect acidulous radicals with facility and precision. For this purpose he may finish the analyses of the salts or solutions he has already examined for metals, or he may have aqueous solutions of salts, or the salts themselves, specially prepared for present use, the metals of the salts being stated. He will then be in a position to effectively study the analysis of salts which may or may not be soluble in water, examining them for both basylous and acidulous radicals.

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REMARKS ON THE PRECEDING TABLE.

The first point of value to be noticed in connexion with this Table is one of a negative character; namely, if either of the reagents gives no reaction, it is self-evident that the salts which it decomposes with production of a precipitate must be absent. Then, again, if the action of one of the reagents indicates the absence of certain acidulous radicals, those radicals cannot be precipitated by the other reagents; thus, if the action of sulphuric acid points to the absence of sulphides, sulphites, carbonates, cyanides, and acetates, these salts may be struck out of the other lists, and the examination of subsequent precipitates be so far simplified. Or, if the barium precipitate is soluble in hydrochloric acid and the calcium precipitate in acetic acid, neither sulphates nor oxalates can be present. Observing these and other points of difference, which will be seen on careful and thoughtful reflection, and remembering the facts suggested by a knowledge of what basylous radicals are present, one acidulous radical after the other may be struck off as absent or present, leaving only one or two as the objects of special experiment. Among the chief difficulties to be encountered will be the separation from each other of chlorides, bromides, iodides, and cyanides, or of tartrates from citrates, and confirmatory tests of the presence of borates &c. These may all be surmounted on referring back to the reactions of the various radicals, as described under their hydrogen salts, the acids.

The rarer acidulous radicals will seldom be met with. Formiates, hypochlorites, hyposulphites, nitrites, and valerianates show themselves under the sulphuric treatment. Ferrocyanides, ferridcyanides, sulphocyanates, tannates, and gallates appear among the salts whose presence is indicated by ferric chloride; formiates, malates, and others by nitrate of silver.

In actual practice the analyst nearly always has some clue to the nature of rarer substances placed in his hands.

If chromium and arsenicum have been detected among the basylous radicals, those elements may be present in the form of chromates, arseniates, and arsenites, yielding with chloride of barium yellow chromate of barium and white arseniate and arsenite of barium, and with nitrate of silver red chromate, brown arseniate, and yellow arsenite of silver.

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ANALYSIS OF SALTS,

SINGLE OR MIXED, SOLUBLE OR INSOLUBLE.

Thus far we have regarded all material substances, especially those of pharmaceutical interest, as being definite compounds, and as having certain well-defined parts, termed, for convenience, basylous and acidulous respectively. Moreover attention has been designedly restricted to those definite compounds which are soluble in water. But there are many substances having no definite or known composition; and of those having definite composition there are many having no definite or ascertained parts; and, again, of those having definite composition, and whose constitution admits of the entertainment of theory, there are many insoluble in water.

Chemical substances of whose composition or constitution nothing is at present known, are chiefly of animal and vegetable origin, and figure in tables of analyses &c. under the convenient collective title of "extractive matter" &c.; they are not of immediate importance, and may be omitted from consideration. Of the substances which are definite in composition, but whose parts or radicals, if they have any, are unknown or imperfectly known, there are only a few, such as the alkaloids, amylaceous and saccharine matters, the glucosides, alcoholic bodies, and albumen, which have any considerable amount of pharmaceutical interest; these will be noticed subsequently. Definite salts having definite parts are the substances which most frequently present themselves; and of these by far the larger proportion (namely, the salts soluble in water) have already been fully studied. There remain, however, many salts which are insoluble in water, but which must be brought into a state of solution before they can be effectively studied from an analytical, pharmaceutical, or a physiological point of view. The next thing to be done therefore is to go through the analysis of substances which may or may not be soluble in water. This will involve no other analytical schemes than those which have been given, will in only one or two cases increase the difficulty of the analysis of a precipitate produced by a group reagent, but will give roundness, completeness, and a practical bearing to the student's analytical know-

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ledge. Such a procedure will at the same time bring before him the methods by which substances insoluble in water are manipulated for pharmaceutical purposes, or made available for use as food by plants, or as food and medicine by man and animals generally.

Preliminary examination of Solid Salts.

Before attempting to dissolve a salt for analysis, its appearance and other physical properties should be noted, and the influence of heat and strong sulphuric acid be ascertained. If the student knows how to interpret what is thus observed, and to what extent to place confidence in the observations, he may more certainly obtain a high degree of precision in analysis, and will always gain some valuable negative information. But if he has only slight experience of the appearance and general properties of bodies, or has the habit of turning what should be inferences from tentative processes into foregone conclusions, he should omit the preliminary examination altogether, or only follow it out under the guidance of a judicious tutor. For it is impracticable here to do more than hint at the results which may be obtained by such an examination, or to so adapt descriptions as to prevent a student from allowing unnecessary weight to preconceived ideas.

Whatever be the course pursued, short memoranda describing results should invariably be entered in the note-book.

Examine the physical characters of the salt in various ways, but never, or only rarely, by the palate, on account of the danger to be apprehended.

If the salt is white, coloured substances cannot be present; if coloured, the tint may indicate the nature of the substance or of one of its constituents, supposing that the student is already acquainted with the colours of salts. Closer observation, aided perhaps by a lens, may reveal the occurrence, in a pulverulent mixture, of small crystals or pieces of a single substance; these may be picked out by a needle and examined separately. The body may present an undoubted metallic appearance, in which case only the metals existing under ordinary atmospheric conditions need be sought. Odour may reveal the presence of ammonia, hydrocyanic acid, hydrosulphuric acid, &c. Between the fingers the substance may be hard, soft, or gritty, and consequent inferences may be drawn. Or the matter may be heavy, like the

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salts of barium or lead, or light, like the carbonates and hydrates of magnesium.

Place a grain or two of the salt in a small dry test-tube or in a piece of ordinary tubing, closed at one end, and heat it, at first gently, then more strongly, and finally, if necessary, by the blowpipe.

Gases or vapours of characteristic appearance or odour may be evolved; iodine, nitrous fumes, sulphurous, hydrocyanic, or ammoniacal gases, &c. Much steam given by a dry substance indicates hydrates or salts containing water of crystallization. A sublimate may be obtained, due to salts of mercury or arsenicum, to oxalic or benzoic acids, or to sulphur free or as a sulphide, &c., a salt wholly volatile containing such substances only. The compound may blacken, pointing to the presence of organic matter, which, in common definite salts, will probably be in the form of acetates, tartrates, and citrates, or as salts of the alkaloids morphine, quinine, strychnine, &c., or as starch, sugar, salicin, or in other definite or indefinite forms common in pharmacy and for which tests will be given in subsequent pages. If no charring occur, the important fact that no organic matter is present is established. The residue may change colour from presence or development of oxide of zinc, oxide of iron, &c.; or it may melt from the presence of a fusible salt and absence of any large proportion of infusible salt; or it may be unaltered, showing the absence of any large amount of such substances.

Place a grain or two of the salt in a test-tube, add a drop or two of strong sulphuric acid, cautiously smelling any gas that may be evolved; afterwards slowly heat the mixture, noticing the effect, and stopping the experiment when any sulphuric fumes begin to escape.

Iodine, bromine, and nitrous or chlorinoid fumes will reveal themselves by their colour, indicating the presence of iodides, bromides, iodates, bromates, nitrates, and chlorates. The evolution of a colourless gas fuming on coming in contact with air, and having an irritating odour, points to chlorides, fluorides, or nitrates. Gaseous products having a greenish colour and odour of chlorine indicate chlorates, hypochlorites, or chlorides mixed

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with other substances. Slight sharp explosions indicate chlorates. Evolution of colourless gas may proceed from cyanides, acetates, sulphides, sulphites, carbonates, or oxalates. Charring will be due to citrates, tartrates, or other organic matter. If none of these effects are produced, most of these bodies are absent or only present in minute quantity. The substances apparently unaffected by the treatment are metallic oxides, borates, sulphates, and phosphates.

Exposure of the substance to the blowpipe-flame, on platinum wire with or without a bead of borax or of microcosmic salt (phosphate of sodium, ammonium, and hydrogen, $NaAmHPO_4$)—on platinum foil with or without carbonate of sodium—on charcoal, alone or in conjunction with carbonate of sodium, cyanide of potassium, or nitrate of cobalt, will sometimes yield important information, especially to one who has devoted much attention to reactions producible by the blowpipe-flame. The pharmaceutical student, however, will seldom have time to work out this subject to an extent sufficient to make it a trustworthy guide in analysis. (See Plattner and Muspratt 'On the Use of the Blowpipe,' and a chapter in Galloway's 'Manual of Qualitative Analysis.')

Methods of dissolving and analyzing single or mixed solid substances.

Having submitted the substance to preliminary examination, proceed to dissolve and analyze by the following methods. These methods consist in treating a substance consecutively with cold or hot water, hydrochloric acid, nitric acid, nitro-hydrochloric acid, or fusion with alkaline carbonates and solution of the product in water and acid. Resulting liquids are analyzed in the manner already described, or by slightly modified processes as detailed in the following paragraphs.

Boil about a grain of the salt presented for analysis in about a third of a test-tubeful of water. If it dissolves, prepare a solution of about 20 or 30 grains in about half an ounce of water, and proceed with the analysis in the usual way, testing first for the

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basylous radical or radicals by the proper group-reagents (HCl, H_2S, AmHS, Am_2CO_3, Am_2HPO_4), pp. 136 or 165, and then for the acidulous radical or radicals, directly or by aid of the prescribed reagents (H_2SO_4, $BaCl_2$, $CaCl_2$, $AgNO_3$, Fe_2Cl_6), p. 239.

If the salt is not wholly dissolved by the water, ascertain whether or not any has entered into solution by filtering, if necessary, and evaporating a drop or two of the clear liquid to dryness on platinum foil; the presence or absence of a residue gives the information sought. If anything is dissolved, prepare a sufficient quantity of solution for analysis and proceed as usual, reserving the insoluble portion of the mixture, after thoroughly exhausting with water, for subsequent treatment by acids.

If the salt is insoluble in water, digest about a grain of it (or of the insoluble portion of a mixed salt) in a few drops of hydrochloric acid, adding water, and boiling if necessary. If the salt wholly dissolves, prepare a sufficient quantity of the liquid, noticing whether or not any effervescence (due to the presence of sulphides, sulphites, carbonates, or cyanides) occurs, and proceed with the analysis as before, except that the first step, the addition of hydrochloric acid, may be omitted.

The analysis of this solution will in most respects be simpler than that of an aqueous solution, inasmuch as the majority of salts (all those soluble in water) will be absent. This acid solution will, in short, only contain:—chlorides produced by the action of the hydrochloric acid on sulphides, sulphites, carbonates, cyanides, oxides, and hydrates; and certain borates, oxalates, phosphates, tartrates, and citrates (possibly silicates and fluorides), which are insoluble in water but soluble in acids without apparent decomposition. The first four will have revealed themselves by the occurrence of effervescence during solution; and the presence of oxides and hydrates may often be inferred by the absence of compatible acidulous radicals. The borates, oxalates, phosphates, tartrates, and citrates alluded to will be reprecipitated in the general analysis as soon as the acid of the solution is neutralized; that is, will come down in their original state when ammonia and sulphydrate of ammonium are added in

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the usual course. Of these precipitates, only the oxalate of calcium and the phosphates of calcium and magnesium need occupy the attention of the pharmaceutist; for the borates, tartrates, and citrates met with in medicine or in general analysis are all soluble in water. These phosphates and oxalates, then, will be precipitated in the course of analysis along with iron, their presence not interfering with the detection of any other metal. If, from the unusually light colour of the ferric precipitate, phosphates and oxalates are suspected, the precipitate is treated according to the following Table (reference to which should be inserted in the general Table for the detection of metals, under Fe).

PRECIPITATE OF PHOSPHATES, OXALATES, AND FERRIC OXIDE.

Dissolve in HCl, add a little citric acid, then AmHO, and filter.

<table>
<tr><td rowspan="4">Filtrate
Fe.
Add HCl and
K_4Fcy.
Blue ppt.</td><td colspan="3">Precipitate
$Ca_3 2PO_4$, CaC_2O_4, $Mg_3 2PO_4$.
Boil in acetic acid and filter.</td></tr>
<tr><td>Insoluble
CaC_2O_4.
White.</td><td colspan="2">Filtrate
$Ca_3 2PO_4$ $Mg_3 2PO_4$
add $Am_2C_2O_4$, stir, filter.</td></tr>
<tr><td></td><td>Precipitate
CaC_2O_4.
White, proving
presence of
$Ca_3 2PO_4$.</td><td>Filtrate
add AmHO.
White ppt.
$MgHPO_4$.</td></tr>
<tr><td></td><td></td><td></td></tr>
</table>

In analyzing phosphates and oxalates advantage is also frequently taken of the facts that the phosphoric radical is wholly removed from solution of phosphates in acid by the addition of an alkaline acetate, ferric chloride, and subsequent ebullition, as described under 'Phosphoric Acid' (p. 214), and that dry oxalates are converted into carbonates by heat, as mentioned under 'Oxalic Acid' (p. 208).

Certain arseniates and arsenites, insoluble in water but soluble in hydrochloric acid, may accompany the above phosphates, oxalates, &c. if for any reason hydrosulphuric acid gas has not been previously passed through the solution.

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If the substance insoluble in water does not wholly dissolve in hydrochloric acid, ascertain if any has entered into solution by filtering, if necessary, and evaporating a drop of the clear liquid to dryness on platinum foil; the presence or absence of a residue gives the information sought. If anything is dissolved, prepare a sufficient quantity of solution for analysis, and proceed as usual, reserving the insoluble portion of the mixture, after thoroughly exhausting with hydrochloric acid and well washing with water, for the following treatment by nitric acid.

If the salt is insoluble in water and hydrochloric acid, boil it (or that part of it which is insoluble in those menstrua) in a few drops of nitric acid. If it wholly dissolves, remove excess of acid by evaporation, dilute with water, and proceed with the analysis in the usual way.

This nitric solution can contain only very few substances; for nearly all salts soluble in nitric acid are also soluble in hydrochloric acid, and therefore will have been previously removed. Some of the metals, however (Ag, Cu, Hg, Pb, Bi), as well as amalgams and alloys, unaffected or scarcely affected by hydrochloric acid, are readily attacked and dissolved by nitric acid. Many of the sulphides, also insoluble in hydrochloric acid, are dissolved by nitric acid, usually with separation of sulphur. Calomel is converted, by long boiling with nitric acid, into mercuric chloride and nitrate. The nitrates here produced are soluble in water.

This nitric solution, as well as the hydrochloric and aqueous solutions, should be examined separately. Apparently time would be saved by mixing the three solutions together and making one analysis. But the object of the analyst is to separate every radical from every other; and when this has been partially accomplished by solvents, it would be unwise to again mix and a second time separate. Moreover solvents often do what chemical reagents cannot do—namely, separate *salts* from each other. This is important, inasmuch as the end to be attained in analysis is not only an enumeration of the radicals present, but a statement of the actual condition in which they are present; the analyst must, if possible, state of what salts a given mixture

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was originally formed, how the basylous and acidulous radicals were originally distributed. In attempting this, much must be left to theoretical considerations; but a process by which the salts themselves are separated is of trustworthy practical assistance; hence the chief advantage of analyzing separately the solutions resulting from the action of water, acids, &c. on a solid substance.

If the salt or any part of a mixture of salts is insoluble in water, hydrochloric acid, and nitric acid, digest it in nitro-hydrochloric acid, boiling if necessary; evaporate to remove excess of acid, dilute, and proceed as before.

Sulphide of mercury and substances only slowly attacked by hydrochloric or nitric acid, such as calomel, ignited ferric oxide, &c. are sufficiently altered by the free chlorine of aqua regia to become soluble.

If the substance is insoluble in water and acids, it is one or more of the following substances:—Sand and certain silicates, such as pipeclay and other clays, fluorspar, cryolite ($3NaF,AlF_3$); sulphates of barium, strontium, and possibly calcium; tinstone; glass; felspar (double silicate of aluminium and other metals); chloride of silver; sulphate of lead. It may also be or contain carbon or carbonaceous matter, in which case it is black and combustible, burning entirely or partially away when heated in the air; or be or contain sulphur, in which case sulphurous gas is evolved, detected by its odour, when the substance is exposed to heat. For the other substances proceed according to the following (Bloxam's) method:—

Four or five grains of the substance are intimately mixed with twice the quantity of dried carbonate of sodium, and this mixture well rubbed in a mortar with five times its weight of *deflagrating flux* (1 of finely powdered charcoal to 6 of nitre). The resulting powder is placed in a thin porcelain dish, or crucible, or clean iron tray, and a lighted match applied to the centre of

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the heap. Deflagration ensues, and decomposition of the various substances occurs, the acidulous radicals going to the alkali-metals to form salts soluble in water, the basylous radicals being simultaneously converted into carbonates or oxides. The mass is boiled in water for a few minutes, the mixture filtered, and the residue well washed. The filtrate may then be examined for acidulous radicals and aluminium in the usual way, and the residue dissolved in dilute hydrochloric acid and analyzed by the ordinary method.

The only substance which resists this treatment is chrome iron-ore.

To detect alkali in felspar, glass, or cryolite, Bloxam recommends deflagration of the powdered mineral with one part of sulphur and six of nitrate of barium. The mass is boiled in water, the mixture filtered, hydrate and carbonate of ammonium added to remove barium, the mixture again filtered, and the filtrate evaporated and examined for alkalies by the usual process.

QUALITATIVE ANALYSIS OF SUBSTANCES HAVING UNKNOWN PROPERTIES.

Substances are presented to the analyst in one of the three forms in which all matter exists—namely, solid, liquid, or gaseous.

The method of analysis in the case of solid bodies has just been described (pp. 242 & 244).

In the case of liquids, the solvents as well as the dissolved matters claim attention. A few drops are evaporated to dryness on platinum foil to ascertain if solid matter of any kind is present; the liquid is tested by red and blue litmus paper to ascertain if free alkalies, free acids, or neither are present; a few drops are heated in a test-tube and the odour of any vapour noticed, a piece of glass tubing bent to a right angle being, if

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necessary, adapted to the test-tube by a cork in the ordinary way, and some of the distilled liquid collected and examined; finally, the usual group-reagents for the several basylous and acidulous radicals are consecutively applied.

Proceeding in this way the student, who has already had some experience in pharmacy, will not be likely to overlook such solvents as water, acids, alcohol, ether, fixed oils, essential oils, &c., nor to miss the substances which these menstrua may hold in solution. He must not, however, suppose that he will always be able to qualitatively analyze, say, a bottle of medicine; for the various infusions, decoctions, tinctures, wines, syrups, liniments, confections, extracts, pill-masses, and powders contain vegetable matters most of which at present are quite beyond the reach of the analyst. Neither the highest skill in analysis nor the largest amount of experience concerning the odour, appearance, taste, and uses of drugs is sufficient for the detection of all these vegetable matters. Skill and experience combined will, however, do much; and even so difficult a task as that just mentioned may be, in most cases, accomplished with reasonable success. Qualitative analysis alone will not enable the experimenter to produce a mixture of substances similar to that analyzed; to this end recourse must be had to quantitative analysis, a subject reserved for subsequent consideration.

Gas-analysis, or Eudiometry (from εὐδία, *eudia*, calm air, and μέτρον, *metron*, a measure, in allusion to the *eudiometer*, an instrument used in measuring the proportion and, as the early chemists thought, the salubrity of the gases of the air), is a branch of experimental investigation, chiefly of a quantitative character, concerning which information must be sought in other treatises. The analysis of atmospheric air from various localities, coal-gas, and the gases obtained in chemical researches involves operations which are scarcely within the sphere of Pharmaceutical Chemistry. Beyond the recognition, therefore, of oxygen, hydrogen, nitrogen, carbonic, sulphurous, and hydrosulphuric acid gases, the experimental consideration of the chemistry of gaseous bodies may be omitted. Their study should not, however, be neglected, as existing conceptions of the constitution of chemical substances are largely dependent on the observed relations of the volumes of gaseous compounds to their elements. The best work on this subject is a small book by Hofmann, 'Introduction to Modern Chemistry.'

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Spectrum-Analysis.—It may be as well to state here that the preliminary and final examinations of minute quantities of solid matter may, in certain cases, profitably include their exposure to a temperature at which they emit light, the flame being physically analyzed by a spectroscope. A spectroscope consists essentially of a prism to decompose a ray of light into its constituent colours, with tubes and lenses to collect and transmit the ray or rays to the eye of an observer. The material to be examined is placed on the end of a platinum wire, which is then brought within the edge of a spirit-lamp or other smokeless flame; volatilization, attended usually in the case of a compound by decomposition, at once occurs, and the whole flame is tinged of characteristic hue. A flat ribbon of rays is next cut off by bringing near to the flame a brass tube, the cap of which is pierced by a narrow slit. At the other end of the tube, at focal distance for parallel rays, is a lens, through which the ribbon of light passes to a prism; the prism decomposes the ribbon, spreading out its constituent colours like a partially opened fan, and the spectrum thus produced is then examined by help of a telescope attached by a moveable joint to the stand which carries the prism and object-tube. Sodium compounds, under these circumstances, give yellow light only, indicated by a double band of light in a position corresponding to the yellow part of an ordinary solar spectrum. The potassium spectrum is mainly composed of a red and violet band; lithium a crimson, and at very high temperatures a blue band. Most of the other elements give equally characteristic spectra.

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SPECIAL CHEMICAL OPERATIONS ON SUBSTANCES OF VEGETABLE AND ANIMAL ORIGIN.

Except alcohol and a few acids, the compounds which have hitherto engaged our notice have been of mineral origin. But many medicinal substances, obtained from animals and vegetables, when discovered were producible only by highly organized living structures, and were hence termed organic compounds*.

A few of these compounds, of common occurrence in pharmacy and possessing prominent characteristics, may now occupy attention; reactions of the alkaloids and some other principles may be performed, and the methods of examining morbid urine be experimentally studied. There will then remain certain substances, solid and liquid, which can only be fairly regarded from a synthetical point, and a still larger number, doubtless, not yet brought within the grasp of the chemist, and of which, therefore, we must at present be content to remain in ignorance. An opportunity, however, will be afforded of noticing the effect of a mixture of definite and indefinite organic matter, such as a vomit or the contents of a stomach, in masking or preventing the reactions by which mineral and vegetable poisons are detected.

ALKALOIDS.

The alkaloids, or alkali-like (*εἶδος, eidos,* likeness) bodies have many analogies with ammonia. Their constitution is not yet

* A large number of these compounds can now be obtained artificially—without the aid of a living organism; hence the distinction formerly drawn between organic and inorganic compounds, organic and inorganic chemistry, is fast breaking down.

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known; but they are probably derivatives of a single molecule of ammonia (NH_3), or of double, triple, quadruple, &c. molecules (N_2H_6, N_3H_9, N_4H_{12}). A large number of artificial alkaloids or organic bases having such a constitution have already been formed. These are termed *amines*, and are primary, secondary, and tertiary according as one, two, or three atoms of hydrogen in ammonia (the tri-hydrogen amine) have been displaced by radicals, as seen in the following general formula (R = any radical)—

$$\left.\begin{matrix}R\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}R\\R\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}R\\R\\R\end{matrix}\right\}N;$$

or in the following examples—

$$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N.$$

Ethylamine. Diethylamine. Triethylamine.

The three classes have also been termed amidogen-, imidogen-, and nitrile-bases.

The displacing radicals may be similar or different; and while the radical displacing one atom of hydrogen is keeping its place any of the many known radicals may occupy the position of one or both of the other atoms of hydrogen. Thus, for example, we have methyl-ethyl-amyl-amine ($NCH_3C_2H_5C_5H_{11}$, or NMeEtAy), a colourless, oily body, of agreeable aromatic odour.

The organic bases derived from one molecule of ammonia are termed monamines; from two molecules, diamines; from three, triamines; and from four, tetramines:—

$$\left.\begin{matrix}R\\R\\R\end{matrix}\right\}N \qquad \left.\begin{matrix}R_2\\R_2\\R_2\end{matrix}\right\}N_2 \qquad \left.\begin{matrix}R_3\\R_3\\R_3\end{matrix}\right\}N_3 \qquad \left.\begin{matrix}R_4\\R_4\\R_4\end{matrix}\right\}N_4$$

In these amines, any bivalent, trivalent, or quadrivalent radical may occupy the place of two, three, or four univalent radicals.

Attempts to form artificially the natural organic bases have hitherto failed; but the primary, secondary, or tertiary character of some of them has been indicated by the introduction or elimination of methyl, ethyl, &c., for hydrogen.

The names of the salts of the alkaloids are given on the assumption that the acid unites with the alkaloid without de-

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composition. Thus hydrochlorate of morphine is regarded as morphine with hydrochloric acid, just as we might assume sal ammoniac to be ammonia (NH_3) with hydrochloric acid (HCl), and name it hydrochlorate of ammonia (NH_3HCl) instead of chloride of ammonium (NH_4Cl).

Antidotes.—In cases of poisoning by alkaloids, emetics and the stomach-pump must be relied on rather than chemical agents. Astringent liquids may be administered, as tannic acid precipitates many of the alkaloids from their aqueous solution, absorption of the poison being thus possibly retarded.

MORPHINE, OR MORPHIA.

Formula $C_{17}H_{19}NO_3$, H_2O. Molecular weight 303.

Morphine occurs in opium as meconate of morphine. The hydrochlorate (*Morphiæ Hydrochloras*, B. P.) is prepared by simply decomposing an aqueous infusion of opium with chloride of calcium, meconate of calcium and hydrochlorate of morphine being produced. The salt is partially purified by crystallization, then by treatment of the solution of the impure hydrochlorate by animal charcoal, and lastly by precipitation of the morphine from the still coloured liquid by ammonia and re-solution of the morphine in hot dilute hydrochloric acid; hydrochlorate of morphine separates out on cooling. Acetate of morphine ($C_{17}H_{19}NO_3C_2H_4O_2$) (*Morphiæ Acetas*, B. P.) is prepared by dissolving morphine in acetic acid, the morphine being prepared from a solution of the hydrochlorate by precipitation with ammonia. Both the hydrochlorate and acetate of morphine are soluble in water, but the solution is not stable unless acidulated and containing alcohol; hence the officinal solutions (*Liquor Morphiæ Hydrochloratis* and *Liquor Morphiæ Acetatis*) consist of three parts water and one part rectified spirit, a few minims per ounce of hydrochloric or acetic acid being added. The other officinal preparations are *Suppositoria Morphiæ*, *Trochisci Morphiæ*, and *Trochisci Morphiæ et Ipecacuanhæ*.

Reactions.

First Analytical Reaction.—To a drop or two of a solution of a salt of morphine add a drop of a *neutral* solution of perchloride of iron; a dark-bluish colour is produced.

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Second Analytical Reaction.—To a drop or two of a solution of a morphine salt add a minute fragment of iodic acid (prepared by oxidizing iodine with nitric acid, evaporating to dryness, and recrystallizing from water); iodine is set free. Into the upper part of the tube insert a glass rod covered with mucilage of starch, and warm the solution; dark-blue starch-iodide is produced.

This reaction is only confirmatory of others, as albuminous matters also reduce iodic acid.

Third Analytical Reaction.—To a few drops of an aqueous infusion of opium add a drop of *neutral* solution of perchloride of iron; a red solution of meconate of iron is produced. Add solution of corrosive sublimate; the colour is not destroyed (as it is in the case of sulphocyanide of iron, a salt of similar tint).

In cases of poisoning by laudanum or other preparation of opium, this reaction is almost as conclusive as a direct reaction of morphine, the poison itself.

Other Reactions.—Add carbonate of sodium to a solution of a salt of morphine; a white precipitate of morphine falls, slowly and of a crystalline character if the solution is dilute. Collect this precipitate and moisten it with neutral solution of perchloride of iron; the bluish tint above referred to is produced.

Heat morphine or its hydrochlorate on platinum foil; it burns entirely away.

QUININE, OR QUINIA.

Formula $C_{20}H_{24}N_2O_2, 3H_2O$. Molecular weight 378.

Quinine exists in yellow cinchona bark as kinate of quinine. Sulphate of quinine (*Quiniæ Sulphas*, B. P.) is prepared by treating the bark with dilute hydrochloric acid, precipitating the quinine by soda, and redissolving in the proper proportion of hot dilute sulphuric acid. The salt crystallizes out on cooling, in

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acicular crystals containing two atoms of quinine ($2C_{20}H_{24}N_2O_2$), one of sulphuric acid (H_2SO_4), and seven of water of crystalization ($7H_2O$). This sulphate, or, more correctly, disulphate, is only slightly soluble in water; on the addition of dilute sulphuric acid a neutral sulphate is formed which is freely soluble. The latter salt may be obtained in large rectangular prisms, having a composition expressed by the formula $C_{20}H_{24}N_2O_2$, H_2SO_4, $7H_2O$. The ordinary disulphate of quinine is more soluble in alcohol or alcoholic liquids than in water; hence the *Tinctura Quiniæ*, B. P., which is a solution of the salt in tincture of orange-peel (eight grains in the ounce). Quinine wine (*Vinum Quiniæ*, B. P.) is a solution of neutral sulphate and citrate of quinine in orange wine, made by dissolving the disulphate (one grain in the ounce) in orange-wine by the help of citric acid. The only officinal preparation of the pure disulphate is *Pilula Quiniæ*, containing three parts salt to one of confection of hips. The remaining Pharmacopœial preparation of quinine is the mixed citrates of iron, ammonium, and quinine (*Ferri et Quiniæ Citras*, B. P.), the well-known scaly compound. It is made by dissolving ferric hydrate, prepared from ferric sulphate, and quinine prepared from the sulphate, in solution of citric acid, ammonia also being added: the liquid, evaporated to a syrupy consistence and dried in thin layers on glass plates, yields the usual greenish-yellow scales.

Reactions.

First Analytical Reaction.—To a solution of quinine or its salts in acidulated water add chlorine water and then solution of ammonia; a green coloration is produced.

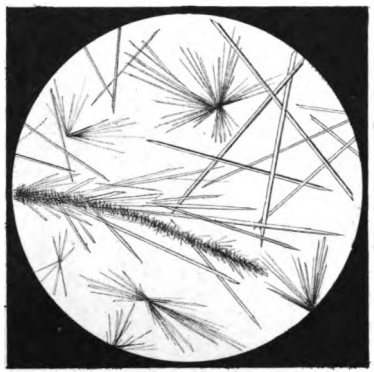
Second Analytical Reaction.—Repeat the foregoing reaction, but precede the addition of ammonia by solution of ferrocyanide of potassium; an evanescent red coloration is produced (Livonius and Vogel).

Third Analytical Reaction.—Quinine may be impure from the presence of the other alkaloids (chiefly quinidine and cinchonine) of cinchona bark; the following tests will determine the point. The first is Stoddart's modification of Liebig's process.

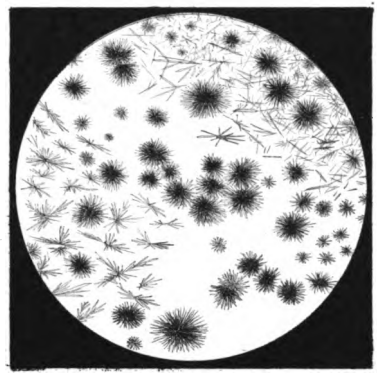
Into a glass tube or bottle put ten grains of the suspected salt, dissolve in 10 minims of dilute sulphuric acid and 60 minims of

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SULPHOCYANIDE OF QUININE.



SULPHOCYANIDE OF QUINIDINE.



SULPHOCYANIDE OF CINCHONINE.

All magnified 230 diam.s

H.B. Brady del. ad nat. Tuffen West sc.

W. West imp.

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distilled water; to this add 150 minims of *pure* ether, 3 minims of alcohol, and 40 minims of a solution of soda (1 part of solid hydrate to 12 of water). Agitate well and set aside for twelve hours, when, if the slightest trace of quinidine or cinchonine be present, they will be seen at the line of separation between the ether and solution of sulphate of sodium.

If only a small percentage of quinidine be present, it will appear as an oily substratum, appearing under a lens as dust, from the minuteness of its particles. Cinchonine will appear more decidedly crystalline. With a little practice the eye will easily distinguish which of the alkaloids is deposited.

Fourth Analytical Reaction.—This is Stoddart's chemico-microscopic test. Into an ounce of distilled water drop 10 drops of dilute sulphuric acid (British Pharmacopœia). To this add 14 grains (or as much as will saturate the acid) of the suspected salt. Filter through paper, and to a little of the filtered solution add a few drops of solution of sulphocyanide of potassium (180 grains in $1\frac{1}{2}$ ounce of water). An immediate precipitate of the several alkaloids takes place, each of which (see the accompanying plates) is distinct and characteristic. If quinine, quinidine, and cinchonine be present they will all be seen on the slide, distinct from each other, becoming more so every minute. A good plan is to place on a glass slip a minute drop of the solution to be tested, and to put another of the sulphocyanide by its side. Over both place a piece of thin glass, which will cause the drops to touch. Examine the line of junction under a half-inch object-glass, when the crystals are readily seen and recognized. By this method $\frac{1}{10000}$ of a grain of quinidine or cinchonine may easily be detected. The particles arrange themselves into the respective groups—the long slender needles of the quinine salt, the round crystalline masses of the quinidine, and the large well-formed prisms of the cinchonine salts. So remarkably constant is this reaction, that an observer who has accustomed himself

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to the general appearance can at once distinguish with ease the respective salts from each other.

The sulphocyanide-of-potassium solution should be of the strength indicated. It may readily be made thus:—Cyanide of potassium (fused), sublimed sulphur, of each 120 grains; distilled water an ounce and a half. Boil in a glass flask for fifteen minutes, filter, and make up the quantity to 1½ ounces with sufficient distilled water.

A small quantity of quinine in much cinchonine or quinidine cannot be recognized by the above reaction. Therefore, before concluding that no quinine is present in a specimen of those alkaloids, the sample should be treated with ether, filtered, the solution evaporated to dryness, and the residue, if any, examined for quinine.

Other characters.—Concentrated sulphuric acid dissolves quinine with production of only a faint yellow colour; salicin, with which quinine may possibly be adulterated, slowly gives, under the same circumstances, a deep red.

Concentrated nitric acid dissolves quinine, yielding a colourless solution; on heating, the solution becomes yellowish.

Quinine and its salts, heated on platinum foil, burn entirely away.

STRYCHNINE, OR STRYCHNIA.

Formula $C_{21}H_{22}N_2O_2$. Molecular weight 334.

This alkaloid exists in Nux Vomica (*Strychnos Nux Vomica*) and in St. Ignatius's bean (*Strychnos Ignatius*), chiefly in combination with lactic acid. According to the officinal process for its preparation (*Strychnia*, B. P.) the disintegrated nuts are exhausted with spirit, the latter removed by distillation, the extract dissolved in water, colouring and acid matters precipitated by acetate of lead, the filtered liquid evaporated to a small bulk, the strychnine precipitated by ammonia, the precipitate washed, dried, and exhausted with spirit, the spirit recovered by distillation, and the residual liquid set aside to crystallize.

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Crystals of strychnine having formed, the mother liquor (which contains the brucine of the seeds) is poured away, and the crystals of strychnine washed with spirit and recrystallized.

Reactions.

First Analytical Reaction.—Place a minute particle of strychnine on a white plate, and near to it a small fragment of red chromate of potassium; to each add one drop of concentrated sulphuric acid: after waiting a minute or so for the chromate to fairly tinge the acid, draw the latter, by a glass rod, over the strychnine spot; a beautiful purple colour is produced, quickly fading into a yellowish red. The following oxidizing agents may be used in the place of the chromate:—Puce-coloured oxide of lead, fragments of black oxide of manganese, ferridcyanide of potassium, or permanganate of potassium.

This reaction is highly characteristic; a minute fragment dissolved in much dilute alcohol, or, better, chloroform, and one drop of the liquid evaporated to dryness on a porcelain crucible-lid or other white surface, yields a residue which immediately gives the purple colour on being oxidized in the manner directed.

Other Reactions.—Strong sulphuric acid does not act on strychnine, even at the temperature of boiling water, a fact of which advantage is taken in separating strychnine from other organic matter for purposes of analysis.

Sulphocyanide of potassium produces, even in dilute solutions of strychnine, a white precipitate, which, under the microscope, is seen to consist of tufts of acicular crystals.

Strong nitric acid does not colour strychnine in the cold, and on heating only turns it yellow.

The Physiological Test.—A small frog placed in an ounce of water to which $\frac{1}{100}$ of a grain of a salt (acetate) of strychnine is added, is, in two or three hours, seized with tetanic spasms on the slightest touch, and dies shortly afterwards.

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Strychnine has an intensely bitter taste. Cold water dissolves only $\frac{1}{2000}$ part; yet this solution, even when largely diluted, is distinctly bitter. Alcohol is a somewhat better solvent. The salts of the alkaloid are more soluble. The officinal solution (*Liquor Strychniæ*, B. P.) contains four grains of strychnine to the ounce, the solvent being three parts water, one part spirit, and a few minims of hydrochloric acid (rather more than sufficient to form hydrochlorate of strychnine).

Brucine, or Brucia ($C_{23}H_{26}N_2O_4, 4H_2O$), is an alkaloid accompanying strychnine in Nux Vomica. It is readily distinguished by the intense red colour produced when nitric acid is added to it. *Igasurine* is another alkaloid existing in no less than nine varieties of Nux Vomica.

ALKALOIDS OF LESS FREQUENT OCCURRENCE.

Aconitine, Aconitina, or Aconitia ($C_{30}H_{47}NO_7$), is an alkaloid obtained from aconite root (*Aconitum Napellus*). The alkaloid itself is almost insoluble in water; but it occurs in the plant in combination with a vegetable acid, forming a soluble salt. The officinal process for its preparation (*Aconitia*, B. P.) consists in dissolving out the natural salt of the alkaloid from the root by rectified spirit, recovering the latter by distillation, mixing the residue with water, filtering, precipitating the aconitine by ammonia, drying the precipitate and digesting it in ether (in which some of the accompanying impurities are insoluble), recovering the ether by distillation, dissolving the dry residue in the retort in water acidulated by sulphuric acid, again precipitating the alkaloid by ammonia, and finally washing and drying.

The chemical reactions of aconitine are not sufficiently well marked to admit of application as qualitative tests. It is one of the most violent poisons known. *Unguentum Aconitiæ*, B. P., contains eight grains of the alkaloid to one ounce of prepared lard.

Atropine, or Atropia ($C_{17}H_{23}NO_3$), exists in the Belladonna root (*Atropa Belladonna*) as soluble acid malate of atropine. It is obtained in the pure state by exhausting the root with spirit, precipitating the acid and some colouring-matter by lime, filtering, adding sulphuric acid to form sulphate of atropine (which is

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somewhat less liable to decomposition during subsequent operations than the alkaloid itself), recovering most of the spirit by distillation, adding water to the residue, and evaporating till the remaining spirit is removed; solution of carbonate of potassium is then poured in till the liquid is nearly but not quite neutral, by which resinous matter is precipitated; the latter is filtered away, excess of carbonate of potassium then added, and the liberated atropine dissolved out by shaking the liquid with chloroform. The latter solution having subsided is removed, the chloroform recovered by distillation, the residual atropine dissolved in warm spirit, colouring-matter separated by digesting the liquid with animal charcoal, the solution filtered, evaporated, and set aside to deposit crystals.

Atropine solutions give, with perchloride of gold, a yellow precipitate. One drop of a dilute aqueous solution (two grains to the ounce) powerfully dilates the pupil of the eye. It is applied on a piece of thin tissue paper or small disk placed between the eyelid and the eye. The alkaloid itself (*Atropia*), its sulphate (*Atropiæ Sulphas*, made by neutralizing atropine with sulphuric acid), their solutions (*Liquor Atropiæ*, four grains per ounce, and *Liquor Atropiæ Sulphatis*, four grains per ounce), and an ointment (*Unguentum Atropiæ*, eight grains per ounce) are the preparations officinal in the British Pharmacopœia.

Beberine, or Beberia ($C_{38}H_{42}N_2O_6$), is an alkaloid existing in Bebeeru bark (*Nectandra Rodiei*). According to the British Pharmacopœia, it, or rather its sulphate (*Beberiæ sulphas*, B. P.), may be prepared by exhausting the bark with water acidulated by sulphuric acid, concentrating, removing most of the acid by lime, filtering, precipitating the alkaloid by ammonia, filtering, drying, dissolving in spirit (in which some accompanying matters are insoluble), recovering most of the spirit by distillation, neutralizing by dilute sulphuric acid, evaporating to dryness, dissolving the residual sulphate in water, evaporating to the consistence of a syrup, and spreading on glass plates, drying the product at 140°. Thus obtained, it occurs in thin dark-brown translucent scales.

Alkalies give a pale yellow precipitate of beberine when added to an aqueous solution of a salt of the alkaloid; the precipitate is soluble in ether. With red chromate of potassium and sulphuric acid beberine gives a black resin, and with nitric acid a yellow resin.

Berberine, or Berberia ($C_{20}H_{17}NO_4$), is an alkaloid existing in several plants of the natural order *Berberideæ*, in Calumba and

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in many other yellow woods. The colour of the tissues of these vegetables is evidently due to berberine; for the alkaloid itself is remarkable for its beautiful yellow colour. When a dilute solution of iodine in iodide of potassium is added to solution of any salt of berberine in hot spirit, excess of iodine being carefully avoided, brilliant green spangles are deposited. The reaction is sufficiently delicate to form, according to Perrins, an excellent test of the presence of berberine. This iodo-compound polarises light, and has other analogies with a similar quinine-salt termed herapathite. Berberine is not an officinal alkaloid; but the plants in which it occurs are used as medicinal agents in all parts of the world. It is readily extracted by boiling the raw material with water, evaporating the strained liquid to a soft extract, digesting the residue in alcohol, recovering the alcohol by distillation, boiling the residue with diluted sulphuric acid, filtering and setting aside; the sulphate of berberine separates out, and may be purified by recrystallization from hot water. The alkaloid itself is obtained by shaking hydrated oxide of lead with a hot aqueous solution of the sulphate of berberine (Proctor).

Podophyllum root contains berberine. In preparing the resin of podophyllum (*Podophylli Resina*, B. P.) an alcoholic extract of the root is poured into water acidulated by hydrochloric acid, whereby the whole of the hydrochlorate of berberine, which is almost insoluble in dilute mineral acids, is precipitated with the resin (Maisch).

Conine, Conicine, Cicutine, Conia, or Conylia.—Formula $C_8H_{15}N$, or $(C_8H_{14})''HN$. This alkaloid is a volatile liquid, occurring in hemlock (*Conium maculatum*). It is not officinal. It may be obtained by distilling hemlock seeds with water rendered slightly alkaline by caustic soda or potash, or by similarly treating the fresh juice of the leaves. The alkaloid is a yellow oily liquid, floating on the water that distils over; by redistillation it is obtained colourless and transparent. The salts of conine have no odour, but when moistened with solution of an alkali yield the alkaloid, the strong smell of which, at once recalling hemlock, is characteristic. Extract of hemlock, to which solution of potash and boiling water have been added, forms the officinal Inhalation of Conine (*Vapor Coniæ*, B. P.).

Sulphuric acid turns conine purplish-red, changing to olive-green, nitric acid a blood-red; perchloride of gold produces a yellowish-white precipitate, perchloride of platinum no precipitate, in aqueous solutions.

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Hemlock also contains methyl-conine $(C_8H_{14})''C_2H_3N$ (Kekulé and Von Planta).

NICOTINE, NICOTINA, OR NICOTYLIA.—Formula $C_{10}H_{14}N_2$, or $(C_5H_7)'''_2N_2$. This is also a volatile alkaloid, forming the active principle of tobacco (*Nicotiana tabacum*), malate and citrate of nicotine being the forms in which it occurs in the plant. Its odour is characteristic; like conine, it yields a precipitate with perchloride of gold; but, unlike that alkaloid, its aqueous solutions are precipitated yellowish-white by perchloride of platinum. It is not officinal.

THEINE, OR CAFFEINE $(C_8H_{10}N_4O_2+H_2O)$.—This alkaloid occurs in tea, coffee, Paraguay tea, guarana, and the kola-nut. Infusions and preparations of these vegetable products are used chiefly as beverages by three-fourths of the human race. It is remarkable that the instinct of man, even in his savage state, should have led him to select, as the bases of common beverages, &c., just the four or five plants which out of many thousands are the only ones, so far as we know, containing theine.

Concentrated nitric acid, or a mixture of chlorate of potassium and hydrochloric acid, rapidly oxidizes theine, forming compounds which with ammonia yield a beautiful purple-red colour, resembling the murexid obtained under similar circumstances from uric acid; the oxidation must not be carried too far. Theine boiled with caustic potash yields methylamine (CH_3HHN), the vapour of which has a peculiar, characteristic odour.

The chemical action of theine on the system is not yet made out. Liebig thinks it may aid in the production of a substance a normal amount of which is so necessary, an abnormal so unpleasant—namely, bile. Most chemists agree that it arrests the rapid consumption of tissue and consequent feeling of fatigue which is especially experienced after hard work with mind or body.

VERATRINE, OR VERATRIA $(C_{32}H_{52}N_2O_8)$.—This alkaloid occurs as gallate of veratrine in various species of *Veratrum* (Hellebore), in *Cevadilla*, and in the corms of *Colchicum autumnale*. A mere trace of it brought into contact with the mucous membrane of the nose causes violent fits of sneezing. Fuming sulphuric acid colours it yellow, red, and violet in succession.

The officinal process for the preparation of the alkaloid (*Veratria*, B. P.) consists in exhausting the disintegrated cevadilla seeds by alcohol, recovering most of the spirit by distillation pouring the residue into water, by which much resin is precipitated, filtering, and precipitating the veratrine from the aqueous

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solution by ammonia. It is purified by washing with water, solution in dilute hydrochloric acid, decolorization of the liquid by animal charcoal, reprecipitation by ammonia, washing and drying. *Unguentum Veratriæ*, B. P., contains eight grains of the slightly impure alkaloid obtained as just described, rubbed down with half a drachm of olive-oil and diffused through one ounce of prepared lard.

AMYLACEOUS AND SACCHARINE SUBSTANCES.

STARCH.

Formula $C_6H_{10}O_5$.

Rasp or grate, or, with a knife, scrape a portion of a clean raw potato, letting the pulp fall on to a piece of muslin placed over a small dish or test-glass, and then pour a slow stream of water over the pulp; minute particles or *granules* of starch pass through the muslin and sink to the bottom of the vessel, fibrous matter remaining on the sieve. This is potato-starch. Wheat-starch (*Amylum*, B. P.) may be obtained by tying up some flour in a piece of calico and kneading the bag in a slow stream of water flowing from a tap, the washings running into a deep vessel, at the bottom of which the starch collects: the sticky matter remaining in the bag is *gluten*.

Gluten is the body which gives tenacity to dough and bread. It seems to be a mixture of vegetable fibrin, vegetable casein, and an albuminous matter termed glutin. These substances and gluten itself are closely allied; each contains about 16 per cent. of nitrogen.

Mix two or three grains of starch with first a little and then more water, and heat the mixture to the boiling-point; mucilage of starch (*Mucilago Amyli*, B. P.) results.

This mucilage or paste is not a true solution; the starch is simply in a condition of excessive hydration; by long boiling, however, a portion becomes dissolved.

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To a portion of the mucilage add a little free iodine; a deep blue colour is produced.

This reaction is a very delicate test of the presence of either iodine or starch. The starch must be in the state of mucilage; hence in testing for starch the substance supposed to contain it must be first boiled with water. The solutions used in the reaction should also be cold, or nearly so, as the blue colour disappears on heating, though it is partially restored on cooling. The iodine reagent may be iodine-water or tincture of iodine. In testing for iodine its occurrence in the free state must be ensured by the addition of a drop, or even less, of chlorine-water. Excess of chlorine must be avoided, or chloride of iodine will be formed, which does not colour starch.

The so-called *iodide of starch* scarcely merits the name of a chemical compound, the state of union of its constituents being but feeble. All substances that attack iodine remove that element from iodide of starch. The alkalies, hydrosulphuric acid, sulphurous acid, and all reducing agents, destroy the blue colour.

All kinds of starch yield this blue colour with iodine, showing their chemical similarity. But physically the granules of starch from different sources differ much in size and appearance when examined by the microscope with or without the aid of polarized light. The granules of potato-starch are large, of rice-starch very small, arrowroot and wheat-starch being intermediate. By polarized light the granules of potato-starch appear as if traversed by a black cross, the wheat-starch granules, as seen in common flour, yielding no such effect. (See the frontispiece plates of the original edition of Pereira's 'Materia Medica.')

Dextrin.—Mix a grain or two of starch with about half a test-tubeful of cold water and a drop or two of sulphuric acid, and boil the mixture for a few minutes; no mucilage is formed, and the liquid, if sufficiently boiled, yields no blue colour with iodine: the starch has become converted into *dextrin*. The same effect is produced if the starch is maintained at a temperature of about 320° F. for a short time. Dextrin is now largely manufactured in this way, and a paste of it used by calico-printers as a vehicle for colours; it is termed *British gum*. The change may also be effected by *diastase*, a peculiar ferment existing in malt. Mix

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two equal quantities of starch with equal amounts of water, adding to one a little ground malt, then heat both slowly to the boiling-point; the mixture without malt thickens to a paste or pudding, that with malt remains thin, its starch having become converted into dextrin.

Diastase is probably gluten in a state of decomposition; it is so named from διάστασις (*diastasis*), separation, in allusion to the separation, or rather alteration, it effects among the constituent atoms of starch.

Malt is simply barley which has been softened by steeping in water, allowed to germinate slightly, and further change then arrested by the application of heat in a kiln. During germination the gluten breaks up and yields diastase; and a portion of this reacting on the starch of the barley converts it into dextrin, and, indeed, carries conversion to the further stage of grape-sugar, as will be explained immediately. The temperature to which the malt is heated is made to vary, so that the sugar of the malt may or may not be partially altered to a dark-brown colouring material; if great, the malt is said to be *high-dried*, and is used in porter-brewing; if low, the product is of lighter colour, and is used for ale. The diastase remaining in malt is still capable of converting a large quantity of starch into dextrin and sugar; hence the makers or distillers of the various spirits operate on a mixture of malted and unmalted grain in preparing liquors for fermentation. The word malt is said to be derived from the Welsh *mall*, soft.

Isomerism.

The composition of dextrin is represented by the same formula as that of starch, namely $C_6H_{10}O_5$; for it has the same percentage composition as starch. There are many other bodies similar in centesimal composition, but dissimilar in properties; such substances are termed *isomeric* (from ἴσος, *isos*, equal, and μέρος, *meros*, part); and their condition is spoken of as one of *isomerism*. There is sometimes good reason for doubling or otherwise multiplying the formula of one of two isomeric bodies. Thus olefiant gas (ethylene), the chief illuminating constituent of coal-gas, is represented by the formula C_2H_4, while amylene, an anæsthetic liquid hydrocarbon, obtained from amylic alcohol, though having the same percentage composition as olefiant gas, is represented by the formula C_5H_{10}; for the latter, when gaseous,

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is about twice and a half as heavy as the former, and must contain, therefore, in equal volumes, twice and a half as many atoms: its formula is, consequently, for this and other reasons, constructed to represent those proportions. This variety of isomerism is termed *polymerism* (from πολὺς, *polus*, many or much, and μέρος, part). An illustration of a second variety is seen in the case of cyanate of ammonium and urea, bodies already alluded to in connexion with cyanic acid. These and several other pairs of chemical substances have dissimilar properties, yet are similar not only in elementary composition and in the centesimal proportion of the elements, but also in the fact that each molecule possesses the same number of atoms. But the reactions of these bodies indicate the probable nature of their construction; and this is shown in their formula by the disposition of the symbols. Thus cyanate of ammonium is represented by the formula NH_4CNO, urea by CH_4N_2O. Such bodies are termed *metameric* (from μετὰ, *meta*, a preposition denoting change, and μέρος), and their condition spoken of as one of *metamerism*. The isomerism of starch and dextrin may be of a polymeric or of a metameric character; but we do not yet know which, and must therefore at present give them identical formulæ. *Cellulose*, or the woody fibre of plants, a substance familiar, in the nearly pure state, under the forms of cotton, wool (*Gossypium*, B. P.), paper, linen, pith, &c. is another substance isomeric, probably polymeric, with starch.

By the action of nitric acid of various strengths on cellulose, two, four, or six atoms of hydrogen are substituted by peroxide of nitrogen (N_2O_4), mono-, di- and trinitrocellulose being formed:—

$$\underset{\text{Cellulose.}}{C_{12}H_{20}O_{10}} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Nitrocellulose.}}{C_{12}\left\{\begin{matrix}H_{18}\\N_2O_4\end{matrix}\right\}O_{10}} + \underset{\text{Water.}}{2H_2O}$$

$$\underset{\text{Cellulose.}}{C_{12}H_{20}O_{10}} + \underset{\text{Nitric acid.}}{4HNO_3} = \underset{\text{Dinitrocellulose.}}{C_{12}\left\{\begin{matrix}H_{16}\\2N_2O_4\end{matrix}\right\}O_{10}} + \underset{\text{Water.}}{4H_2O}$$

$$\underset{\text{Cellulose.}}{C_{12}H_{20}O_{10}} + \underset{\text{Nitric acid.}}{6HNO_3} = \underset{\text{Trinitrocellulose.}}{C_{12}\left\{\begin{matrix}H_{14}\\3N_2O_4\end{matrix}\right\}O_{10}} + \underset{\text{Water.}}{6H_2O}$$

Trinitrocellulose is highly explosive gun-cotton, dinitrocellulose is not sufficiently explosive for use instead of gunpowder, mononitrocellulose is scarcely at all explosive. The first and third

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are insoluble in a mixture of alcohol and ether; the second (*Pyroxylin*, B. P.) is soluble, the solution forming ordinary collodion (*Collodium*, B. P.). Flexible collodion (*Collodium Flexile*, B. P.) is a mixture of collodion, Canada balsam, and castor-oil.

SUGAR.

Formula $C_{12}H_{22}O_{11}$.

Dissolve a grain or two of common cane-sugar in water. To a portion of this solution placed in a test-tube add more water, two or three drops of solution of sulphate of copper, about half its bulk of solution of potash or soda, and heat the mixture to the boiling-point; no obvious change occurs. To another portion of the syrup add a drop of sulphuric acid, and boil for a few minutes, then add the copper solution and alkali, and heat as before; a yellow, red, or yellowish-red precipitate of suboxide of copper (Cu_2O), in a hydrated state, falls.

The above reaction is due to the conversion of the *cane-sugar* ($C_{12}H_{22}O_{11}$) into *grape-sugar* ($C_{12}H_{24}O_{12}$, or $2C_6H_{12}O_6$). The formation of a precipitate immediately, without the action of acid, shows the presence of grape-sugar,—its formation only after ebullition with acid indicating, in the absence of starch or dextrin, cane-sugar.

Cane-sugar or *sucrose* (*Saccharum Purificatum*, B. P.) is a frequent constituent of vegetable juices, but is most plentiful in that of the sugar-cane. Grape-sugar or glucose (from γλυκὺς, *glucūs*, sweet) is often seen in the crystallized state, in dried grapes or raisins and other fruits; it is also the variety of sugar met with in diabetic urine. Both varieties twist a ray of polarized light from left to right, to an extent dependent on the amount of sugar present—a fact easy of application in estimating the amount of sugar in syrups or in diabetic urine.

Ferment two or three grains of sugar by dissolving in a test-tube full of water, adding a little yeast or a piece of the so-called German or dried yeast, and setting the whole aside in a warm place at a temperature of 70° or 75°; carbonic acid gas is evolved,

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and, if the tube be inverted in a small dish containing water, may be collected in the upper part of the tube and subsequently tested: the solution contains alcohol. If the experiment be made on an ounce or two of sugar, the fermented liquid may be distilled, one half being collected, shaken with a little lime to neutralize any acetic acid, and again fractionally distilled; the product is dilute spirit of wine.

Both cane-sugar and grape-sugar yield alcohol by fermentation, the cane-sugar probably always passing into grape-sugar before the production of alcohol commences.

$$\underset{\text{Grape-sugar.}}{C_6H_{12}O_6} = \underset{\text{Alcohol.}}{2C_2H_5HO} + \underset{\text{Carbonic acid gas.}}{2CO_2}$$

Hence the spirit of the various kinds of wine, beer, liqueurs, &c. *Milk-sugar* or *lactose* (*Saccharum Lactis*, B. P.), the sweet principle of the milk of various animals, is not susceptible of alcoholic or vinous fermentation; but it resembles grape-sugar in reducing an alkaline solution of copper with precipitation of suboxide.

To a little solution of grape-sugar add solution of potash or soda, or solution of carbonate of potassium, and warm the mixture; the liquid is darkened in colour from amber to brown, according to the amount of sugar present.

The copper reaction, the fermentation process, and the effect of alkalies form three good tests of the presence of grape-sugar, and, indirectly, of cane-sugar. A piece of merino or other woollen material, previously dipped in a solution of stannic chloride and dried, becomes of a brown or black colour when dipped in a solution of glucose and heated to about 300° F. by holding before a fire.

Boil starch with a little water and a drop of sulphuric acid as for dextrin, but continue the ebullition for several minutes: on testing a portion of the cooled liquid with iodine, and another portion with the alkaline solution of a copper salt as described on the previous page, it will be found that the starch has become

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converted into grape-sugar, or *starch-sugar* as it is sometimes termed. If made on rather a larger scale, the acid may be neutralized by chalk, the mixture filtered, the liquid evaporated to a thick syrup and set aside; in a few days it crystallizes to a granular mass resembling honey.

The sugar in fresh fruits is mainly cane-sugar; but by action of the acid, or possibly of a ferment in the juice, it is gradually converted into *inverted sugar*, a variety only differing from cane-sugar in having an inverted or opposite influence on polarized light, twisting the ray from right to left. Fruit-sugar, as gathered in the form of syrup by bees, is probably a mixture of these two varieties. It is gradually altered to a crystalline or granular mass of grape-sugar, as seen in dried fruits and in solidified honey (*Mel*, B. P.). Honey often contains flocculent matters which cause it to ferment; hence for use in medicine it is directed (*Mel Depuratum*, B. P.) to be clarified by melting and straining while hot through flannel previously moistened with warm water.

Barley-sugar is made by simply heating cane-sugar till it fuses, a change from the crystalline to the uncrystallizable condition occurring. *Treacle* (*Theriaca*, B. P.) chiefly results from the application of too much heat in evaporating the syrups of the sugar-cane; it is a mixture of cane-sugar with uncrystallizable sugar, colouring-matter, &c.

Carefully heat a grain or two of sugar in a test-tube until it blackens; the product is *caramel* or *burnt sugar* (the *Saccharum Ustum* of pharmacy). It is used as a colouring agent for gravies, confectionaries, spirits, &c.

Mannite ($C_6H_{14}O_6$).—Boil manna with alcohol, filter, and set aside; mannite crystallizes out.

Mannite is an alcohol, the radical of which is sexivalent $(C_6H_6)^{vi}6HO$ (Wanklyn). It is closely related to the sugars, glucose becoming mannite by action of nascent hydrogen:—

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Mannite.}}{C_6H_{14}O_6}$$

Indeed glucose itself is probably an alcohol of another radical $(C_6H_6)^{vi}6HO$.

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THE GLUCOSIDES.

The glucosides are certain proximate vegetable principles which, by ebullition with dilute acid or other method of decomposition, take up the elements of water and yield glucose, accompanied by a second substance, which differs in each case according to the body operated on. Ten of the glucosides are of pharmaceutical interest, namely:—Amygdalin, Convolvulin, Digitalin, Elaterin, Guaiacin, Jalapin, Salicin, Santonin, Scammonin. Tannin, or tannic acid, is also a glucoside; it has been described among the acids.

AMYGDALIN ($C_{20}H_{27}NO_{11}$, $3H_2O$).—This is a white crystalline substance, existing in the bitter but not in the sweet almond. It is readily extracted from the cake left when the fixed oil has been expressed from bitter almonds.

Make an emulsion of two or three sweet almonds by bruising and rubbing them with water, and notice that it has no odour of essential oil of bitter almonds; add a grain or two of amygdalin, an odour of essential oil of bitter almonds is at once developed. Bruise two or three bitter almonds and rub with water; the volatile oil is again developed.

The source of the hydride of benzoyl, or essential oil of bitter almonds, in these reactions is the amygdalin, which, under the influence of *synaptase* or *emulsin*, a ferment existing in both bitter and sweet almonds, splits up into the essential oil, hydrocyanic acid, and glucose:—

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Hydride of benzoyl.}}{C_7H_5OH} + \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

As each molecule of amygdalin yields one of hydrocyanic acid, a simple calculation shows that 19 grains will be required to form one grain of real hydrocyanic acid, a quantity equivalent to 50 minims of the dilute hydrocyanic acid of the British Pharmacopœia.

The reaction between synaptase and amygdalin is, of course, applicable as a test of the presence of one by the addition of the other.

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CONVOLVULIN.—See JALAPIN.

DIGITALIN ($C_{27}H_{45}O_{15}$).—This is one, if not the active principle of the Purple Foxglove (*Digitalis*, B. P.). Boil a grain or two of digitalin (*Digitalinum*, B. P.) with dilute sulphuric acid for some time; white flocks of *digitaliretin* ($C_{15}H_{25}O_5$) separate, and glucose may be detected in the liquid by the copper test.

$$\underset{\text{Digitalin.}}{C_{27}H_{45}O_{15}} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Digitaliretin.}}{C_{15}H_{25}O_5} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

Digitalin is very poisonous, soluble in alcohol and acids, its solution in hydrochloric acid being first yellow, but finally green. The officinal process for its preparation consists in dissolving the glucoside out of the digitalis leaf by alcohol, recovering the alcohol by distillation, dissolving the residue in water by the help of a small quantity of acetic acid, removing much of the colour from the solution by animal charcoal, neutralizing most of the acetic acid by ammonia, precipitating the digitalin by tannic acid, with which it forms an insoluble compound; washing the precipitate, rubbing and heating it with spirit and oxide of lead, which removes the acid in the form of insoluble tannate of lead, again decolorizing by animal charcoal, evaporating to dryness, washing out impurities still remaining by ether, and drying the residual digitalin.

ELATERIN ($C_{20}H_{28}O_5$).—Boil elaterium (*Elaterium*, B. P.), a sediment from the juice of the squirting cucumber, in a small quantity of spirit of wine, and filter; fibrous and amylaceous matter, &c., remain insoluble, while elaterin, resin, &c. are dissolved. The filtrate, concentrated and poured into a warm solution of potash, yields, on cooling, crystals of elaterin, resin &c. being retained by the alkali. Boil elaterin in dilute sulphuric acid for an hour or two, filter, and test the clear liquid for glucose; a reddish precipitate of cuprous oxide is obtained, indicating the glucosidic character of elaterin.

Elaterin is the active principle of the so-called elaterium. Good specimens of this drug should yield, according to the British

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Pharmacopœia, not less than 20 per cent. of elaterin by the above process. Elaterium is sometimes adulterated with chalk and other substances.

GUAIACIN.—Resin of guaiacum (*Guaiaci Resina*, B. P.) is probably a mixture of several substances, among which are *Guaiaretinic acid* ($C_{20}H_{28}O_4$) (Hlasiwetz) and *Guaiacin*, a glucoside. On boiling guaiacum resin with dilute sulphuric acid for some time glucose is found in the liquid, a green resinous substance (*guaiaretin*) remaining insoluble (Kosmann). Most oxidizing agents, and even atmospheric air, especially under the influence of certain organic substances, produce blue, then green, and finally a brown colour when brought into contact with an alcoholic solution of guaiacum resin.

These effects are said to be due to three stages of oxidation (Jonas). They may be observed on adding the solution to the inner surface of a paring of raw potato.

JALAPIN ($C_{34}H_{56}O_{16}$) AND CONVOLVULIN ($C_{31}H_{50}O_{16}$).—According to Keyser and Meyer, jalap-resin contains two distinct substances —jalapin, chiefly obtained from Mexican male jalap, and convolvulin, most largely contained in the true jalap; the former is soluble in ether, the latter insoluble. Boil jalap-resin with dilute sulphuric acid for some time and filter; a substance, which is probably a mixture of *jalapinol* ($C_{16}H_{30}O_3$) and *convolvulinol* ($C_{13}H_{24}O_3$), separates; and glucose may be detected in the clear liquid.

$$\underset{\text{Jalapin.}}{C_{34}H_{56}O_{16}} + \underset{\text{Water.}}{5H_2O} = \underset{\text{Jalapinol.}}{C_{16}H_{30}O_3} + \underset{\text{Glucose.}}{3C_6H_{12}O_6}$$

Jalap-resin (*Jalapæ Resina*, B. P.) is obtained by digesting and percolating jalap with spirit of wine, and evaporating the tincture to dryness.

SALICIN ($C_{13}H_{18}O_7$).—This substance is contained in and easily extracted from willow-bark. To a small portion of salicin placed

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on a white plate or dish add a drop of strong sulphuric acid; a deep-red colour is produced.

Boil salicin with dilute sulphuric acid for some time; it is converted into *saligenin* ($C_7H_8O_2$) and glucose.

$$\underset{\text{Salicin.}}{C_{13}H_{18}O_7} + \underset{\text{Water.}}{H_2O} = \underset{\text{Saligenin.}}{C_7H_8O_2} + \underset{\text{Glucose.}}{C_6H_{12}O_6}$$

Test a portion of the solution for grape-sugar by the copper test. To another portion, carefully neutralized, add a persalt of iron; a purplish-blue colour is produced, due to the reaction of the saligenin and the ferric salt.

Heat a mixture of about 1 part of salicin, 1 of red chromate of potassium, $1\frac{1}{2}$ of sulphuric acid, and 20 of water in a test-tube; a fragrant characteristic odour is evolved, due to the formation of hydride of salicyl ($C_7H_5O_2H$), an essential oil identical with that existing in meadow-sweet (*Spirea ulmaria*) and in heliotrope.

$$\underset{\text{Salicin.}}{2C_7H_8O_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Hydride of salicyl.}}{2C_7H_5O_2H} + \underset{\text{Water.}}{2H_2O}$$

SANTONIN ($C_{15}H_{18}O_3$).—This substance is a weak acid, insoluble in ammonia, but forming with lime a soluble salt. From a solution of santonate of lime the santonin is precipitated by acids. Boiled for some time with dilute sulphuric acid it yields 87 per cent. of an insoluble resinous substance (*santoniretin*) and glucose (Kosmann). Santonin is officinal in the British Pharmacopœia. The process for its preparation consists in boiling santonica (the unexpanded flower-heads of an undetermined species of *Artemisia*) with milk of lime (whereby santonate of lime is formed), straining, precipitating the santonin or santonic acid by hydrochloric acid, washing with ammonia to remove resin, dissolving in spirit and digesting with animal charcoal to get rid of colouring-matter, setting the spirituous solution aside to

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deposit crystals of santonin, and purifying by recrystallization (Mialhe).

SCAMMONIN ($C_{32}H_{52}O_{16}$).—Boil resin of scammony (*Scammoniæ Resina*, B. P.) with dilute sulphuric acid for some time; glucose may then be detected in the liquid, a resinous acid termed *scammoniol* ($C_{14}H_{18}O_8$?) being produced at the same time.

ALCOHOL AND ALLIED BODIES.

ALCOHOL.

The formation of alcohol by the fermentation of sugar has already been alluded to (p. 269). The weak spirit concentrated by distillation till it contains 84 per cent. by weight of pure alcohol is an ordinary article of commerce; its specific gravity at 60° is 0·8382. This is ordinary *spirit of wine*, the *Spiritus Rectificatus* of the British Pharmacopœia. The officinal *proof spirit** (*Spiritus Tenuior*, B. P.) contains 49 per cent. by weight of alcohol, and is made by adding 60 volumes of water to 100 volumes of rectified spirit. Obviously, proof spirit may be made by diluting with water rectified spirit of any other strength than that mentioned above—than the "sixty over proof" (60° O.P.), as it is commonly and conveniently termed. Thus one hundred fluid ounces of a spirit of "seventy over proof" may have seventy ounces of water added, or the same quantity of a spirit of "fifty over proof" may have fifty ounces of water added, and so on. The specific gravity of proof spirit at 60° is 0·920.

Alcohol, by quantitative analysis, is found to contain the elements carbon, hydrogen, and oxygen in the following proportions:—

Centesimal composition of Alcohol.

Carbon	52·174
Hydrogen	13·043
Oxygen	34·783
	100·000

* *Proof spirit* is so termed from the fact that in olden times a proof of its strength was afforded by moistening a small quantity of gunpowder and setting light to the spirit; if it fired the powder it was said to be "over proof," if not "under proof." The weakest spirit that would stand this test was what we should now describe as of sp. gr. 920.

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From these numbers a formula is obtained in the usual way. Thus, on dividing these figures by the atomic weights of the respective elements, and reducing the products to the simplest whole numbers, alcohol will be found to contain two atoms of carbon to every six of hydrogen and to every one of oxygen, and its possible or *empirical formula* to be C_2H_6O. But there is good reason to believe that alcohol is the hydrate of a basylous radical *ethyl* (C_2H_5 or Et); hence we derive the *rational formula* C_2H_5HO or EtHO. Alcohol is, then, a body analogous in constitution to hydrate of potassium (KHO); and there are other compounds of ethyl analogous in constitution to ordinary inorganic salts such as those of potassium. The oxide of ethyl (Et_2O) is common ether; the nitrite of ethyl ($EtNO_2$) is the body which, dissolved in spirit of wine, constitutes "sweet spirit of nitre;" the acid sulphate of ethyl ($EtHSO_4$), or sulphethylic or sulphovinic acid, is a liquid met with in the preparation of ether. The iodide (EtI), hydride (EtH), acetate ($Et\bar{A}$), &c. are of considerable chemical interest, but not used in medicine.

Aldehyd (C_2H_4O).—Place together, in a capacious test-tube, spirit of wine, black oxide of manganese, sulphuric acid, and water, and gently warm the mixture; aldehyd (*alcohol dehydrogenatus*), a highly volatile liquid, is immediately formed, and its vapour evolved, recognized by its peculiar somewhat fragrant odour. Adapt a cork and rather long bent tube to the test-tube, and let some of the aldehyd slowly distil over into another test-tube, the condensing-tube being kept as cool as possible. Set the distillate aside for a day or two; the aldehyd will have nearly all disappeared, and acetic acid be found in the tube. Test the exposed liquid by litmus paper; it will be found to have an acid reaction: make it slightly alkaline by a drop or two of solution of carbonate of sodium, then boil to remove any alcohol and aldehyd present, add sulphuric acid, and notice the characteristic odour of the acetic acid evolved.

These experiments will enable the student to understand more fully the process of acetification described in connexion with acetic acid. Pure diluted alcohol is not oxidized by expo-

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sure to air; but in presence of fermentive matter, or vegetable matter undergoing decay or change, it is oxidized first to aldehyd and then to acetic acid.

In the above process the black oxide of manganese and sulphuric acid furnish nascent oxygen:—

$$\underset{\text{Black oxide of manganese.}}{2MnO_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Sulphate of manganese.}}{2MnSO_4} + \underset{\text{Oxygen.}}{O_2} + \underset{\text{Water.}}{2H_2O}$$

One molecule of the nascent oxygen then acts on two molecules of the alcohol, just as the oxygen of the air acts on the alcohol in fermented infusion of malt, beer, wine, &c., giving aldehyd:—

$$\underset{\text{Alcohol.}}{2C_2H_6O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Aldehyd.}}{2C_2H_4O} + \underset{\text{Water.}}{2H_2O}$$

The aldehyd rapidly, even when pure (more rapidly when impure), absorbs oxygen and yields acetic acid:—

$$\underset{\text{Aldehyd.}}{2C_2H_4O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetic acid.}}{2C_2H_4O_2}$$

ETHER.

Formula $C_4H_{10}O$, or $(C_2H_5)_2O$, or Et_2O.

Into a capacious test-tube put a small quantity of spirit of wine and about half its bulk of sulphuric acid, and gently warm the mixture; the vapour of ether, recognized by its odour, is evolved. Adapt a cork and long bent tube to the test-tube and slowly distil over the ether into another test-tube. Half the original quantity of alcohol now placed in the generating-tube will again give ether; and this operation may be repeated many times.

On the large scale, and according to the officinal process (*Æther*, B. P.), the addition of alcohol, instead of being intermitting, is continuous, a tube conveying alcohol from a reservoir into the generating-vessel.

On the addition of sulphuric acid to alcohol in equal volumes,

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one molecule of each react and give a molecule of sulphethylic acid and one of water:—

$$\underset{\text{Alcohol.}}{EtHO} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sulphethylic}\\\text{acid.}}}{EtHSO_4} + \underset{\text{Water.}}{H_2O}$$

More alcohol then gives ether and sulphuric acid by the reaction of one molecule of the alcohol on one of sulphethylic acid:—

$$\underset{\text{Alcohol.}}{EtHO} + \underset{\substack{\text{Sulphethylic}\\\text{acid.}}}{EtHSO_4} = \underset{\text{Ether.}}{Et_2O} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4}$$

The water of the first reaction and the ether of the second distil over, while the sulphuric acid, as fast as liberated, is attacked by alcohol and reconverted into sulphethylic acid.

Pure ether is gaseous at temperatures above 95° F.; hence the condensing-tubes employed in its distillation must be kept as cool as possible. At all ordinary temperatures it rapidly evaporates, absorbing much heat from the surface on which it is placed. A few drops evaporated consecutively from the back of the hand produce great cold; if blown in the form of spray, the cooling effect is so rapid and intense as to produce local anæsthesia. Its vapour is very heavy, more than twice and a half that of air, and in a still atmosphere will flow a considerable distance along a table, floor, &c. before complete diffusion occurs; the vapour is also highly inflammable; hence the importance of keeping candle and other flames at a distance during manipulations with ether.

To the ether obtained in the above operation add a strong solution of chloride of calcium and a little slaked lime; the latter absorbs any sulphurous acid that may have been produced by secondary decompositions, while the former absorbs water; on shaking the mixture and then setting aside for a minute or two, the ether will be found floating on the surface of the solution of chloride of calcium.

This ether, redistilled until the distillate has a sp. gr. not higher than 0·735, is the ether of the British Pharmacopœia. It still contains about 8 per cent. of alcohol. The latter may be removed by shaking the ether with water, setting aside, sepa-

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rating the floating ether and again shaking with water; alcohol is thus washed out. This washed ether containing water (for water and ether are to some extent soluble the one in the other; 50 measures agitated with an equal volume of water are reduced to 45 by an absorption of 10 per cent.) is next placed in a retort with solid chloride of calcium and a little caustic lime, and once more distilled; pure dry ether (*Æther Purus*, B. P.) results. Sp. gr. 0·720.

NITROUS ETHER, OR NITRITE OF ETHYL.

Formula $EtNO_2$.

To a third of a test-tubeful of rectified spirit add about a tenth of its bulk of sulphuric acid, rather more of nitric acid, and some copper wire or turnings, and warm the mixture; as soon as ebullition commences, the vapour of nitrous ether is evolved, recognized by its odour. A long bent tube, kept cool, may be adapted by a perforated cork to the test-tube, and thus a few drops of impure nitrous ether be condensed and collected.

The above process, conducted on a larger scale, with definite quantities of materials, temperature regulated by a thermometer, and a well-cooled condenser, is the officinal (Redwood's) process for the preparation of a concentrated solution of nitrous ether in spirit; diluted with alcohol it forms the "sweet spirit of nitre" (*Spiritus Ætheris Nitrosi*, B. P.) of pharmacy.

Disregarding secondary products, the following equation probably represents the decompositions that occur in the operation:—

$$\underset{\text{Alcohol.}}{EtHO} + \underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Copper.}}{Cu} = \underset{\text{Nitrous ether.}}{EtNO_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Sulphate of copper.}}{CuSO_4}$$

The nitrous radical may be detected by adding sulphate of iron and sulphuric acid to some of the spirit of nitrous ether, a brown or black compound being produced, already explained in connexion with nitric acid.

To some spirit of nitrous ether add twice its bulk of a saturated solution of chloride of calcium and mix the liquids; on

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setting aside, nitrous ether will rise to the surface. If the spirit of nitrous ether be of officinal strength, not less than 2 per cent. of its volume will thus separate, indicating the presence of 10 per cent. of the ether, 8 per cent. still remaining dissolved. A graduated tube is obviously most convenient for this experiment.

CHLOROFORM.

Formula $CHCl_3$.

Should the student have the necessary appliances at hand, a small quantity of this liquid may easily be prepared by the officinal process. One fluid ounce and a half of spirit and 24 of water are placed in a retort or flask of at least a quart capacity; 8 ozs. of chlorinated lime and 4 of slaked lime are added, the vessel connected with a condenser, and the mixture heated until distillation commences, the source of heat then being withdrawn. The condensed liquid should fall into a small flask containing water, at the bottom of which a drachm or so of chloroform will slowly collect.

The hypochlorite of calcium (Ca2ClO), believed to be present in the chlorinated lime (see remarks in connexion with hypochlorous acid), readily yields up oxygen and chlorine to organic substances. Thus the alcohol used in making chloroform, omitting secondary actions, is probably first reduced to aldehyd:—

$$\underset{\text{Alcohol.}}{2C_2H_6O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Aldehyd.}}{2C_2H_4O} + \underset{\text{Water.}}{2H_2O}$$

The action of chlorine on aldehyd then probably gives chloral (*chlor-al*dehyd)—

$$\underset{\text{Aldehyd.}}{C_2H_4O} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Chloral.}}{C_2HCl_3O} + \underset{\text{Hydrochloric acid.}}{3HCl},—$$

chloral and hydrate of calcium giving formate of calcium and chloroform—

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$$\underset{\text{Chloral.}}{2C_2HCl_3O} + \underset{\substack{\text{Hydrate of}\\\text{calcium.}}}{Ca2HO} = \underset{\substack{\text{Formate of}\\\text{calcium.}}}{Ca2CHO_2} + \underset{\text{Chloroform.}}{2CHCl_3}$$

Or, neglecting the probable steps in the process, and regarding only the materials and the products, 4 molecules of alcohol and 8 of hypochlorite of calcium give 2 of chloroform, 3 of formate of calcium, 5 of chloride of calcium, and 8 of water, thus:—

$$\underset{\text{Alcohol.}}{4C_2H_6O} + \underset{\substack{\text{Hypochlorite}\\\text{of calcium.}}}{8CaCl_2O_2} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\substack{\text{Formate of}\\\text{calcium.}}}{3(Ca2CHO_2)} + \underset{\substack{\text{Chloride of}\\\text{calcium.}}}{5CaCl_2} + \underset{\text{Water.}}{8H_2O}$$

The free hydrate of calcium in the generating-vessels is not essential, but is useful in preventing secondary decompositions occurring.

Chloroform may be regarded as the chloride of dichlormethyl; it may be formed from methylic compounds, thus:—

$$\underset{\substack{\text{Methylic}\\\text{alcohol.}}}{2CH_4O} + \underset{\substack{\text{Chlorinated}\\\text{lime.}}}{2(CaCl_2, CaCl_2O_2)} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\substack{\text{Oxychloride of}\\\text{calcium.}}}{CaCl_2 3CaO} + \underset{\text{Water.}}{3H_2O}$$

Chlorine converts it into tetrachloride of carbon:—

$$\underset{\substack{\text{Chloride of}\\\text{methyl.}}}{CH_3Cl} \qquad \underset{\substack{\text{Chloride of}\\\text{di-chlor-methyl.}}}{C\left\{\begin{matrix}H\\Cl_2\end{matrix}\right\}Cl} \qquad \underset{\substack{\text{Chloride of}\\\text{tri-chlor-methyl.}}}{CCl_3Cl} \qquad \text{or} \qquad \underset{\substack{\text{Tetrachloride}\\\text{of carbon.}}}{CCl_4}$$

Chloroform is purified by shaking it with water and then with sulphuric acid, which chars and removes hydrocarbons, but does not affect chloroform. It is freed from any trace of acid by agitation with lime, and from moisture by solid chloride of calcium. Its sp. gr. is 1·49.

Iodide of Ethyl (EtI) may be prepared by mixing amorphous phosphorus with absolute alcohol and then adding iodine.

$$\underset{\text{Alcohol.}}{5EtHO} + \underset{\substack{\text{Iodide of}\\\text{phosphorus.}}}{PI_5} = \underset{\substack{\text{Iodide of}\\\text{ethyl.}}}{5EtI} + \underset{\substack{\text{Phosphoric}\\\text{acid.}}}{H_3PO_4} + \underset{\text{Water.}}{H_2O}$$

Ethyl.—This gaseous radical (Et_2) is obtained on digesting together at about 250° F., in a strong sealed tube, dry freshly granulated zinc with iodide of ethyl (Frankland).

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$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Iodide of ethyl.}}{2EtI} = \underset{\text{Iodide of zinc.}}{ZnI_2} + \underset{\text{Ethyl.}}{Et_2}$$

On cautiously opening the tube the ethyl escapes and may be ignited or collected over water. There remains with the iodide of zinc a body termed by Frankland *zinc-ethyl* ($ZnEt_2$); it is a spontaneously inflammable liquid, but may be easily distilled and otherwise manipulated if a few simple precautions be observed. If water be allowed to flow down the tube the solid compound of iodide of zinc and zinc-ethyl is decomposed, a gas, *hydride of ethyl* (EtH), resulting, which also may be inflamed or collected over water:—

$$ZnEt_2 + 2H_2O = Zn2HO + 2EtH.$$

Other Alcohol Radicals.

What has been stated concerning the chemistry of ethyl and its compounds may be applied to other radicals known to exist, some of the compounds of each of which are of common occurrence. These basylous radicals are closely related to each other, to hydrogen, and to the metals. Starting from hydrogen, their formulæ may be built up by successive additions of CH_2, thus:—

Hydrogen	H
Methyl	CH_3, or Me
Ethyl	C_2H_5, or Et
Propyl (or Trityl)	C_3H_7, or Pr
Butyl (or Tetryl)	C_4H_9, or Bu
Amyl	C_5H_{11}, or Ay
Caproyl (or Hexyl)	C_6H_{11}, or Cp

The above list is an illustration of an *homologous* series (from ὁμὸς, *omos*, the same, and λόγος, *logos*, description) of compounds. It will be observed that the relation of the number of hydrogen atoms to carbon is twice as many with one added; hence the series is often termed the C_nH_{2n+1} series (n = any number). The oxides of these radicals are known as *ethers*, their hydrates *alcohols*, their compounds with the acetic and similar acidulous radicals *ethereal salts*, &c. Each alcohol also yields a body corresponding to the aldehyd of spirit of wine, the class being

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termed *aldehyds*; each also yields an acid corresponding with acetic acid. Each of these classes constitutes an homologous series. Or, taking the hydride, oxide, hydrate, acid, &c. of any single radical we get a *heterologous* (ἕτερος, *eteros*, another) series of compounds. Hydride of methyl (MeH) is ordinary *marsh-gas* or *fire-damp*; *formic acid*, the acid of the methyl series; *butyric acid*, the acid of the butyl series; *valerianic acid*, the acid of the amyl series.

METHYLIC ALCOHOL.

Methylic Alcohol (CH_3HO, or MeHO), Wood Spirit, or Pyroxylic Spirit, is a product of the destructive distillation of wood. Spirit of wine containing 10 per cent. of wood-spirit constitutes ordinary *methylated spirit*, a spirit issued duty-free, for the use of manufacturers, the methylic alcohol not interfering with technical applications. From its nauseous taste and odour, however, it cannot take the place of gin, brandy, &c.; hence, while industry is benefited, intemperance is discouraged and the revenue not injured.

Detection of Methylic Alcohol in presence of Ethylic Alcohol.—Three or four methods have been proposed for the detection of methylated spirit in tinctures &c.; that open to least objection is by J. T. Miller. For the application of the test to tinctures and similar spirituous mixtures, some of the spirit is separated by distilling off a drachm or so from about half an ounce of the liquid placed in a small flask or test-tube, having a long bent tube attached. Into a similar apparatus put 30 grains of powdered red chromate of potassium, half an ounce of water, 25 minims of strong sulphuric acid, and 30 or 40 minims of the spirit to be tested. Set the mixture aside for a quarter of an hour and then distil half a fluid ounce. Place the distillate in a small dish, add a very slight excess of carbonate of sodium, boil down to about a quarter of an ounce, add enough acetic acid to impart a distinct but feeble acid reaction, pour the liquid into a test-tube, add a grain of nitrate of silver dissolved in about 30 drops of water, and heat gently for a couple of minutes. If the

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liquid then merely darkens a little, but continues quite translucent, the spirit is free from methylic alcohol; but if a copious precipitate of dark-brown or black metallic silver separates, and the tube, after being rinsed out and filled with clean water, has a distinct film of silver, which appears brown by transmitted light (best seen by holding it against white paper), the spirit is methylated.

This test depends for its action on the reducing-powers of formic acid. In the above operation the ethylic alcohol becomes oxidized to acetic acid, which does not reduce silver salts, a minute quantity only of formic acid being produced, while the methylic alcohol yields formic acid in a comparatively large quantity. Aldehyd, which is also a reducing agent, is simultaneously produced, but removed in the subsequent ebullition with carbonate of sodium.

AMYLIC ALCOHOL.

Amylic Alcohol (*Alcohol Amylicum*, B. P.) ($C_5H_{11}HO$, or AyHO) is a constant accompaniment of ethylic or common alcohol (C_2H_5HO, or EtHO) when the latter is prepared from sugar which has been derived from starch; hence the name, from *amylum* starch. The sugar of potato-starch yields a considerable quantity; hence the alcohol is often called *potato-oil*. It is also termed *fousel-oil*, or *fusel-oil* (from φύω, *phuō*, to produce), in allusion to the circumstance that the supposed oil is not simply educed from a substance already containing it, as is usually the case with oils, but is actually produced during the operation. It was described as oil probably because it resembled oil in not readily mixing with water; but it is soluble to some extent in water, and is a true spirit, homologous with spirit of wine. See also Valerianic Acid.

Acetate of Amyl ($C_5H_{11}C_2H_3O_2$, or Ay$\bar{A}$). To a small quantity of amylic alcohol in a test-tube add some acetate of potassium and a little sulphuric acid, and warm the mixture; the vapour of acetate of amyl is evolved, recognized by its odour, which is that of the jargonelle pear. If a condensing-tube be

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attached, the essence may be distilled over, washed by agitation with water to free it from alcohol, and separated by a pipette.

$K\bar{A}$	+	AyHO	+	H_2SO_4	=	$Ay\bar{A}$	+	$KHSO_4$	+	H_2O
Acetate of potassium.		Amylic alcohol.		Sulphuric acid.		Acetate of amyl.		Acid sulphate of potassium.		Water.

This compound, prepared with the proper equivalent proportions of constituents as indicated by the above equation, is largely manufactured for use as a flavouring agent by confectioners. Valerianate of amyl ($C_5H_{11}C_5H_9O_2$) is similarly used under the name of apple-oil. Butyrate of ethyl ($C_2H_5C_4H_7O_2$) closely resembles the odour and flavour of the pine-apple; œnanthylate of ethyl ($C_2H_5C_7H_{13}O_2$) recalls greengage; pelargonate of ethyl ($C_2H_5C_9H_{17}O_2$) quince; suberate of ethyl ($Et_2C_8H_{12}O_4$) mulberry; sebacate of ethyl ($Et_2C_{10}H_{16}O_4$) melon. Hydride of salicyl ($C_7H_5O_2H$), or salicylous acid, is the essential oil of meadow-sweet (*Spirea Ulmaria*), and may be prepared artificially by the oxidation of salicin (*vide* p. 274). Salicylate of methyl ($CH_3C_7H_5O_3$), or gaultheric acid, is the essential oil of wintergreen (*Gaultheria procumbens*), and may also be prepared artificially from salicin. By mixing these ethereal salts with each other and with essential oils in various proportions, the odour and flavour of nearly every fruit may be tolerably successfully imitated.

What has been stated regarding radicals having the general formula C_nH_{2n+1} and their salts, may be applied to the radicals of other series. The series C_nH_{2n-7} includes *phenyl* (C_6H_5), the hydride of which (C_6H_5H, or PhH) is common *benzol*, a colourless volatile liquid obtained from coal-tar. Benzol is a powerful solvent of grease, and under the name of *Benzine-Collas* was introduced by M. Collas, in 1848, for cleansing stuffs. By the action of strong nitric acid benzol yields *nitrobenzol* ($C_6H_5(NO_2)$), a liquid termed, from its odour, *artificial oil of bitter almonds*, or *essence of mirbane*. The odour of this essence, however, is not exactly that of essential oil of almonds, and its composition is different; so that it is not truly an artificial volatile oil, the natural oil (C_7H_5OH) being a hydride of the negative radical benzoyl, a radical derived from the next higher homologue of phenyl by displacement of hydrogen by oxygen. The hydrate of phenyl (C_6H_5HO), or *phenic alcohol*, or *phenol*, is the *phenic acid* or *carbolic acid* of commerce (*Acidum Carbolicum*, B. P.),

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a colourless crystalline substance, obtained from coal-tar oil by fractional distillation and subsequent purification. It is only slightly soluble in water, but readily dissolved by alcohol, ether, and glycerin (*Glycerinum Acidi Carbolici*, B. P.). In odour and taste it resembles creasote ($C_8H_{10}O$?), a wood-tar-product for which carbolic acid is often substituted. Carbolic acid is a powerful *antiseptic* (*ἀντὶ, anti*, against, and *σήπω, sepo*, to putrefy). Both carbolic acid and benzol are secondary products, obtained in the manufacture of coal-gas; hence, indeed, the word *phenic* and thence *phenyl* (from *φαίνω, phainō*, I light, in allusion to the use of coal-gas). *Aniline*, or *phenylamine*, is a product of the action of nascent hydrogen on nitrobenzol—

$$\underset{\text{Nitrobenzol.}}{C_6H_5NO_2} + \underset{\text{Hydrogen.}}{3H_2} = N\left\{\begin{matrix} C_6H_5 \\ H \\ H \end{matrix}\right. + 2H_2O,—$$

the substance whence, by oxidation &c., aniline-red (magenta), -orange, -yellow, -green, -blue, -violet (mauve), and -black are produced. Tri-nitro-carbolic acid ($C_6H_3(NO_2)_3O$) is the yellow dye known as *picric acid*. In the series C_nH_{2n-1} we have the univalent radical *allyl* (C_3H_5), whose sulphide ($(C_3H_5)_2S$) is *essential oil of garlic*, and sulphocyanide (C_3H_5CyS) the *essential oil of mustard*. Allyl compounds are also met with in several other liliaceous and cruciferous plants. In the C_nH_{2n} series occurs *ethylene* or *olefiant gas* (C_2H_4), a bivalent radical, the alcohol of which is *glycol* ($C_2H_4 2HO$); and in the C_nH_{2n-1} the trivalent hypothetical radical *glyceryl* (C_3H_5), the hydrate of which ($C_3H_5 3HO$) is glycerin (p. 125).

ALBUMEN.

Agitate, thoroughly, white of egg (*Albumen Ovi*, B. P.) with water and strain or pour off the liquid from the flocculent membranous insoluble matter.

Test.—Heat a portion of the solution to the boiling-point; the albumen becomes insoluble, separating in clots or coagula of characteristic appearance.

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Other Reactions.—Add to small quantities of aqueous solution of albumen solutions of corrosive sublimate, nitrate of silver, sulphate of copper, acetate of lead, alum, perchloride of tin, &c.; the various salts not only coagulate but form insoluble compounds with albumen. Hence the value of an egg as a temporary antidote in cases of poisoning by many metallic salts, its administration retarding the absorption of the poison until the stomach-pump or other measures can be applied. Sulphuric, nitric, and hydrochloric acids precipitate albumen; the coagulum is slowly redissolved by aid of heat, a brown, yellow, or purplish-red colour being produced. Neither acetic, tartaric, nor organic acids generally, except gallo-tannic, coagulate albumen. Alkalies prevent the precipitation of albumen.

Albumen is met with in large quantity in the serum of blood, in smaller quantity in chyle and lymph, and in the brain, kidneys, liver, muscles, and pancreas. It is not a normal constituent of saliva, gastric juice, bile, or mucus, but occurs in those secretions during inflammation. It is found in the urine and fæces only under certain diseased states of the system.

The cause of the coagulation of albumen by heat &c. cannot at present be explained.

Albumen has not yet been obtained sufficiently pure to admit of its composition being expressed by a trustworthy formula; Gerhardt regarded it as a sodium compound ($HNaC_{72}H_{110}N_{18}SO_{22},H_2O$).

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TOXICOLOGICAL OPERATIONS.

In cases of murder, suicide, and accidental poisoning, the substances presented to the chemical analyst for examination are usually articles of food, medicines, vomited matters, or the liver, kidney, stomach and contents, removed in course of post-mortem examination. In these cases some special operations are necessary before the poison can be isolated in a state of sufficient purity for the application of the usual tests; for in most instances the large quantity of animal and vegetable, or, in one word, organic matter present prevents or masks the characteristic reactions on which the tests are founded. These operations will now be described*; they form the chemical part of the subject of Toxicology (*τοξικὸν, toxicon*, poison, and *λόγος, logos*, discourse). Substances occurring in the form of an apparently definite salt or unmixed with organic matter need no special treatment, they are analyzed by the ordinary methods already given, attention being restricted, of course, to poisonous compounds only.

EXAMINATION OF AN ORGANIC MIXTURE SUSPECTED TO CONTAIN MERCURY, ARSENICUM, ANTIMONY, LEAD, OR COPPER, SULPHURIC ACID, NITRIC ACID, HYDROCHLORIC ACID, OXALIC ACID, OR HYDROCYANIC ACID, STRYCHNINE OR MORPHINE.

Odour, Appearance, Taste.—Smell the mixture with the view of ascertaining the presence or absence of any notable quantity of free hydrocyanic acid. Look carefully for any small solid particles, such as arsenic, corrosive sublimate, verdigris, &c., and for any appearance which may be regarded as abnormal, any character unusual to the coffee, tea, beer, medicine, vomit, coats of stomach, kidney, liver, or other organ, tissue, or solid matter under examination. If liquid or semifluid, taste the mixture,

* Materials for these experiments are readily obtained for educational purposes by dissolving the poison in infusions of tea, coffee, porter, or in water to which some mucilage of starch or linseed-meal, pieces of bread, potato, fat, &c. have been added.

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or add to a small portion some solution of carbonate of sodium with the view of ascertaining by excessive sourness or strong effervescence the presence of any large poisonous quantity of sulphuric, nitric, or hydrochloric acids.

If this preliminary examination does not indicate the method to be pursued, proceed as follows, treating a portion, not more than one-fourth, of the mixture for the poisonous metals, another for the acids, and a third for alkaloids, reserving the remainder for any special experiments which may suggest themselves in the course of the analysis.

Examination for Mercury, Arsenicum, Antimony, Lead, Copper.

If a liquid, acidulate with hydrochloric acid and boil for a short time. If solid or semisolid, cut up the matter into small pieces, add enough water to form a fluid mixture, with from one-fourth to one-tenth of its bulk of hydrochloric acid, and boil until, from partial aggregation, solution, &c. of the solid matter, filtration can be easily effected.

Heat a portion of the clear liquid with a thin piece of bright copper or copper gauze, about an inch long and a quarter of an inch broad, for about ten or twenty minutes; metallic mercury, arsenicum, or antimony will be deposited on the copper, darkening it considerably in colour. Pour off the liquid from the copper, carefully rinse the latter with a little cold water, dry the piece of metal by holding it over or near a flame (using fingers, not tongs, or it may become sufficiently hot for loss of mercury or arsenicum to occur by volatilization), introduce it into a narrow test-tube or piece of glass tubing closed at one end, and heat the bottom of the tube in a flame, holding it horizontally, that the upper part of the tube may be kept cool, and closing the mouth of the tube with the finger to prevent escape of vapour. Under these circumstances any *Mercury* will volatilize from the copper and condense on the cool part of the tube in a ring or patch of

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white sublimate, readily aggregating into visible globules on being pressed by the side of a thin glass rod inserted into the tube; *Arsenicum* will volatilize from the copper, and, absorbing oxygen from the air in the tube, condense on the cool part of the glass in a ring or patch of white sublimate of arsenic, not running into globules when rubbed, but occurring in small crystals, the characteristic octahedral form of which is readily seen by aid of a good hand lens, or the low power of a microscope; *Antimony* volatilizes from the copper, if strongly heated, and, absorbing oxygen, immediately condenses as a slight white deposit close to the metal.

Nothing short of the production of globules should be accepted as evidence of the presence of mercury. It will usually have existed as corrosive sublimate.

To confirm indications of the presence of arsenicum, a portion of the acid liquid may be subjected to the hydrogen tests; or the tube containing the white crystalline arsenic may be broken, and the part on which the sublimate occurs boiled for some time in water, and the hydrosulphuric-acid, ammonio-nitrate-of-silver, or ammonio-sulphate-of-copper test applied to the aqueous solution.

For antimony, a portion of the acid liquid must always be introduced into the hydrogen-apparatus with the usual precautions. (*Vide* p. 101.)

For *lead* and *copper*, pass hydrosulphuric acid gas through the clear acid liquid for some time, warming the liquid if no precipitate is produced, or diluting and partially neutralizing the acid by ammonia if much acid has been added. Collect on a filter any black precipitate that may have formed; wash, dissolve in a few drops of aqua regia, dilute, and apply the tests of ammonia for copper, sulphuric acid for lead, and any other of the ordinary reagents.

Copper may often be at once detected in a small quantity of acidulated liquid by immersing the point of a penknife or a piece

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of bright iron wire,—a deposit of copper in its characteristic colour quickly or slowly appearing, according to the amount present.

Examination for Mineral Acids, Oxalic Acid, or Hydrocyanic Acid.

To detect sulphuric, nitric, or hydrochloric acids in any liquid containing organic matter, dilute with water and apply to small portions the usual tests for each acid, disregarding indications of small quantities.

Excessive sourness, copious evolution of carbonic acid gas on the addition of carbonate of sodium, and abundant evidence of acid on applying the various tests to small portions of the fluid presented for analysis, collectively form sufficient evidence of the occurrence of a poisonous amount of either of the three common mineral acids. Small quantities of the sulphuric, nitric, and hydrochloric radicals occurring as metallic salts or acids, are common normal constituents of food, hence the direction to disregard insignificant indications. If the fluid under examination is a vomit or the contents of a stomach, and an antidote has been administered, free acid will not be found, but, instead, a large amount of some particular salt.

For oxalic acid, filter or strain a portion of the liquid, if not already clear, and add solution of acetate of lead so long as a precipitate occurs; collect the precipitate, which is partly oxalate of lead, on a filter, wash, transfer it to a test-tube or test-glass, add a little water, and pass hydrosulphuric gas through the mixture for a short time; the lead is thus converted into the insoluble form of sulphide, while oxalic acid is set free in the solution. Filter, boil to get rid of hydrosulphuric gas, and apply the usual tests for oxalic acid (see p. 207) to the clear filtrate.

For hydrocyanic acid, the three chief tests may be applied at once to the liquid or semiliquid organic mixture, whether it has an odour of hydrocyanic acid or not. First:—half fill a small porcelain crucible with the mixture, add eight or ten drops

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of strong sulphuric acid, stir gently with a glass rod, and invert over the mouth of the crucible a watch-glass moistened with a small drop of solution of nitrate of silver; a white film on the silver solution is probably cyanide of silver, formed by action of the gaseous hydrocyanic acid on the nitrate of silver. Second:—prepare a small quantity of the organic mixture as before, slightly moistening the centre of the watch-glass with solution of potash; here again the heat, generated by the action of the strong acid, is sufficient to volatilize some of the hydrocyanic acid, which, reacting on the potash, forms cyanide of potassium. On removing the watch-glass and dropping into it successively solution of a ferrous salt, a ferric salt, and hydrochloric acid, flocks of prussian blue are produced if hydrocyanic acid be present. Third:—proceed as before, moistening the watch-glass with sulphydrate of ammonium; after exposure to the hydrocyanic gas for five or ten minutes, add a drop of solution of ammonia, evaporate to dryness at a low temperature, and add a drop of solution of perchloride of iron; a blood-red colour, due to sulphocyanide of iron, is produced if cyanogen be present.

If the above reactions are not well marked, the organic mixture may be carefully and slowly distilled in a small retort, the neck of which passes into a bottle and dips into a little water at the bottom of the bottle, and the reagents then applied to separate portions of the distillate.

The examination of organic mixtures for hydrocyanic acid must be made without delay, as the poison soon begins to decompose, and in a day or two is usually destroyed.

Examination for Strychnine and Morphine.

Strychnine.—If solid or semisolid, digest the matter with water and about ten per cent. of hydrochloric acid till fluid, filter, evaporate to dryness over a water-bath. If the organic mixture is already liquid, it is simply acidulated with hydrochloric acid and evaporated to dryness. The acid residue is now

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treated with spirit of wine as long as anything is dissolved, the filtered tincture evaporated to dryness over the water-bath, and the residue digested in water and filtered. This slightly acid aqueous solution must now be rendered alkaline by ammonia, and well shaken in a bottle or long tube with about half an ounce of chloroform, and set by till the chloroform has subsided. The chloroform (which contains the strychnine) is then removed by a pipette, the presence of any aqueous liquid being carefully avoided, and evaporated to dryness in a small basin over a water-bath, the residue moistened with concentrated sulphuric acid, and the basin kept over the water-bath for several hours. (It is highly important that the sulphuric acid used in this operation should be free from nitrous compounds. Test the acid, therefore, by adding powdered sulphate of iron, which becomes pink if nitrous bodies are present. If these are found, the acid should be purified by strongly heating with sulphate of ammonium, seventy or eighty grains to a pint.) The charred mass is then treated with water, filtered, excess of ammonia added, the filtrate shaken with about a quarter of an ounce of chloroform, the mixture set aside for the chloroform to separate, and the chloroform again removed. If on evaporating a small portion of this chloroform solution to dryness, adding a drop of sulphuric acid to the residue, and warming, any darkening in colour or charring takes place, the strychnine is not sufficiently pure for chemical detection; in that case the rest of the chloroform must be removed by evaporation, and the residue redigested in warm sulphuric acid for two or three hours. Dilution, neutralization of acid by ammonia, and agitation with chloroform is again practised, and the residue of a small portion of the chloroform solution once more tested with sulphuric acid. If charring still occurs, the treatment must be repeated a third time. Finally a part of the chloroform solution is taken up by a pipette and drop after drop evaporated on one spot of a porcelain crucible-lid until a fairly

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distinct dry residue is obtained. A drop of sulphuric acid is placed on the spot, another drop placed near, a minute fragment of red chromate of potassium placed in the second drop, and when the acid has become tinged with the chromate, one drop drawn across the other; the characteristic evanescent purple colour is then seen if strychnine be present. Other tests (*vide* p. 259) may be applied to similar spots.

This is Girdwood and Rogers's method for the detection of strychnine when mixed with organic matter. It is tedious but trustworthy, and, though apparently complicated, very simple in principle. Strychnine is soluble in acidulated water or alcohol, or in chloroform, readily removed from an alkaline liquid by agitation with chloroform, and not charred or otherwise attacked when heated to 212° F. with sulphuric acid. Much of the organic matter of the food is insoluble in water; of that soluble in water, much is insoluble in alcohol; and of that soluble in both menstrua, all is charred and destroyed by warm sulphuric acid in a shorter or longer time.

Morphine, and the Meconic Acid with which it is associated in Opium.—To the liquid or the semifluid mixture warmed for some time with a small quantity of acetic acid, filtered, and concentrated if necessary, add solution of acetate of lead until no further precipitate is produced. Filter and examine the precipitate for meconic acid, reserving the filtrate for the detection of morphine. Wash the precipitate (meconate of lead &c.) with water, place it in a test-tube or test-glass with a small quantity of water, pass hydrosulphuric acid gas through the mixture for a short time, filter, slightly warm in a small basin, well stirring to promote removal of excess of the gas, and add a drop or two of solution of perchloride of iron; a red colour, due to the formation of meconate of iron, is produced if meconic acid is present. This colour is not destroyed on boiling the liquid, as is the case with the somewhat similarly coloured ferric acetate, nor is it

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bleached by solution of corrosive sublimate, thus distinguishing it from ferric sulphocyanate.

The solution from which meconic acid has been removed by acetate of lead is evaporated to a small bulk over a water-bath, excess of carbonate of potassium added, and evaporation continued to dryness. The residue is then treated with alcohol, which dissolves the morphine. The alcoholic solution evaporated to dryness may leave the morphine sufficiently pure for the application of the usual tests (*vide* page 254) to small portions of the residue. If no reaction is obtained, add a drop of sulphuric acid and a little water to the residue and shake with ether, in which the salt of morphine is insoluble. The treatment with ether may be repeated until nothing more is removed, the acid aqueous liquid saturated with carbonate of potassium, the mixture evaporated to dryness, the residue digested in alcohol, filtered, and portions of the alcoholic liquid evaporated to obtain spots of morphine for the application of the ordinary tests.

The examination for morphine must be conducted with great care, and with as large a quantity of material as can be spared; for its isolation from other organic matter is an operation of considerable difficulty, especially when only a minute proportion of alkaloid is present. Fortunately the detection of meconic acid does not include similar difficulties; and as its reactions are quite characteristic, its presence is held to be strong evidence of the existence of opium in an organic mixture.

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EXAMINATION OF MORBID URINE AND CALCULI.

The various products of the natural and continuous decay of animal tissue and the refuse matter of food are eliminated from the system chiefly as fæces, urine, and expired air. Air exhaled from the lungs carries off from the blood much carbon (about 8 ounces in 24 hours) in the form of carbonic acid gas, and some aqueous vapour—the latter, together with a small amount of oily matter, also escaping by the skin. Directing the breath to a cold surface renders moisture evident; and breathing through a tube into lime-water demonstrates the presence of a considerable quantity of carbonic acid gas. The fæces consist mainly of the insoluble *débris* of the system, the soluble matters and water forming the urine. These excretions vary considerably, according to the food and general habits of the individual and external temperature. But in disease the variations become excessive; their detection by the medical practitioner, or by the pharmaceutist is therefore a matter of importance.

A complete analysis of fæces, urine, or expired air cannot be performed in the present state of our knowledge. Nor can any analysis of fæces or air be made with sufficient ease and rapidity to be practically available in medical diagnosis. But with regard to urine, certain abnormal substances and abnormal quantities of normal constituents may be chemically detected in the course of a few minutes by any one having already some knowledge of chemical manipulation.

Examination of Morbid Urine for Albumen, Sugar, and excess of Urea; and Urinary Sediment for Urates (or Lithates), Phosphates, Oxalate of Calcium, and Uric Acid.

Albumen.—To detect albumen, acidulate a portion of the clear urine in a test-tube with a few drops of acetic acid (to keep phosphates in solution) and boil; flocks or coagula will separate if albumen be present.

This experiment should first be made on normal urine containing a drop or two of solution of white of egg. A coagulum

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of pure albumen is white, greenish if bile-pigment is present, and brownish-red if the urine contains blood. The influence of acids and alkalies on the precipitation of albumen is noticed on page 287.

The occurrence of albumen in the urine may be temporary and of but little importance; or it may indicate the existence of a serious affection, known as Bright's disease.

Sugar.—To a portion of the clear urine in a test-tube add a few drops of solution of sulphate of copper, and then pour in solution of potash or soda until the precipitate first formed is redissolved; slowly heat the solution to near the boiling-point: a yellow, yellowish-red, or red precipitate (cuprous oxide) is formed if sugar be present.

This experiment should first be made on urine containing a drop or two of solution of grape-sugar. The hydrate of copper first precipitated by the alkali is insoluble in excess of pure potash or soda, but readily dissolves if organic matter, especially sugar, be present.

Other tests may be applied if necessary (*vide* page 268).

Excess of Urea.—Nearly one half of the solid matter in the urine is urea. Its proportion varies considerably, but 1½ per cent. may be regarded as an average amount. Concentrate urine slightly by evaporation in a small dish, pour the liquid into a test-tube, set the tube aside till cold, or cool it by letting cold water run over the outside, add an equal bulk of strong nitric acid and again set aside; scaly crystals of nitrate of urea are deposited more or less quickly.

With regard to the amount of urea in urine, it is impossible to sharply define excess or deficiency. If nitric acid gives crystals without concentration, excess is certainly present. A rough estimate may be formed by mixing a few drops of the urine and acid on a piece of glass and setting aside; the time which elapses before crystals form is an indication of the quantity in the specimen. The time will vary according to the temperature and state of moisture of the atmosphere, but with care some useful comparative results may in this way be obtained.

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The empirical formula of urea is CH_4N_2O. Its rational formula may be thus written:— $\left.\begin{matrix}(CO)'' \\ H_2 \\ H_2\end{matrix}\right\} N_2$; that is, it may be regarded as one of the organic bases already referred to, a primary diamine, in which the bivalent radical CO occupies the place of H_2. The other atoms of hydrogen may be displaced by various radicals, and many *compound ureas* be thus obtained.

Urinary Sediments.

Warm the sediment with the supernatant urine and filter:—

<table>
<tr>
<td colspan="2">Insoluble.
Phosphates, calcic oxalate, and free uric acid.
Warm with acetic acid and filter:—</td>
<td>Soluble.
Urates — of ammonium, calcium, or sodium, chiefly the latter.
They are redeposited as the liquid cools, and if sufficient in quantity may be further examined for ammonium, calcium, sodium, and the uric radical by the appropriate tests.</td>
</tr>
<tr>
<td>Insoluble.
Calcic oxalate and uric acid.
Warm with hydrochloric acid, filter:—</td>
<td>Soluble.
Phosphates.
Add ammonia, white ppt. = calcic phosphate, ammonio-magnesian phosphate, or both.</td>
<td></td>
</tr>
<tr>
<td>Insoluble.
Uric acid.
Apply murexid test.</td>
<td>Soluble.
Calcic oxalate.
May be reprecipitated by ammonia.</td>
<td></td>
</tr>
</table>

Urinary deposits are seldom of a complex character; the action of heat and acetic and hydrochloric acids generally at once indicates the character of the deposit, rendering filtration and precipitation unnecessary.

The urates are often of a pink or red colour, owing to the presence of a pigment termed *purpurine*, hence the common name of *red gravel* for such deposits. Purpurine is soluble in alcohol, and may be removed by digesting a red deposit in that solvent. It is seldom necessary to determine whether the urate be that of ammonium, calcium, or sodium (see also Uric Acid, page 233).

The calcic phosphate and the ammonio-magnesian phosphate are usually both present in a phosphatic deposit, the magnesium

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salt forming the larger proportion. They may, if necessary, and if sufficient in quantity, be separated by collecting on a filter, washing, and boiling with solution of carbonate of sodium. The carbonates of calcium and magnesium thus formed are collected on a filter, washed, dissolved in a drop or two of hydrochloric acid, chloride of ammonium, ammonia, and carbonate of ammonium added, the mixture boiled and filtered; any calcium originally present will then remain insoluble as carbonate of calcium, while any magnesium will be reprecipitated from the filtrate as ammonio-magnesian phosphate on the addition of phosphate of sodium, the mixture being also well stirred.——The chief portion of excreted phosphates is carried off by the fæces, that remaining in the urine being kept in solution by the influence of acid phosphate of sodium and, frequently, lactic acid.——Occasionally, an hour or two after a hearty meal, the urine becomes sufficiently alkaline for the phosphates to be deposited, and the urine when passed is turbid from their presence.——The ammoniacal constituent of the magnesium salt does not occur normally, but is produced from urea as soon as urine becomes alkaline.

Calcic oxalate is seldom met with in excessive amounts, but very often in small quantities mixed with phosphates.

Free uric acid is in most cases distinctly crystalline, and nearly always of a yellow, red, or brown colour.

Other deposits than the foregoing are occasionally observed. Thus *hippuric acid* ($HC_9H_8NO_3$), a normal constituent of human urine, and largely contained in the urine of herbivorous animals, is sometimes found associated with uric acid in urinary sediment, especially in that of patients whose medicine contains benzoic acid. Its appearance, as observed by aid of the microscope, is characteristic — namely, slender four-sided prisms, having pointed ends. *Cystin* ($C_3H_7NSO_2$) (from κύστις, *kustis*, a bladder, in allusion to its origin), rarely occurs as a deposit in urine. It is not soluble in warmed urine or dilute acetic acid, and scarcely in dilute hydrochloric acid, hence would be met with in testing for free uric acid. It is very soluble in ammonia, recrystallizing from a drop of the solution placed on a piece of glass in characteristic microscopic six-sided plates. *Organized sediments* may be due to the corpuscles of pus, mucus, or blood, fat-globules, spermatozoa, cylindrical casts of the tubes of the kidneys, epithelial cells from the walls of the bladder, or foreign matters, such as fibres of wool, cotton, &c.; these are best recognized by the microscope.

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Microscopic Examination of Urinary Sediments.

Urine containing insoluble matter is usually more or less opaque. For microscopic examination, a few ounces should be set aside in a conical test-glass for an hour or two, the clear supernatant urine poured off from the sediment as far as possible, a small drop of the residue placed on a slip of glass and covered with a piece of thin glass, and examined under the microscope with different magnifying-powers.

The respective appearances of the various amorphous, crystalline, and organized matters are given in the Frontispiece, the figures of which were drawn from natural specimens in the collections of St. Bartholomew's Hospital, H. B. Brady, F.L.S., Dr. Sedgwick, Mr. Stoddart, Mr. Waddington, and the author.

Uric Acid occurs in many forms, most of which are given in the first Plate. Flat, more or less oval crystals, sometimes attached to each other, their outline then resembling an 8, a cross, a star, &c., are common. Single and grouped quadratic prisms, aigrettes, spiculæ, and crystals resembling dumbbells are met with. From acidulated urine square crystals, two opposite sides smooth and two jagged, are generally deposited. A drop of solution of potash placed on the glass slip will dissolve a deposit of uric acid, a drop of hydrochloric acid reprecipitating it in minute but characteristic crystals.

Cystin is very rarely met with as a urinary deposit; that from which the figure on Plate I. was taken was found in the urine of a patient at St. Bartholomew's Hospital, and was given to the author by Mr. F. Wood. Lamellæ of cystin always assume an hexagonal character, but the angles are sometimes ill defined and the plates superposed; in the latter case, a drop of solution of ammonia placed on the glass at once dissolves the deposit, well-marked six-sided crystals appearing as the drop dries up.

Triple Phosphate (phosphate of magnesium and ammonium) is deposited as soon as urine becomes alkaline, the ammoniacal constituent being furnished by the decomposition of urea. It occurs in large prismatic crystals, forming a beautiful object when viewed by polarized light,—sometimes also in ragged stellate crystals, resembling those of snow.

Amorphous deposits are either *earthy phosphates* (a mixture of phosphates of magnesium and calcium) or *urates* (of calcium, magnesium, ammonium, potassium, or sodium—chiefly the latter). Place a drop of acetic acid near the sediment on the glass slip and

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watch its effect under the microscope; phosphates will dissolve, while urates will gradually assume characteristic forms of uric acid.

Urates of Sodium and Magnesium, though generally amorphous, occasionally take a crystalline form—bundles or tufts of small needles—as shown in the Plate.

Calcic Oxalate generally occurs in octahedra, requiring high magnifying-power for their detection. The crystals are easily overlooked if other matters are present, but are more distinctly seen after phosphates have been removed by acetic acid. In certain aspects the smaller crystals look like square plates traversed by a cross. A dumbbell-form of this deposit is also sometimes seen, resembling certain forms of uric acid and the coalescing spherules of a much rarer sediment—calcic carbonate. Oxalate of calcium is insoluble in acetic but soluble in hydrochloric acid.

Calcic Carbonate is rarely found in the urine of man, but frequently in that of the horse and other herbivorous animals. Its appearance is that of small circular bodies, composed, apparently, of a mass of radiating needles, some of the spherical groups uniting to form dumbbells. Acetic acid dissolves calcic carbonate, liberating carbonic acid gas, with visible effervescence (under the microscope) if the slide has been previously warmed and a group of crystals be attacked.

Hippuric Acid.—The pointed rhombic prisms and acicular crystals are characteristic, and easily recognized. The broader crystals may possibly be mistaken for triple phosphate, and the narrower for certain forms of uric acid; but insolubility in acetic acid distinguishes them from the former, and solubility in alcohol from the latter. These tests may be applied while the deposit is under microscopic observation. An alcoholic solution of hippuric acid evaporated to dryness, and the residue treated with water, gives a solution from which characteristic crystalline forms of hippuric acid may be obtained on allowing a drop to dry up on a slip of glass.

The organized deposits in urine entail greater care in their determination, and usually require a higher magnifying-power for their proper examination than those of crystalline form. The figure on Plate II. of the Frontispiece are drawn to 230 diameters. The following notes will assist the student.

Casts of uriniferous tubuli are fibrous masses often of considerable length, and of various forms—sometimes delicate and transparent, occasionally granular, and often beset with fat-globules. Epithelial *débris* is frequently present in urine in the

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form of nucleated cells, regular and oval when full, but irregular and angular when partially emptied of their contents—sometimes perfect, but more frequently a good deal broken up.

Blood is easily recognized. Urine containing it is high-coloured, and the corpuscles appear under the microscope as reddish circular disks, either single or laid together in strings, resembling piles of coin. Their colour and somewhat smaller size serve to distinguish them from pus-corpuscles: in doubtful cases a drop of blood from the finger should be diluted with water and used for comparison. After urine containing blood has stood for some time, the corpuscles lose their regular rounded outline and become angular. (See *a* in the figure.)

Pus and Mucus.—Purulent urine deposits, on standing, a light-coloured layer easily diffused through the liquid by shaking. Acetic acid does not dissolve the sediment, and solution of potash of officinal strength converts it into a gelatinous mass. Under the microscope, pus-corpuscles appear rounded and colourless, rather larger than blood-disks, and somewhat granular on the surface. They generally show minute nuclei, which are more distinctly seen after treating with acetic acid. (See the portion of the figure marked *a*.) Mucus possesses no definite microscopic characters, but commonly has imbedded in it pus, epithelium, and air-bubbles. Mucus is coagulated in a peculiar and characteristic manner by acetic acid; and this reaction, together with the ropy appearance it imparts to urine, prevents its being confounded with pus.

Fatty matter occurs either as minute globules partially diffused through the urine (as shown at *a*) or in more intimate emulsion (as at *b* in the figure). When present in larger quantity, it collects as a sort of skim on the surface after standing.

Spermatozoa are liable to escape notice, on account of their small size and extreme transparency. Suspected urine should be allowed to settle some hours in a conical test-glass, and the drop at the bottom examined under a high power. The drawing shows their tadpole-like appearance.

Sarcina Ventriculi is an alga of very rare occurrence in urine, though not unfrequent in the matters vomited during certain diseases of the stomach. The upper figures (*a*) are copied from Dr. Thudichum's drawing (from urine), the larger fronds (*b*) are from vomited matter.

Extraneous bodies, such as hair, wool, or fragments of feathers, are often found in urinary deposits, and ludicrous mistakes have been made by observers not on their guard in respect to such casual admixtures.

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Examination of Urinary Calculi.

Urinary calculi have the same composition as unorganized urinary sediments. They consist, in short, of sediments that have been deposited slowly within the bladder, particle on particle, layer on layer, the several substances becoming so compact as to be less easily acted on by reagents than when deposited after the urine has been passed,—the urates less readily soluble in warm water, the calcic phosphate insoluble in acetic acid until it has been dissolved in hydrochloric acid and reprecipitated by an alkali. The term *calculus* is the diminutive of *calx*, a lime- or chalk-stone.

If the calculus is whole, saw it in two through the centre, and notice whether it is built up of distinct layers or apparently consists of one substance. If the latter, use about a grain of the sawdust for analysis; if the former, carefully scrape off portions of each layer, and examine them separately. If the calculus is in fragments, select fair specimens of about half a grain or a grain each, and reduce to a fine powder by placing on a hard surface and crushing under the blade of a knife.

Boil about half a grain of the finely-powdered calculus in half a test-tubeful of distilled water for three or four minutes and pour it on a small filter. Proceed according to the following Table:—

<table>
<tr><td colspan="2">Insoluble.
Phosphates, calcic oxalate, and free uric acid.
Boil with two or three drops of hydrochloric acid and filter.</td><td rowspan="3">Soluble.
Urates.
They will probably be redeposited as the solution cools. Small quantities may be detected by evaporating the solution to dryness. They are tested for ammonium, sodium, calcium, and the uric radical by the appropriate reagents.</td></tr>
<tr><td>Insoluble.
Uric acid.
Apply the murexid test.</td><td>Soluble.
Phosphates and calcic oxalate.
Add excess of ammonia, and then excess of acetic acid; filter.</td></tr>
<tr><td colspan="2"><table><tr><td>Insoluble.
Calcic oxalate.</td><td>Soluble.
Phosphates.
They may be reprecipitated by ammonia.</td></tr></table></td></tr>
</table>

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Calculi composed entirely of uric acid are common; a minute portion heated on platinum foil chars, burns, and leaves scarcely a trace of ash. The phosphates frequently occur together, forming what is known as the *fusible calculus*, from the readiness with which a fragment aggregates, and even fuses to a bead, when heated on a loop of platinum wire in the blowpipe-flame. The phosphates may, if necessary, be further examined by the method described in connexion with urinary deposits. Calcic oxalate often occurs alone, forming a dark-coloured calculus having a very rough surface, hence termed the *mulberry calculus*. Smaller calculi of the same substance are called, from their appearance, *hempseed calculi*. Calculi of *cystin* are rarely met with. *Xanthin* (from ξανθὸς, *xanthos*, yellow, in allusion to the colour it yields with nitric acid) still less often occurs as a calculus.

The earthy concretions, or *chalk-stones*, which frequently form in the joints of gouty persons, are composed chiefly of urates, the sodium salt being that most commonly met with. *Gall-stones*, or *biliary calculi*, occasionally form in the gall-bladder: they contain *cholesterin* (from χολὴ, *chole*, bile, and στερεὸς, *stereos*, solid), a fatty substance soluble in alcohol or ether, and crystallizing from such solutions in well-defined, square, scaly crystals. Calculi of many pounds weight are often found in the stomach and larger intestines of animals.

Experience in manipulation having been gained by the analysis of fragments weighing half a grain or a grain, still smaller quantities of a calculus may be examined by directly testing for each common ingredient, always beginning by heating a minute portion on platinum foil to ascertain whether organic matter, inorganic matter, or both, are present. If organic matter only, the calculus will in nearly all cases be uric acid, the indication being confirmed by applying the murexid test in a watch-glass to another fragment, half the size of a small pin's head. If inorganic, the ash on the platinum foil may be examined for phosphates, and a separate portion of the calculus for oxalates. Even a single drop of liquid obtained in any of these experiments may be filtered by placing on a filter not larger than a sixpence, and previously moistened with water, and adding three or four drops of water one after the other as each passes through the paper.

Knowledge of the composition of a calculus or urinary deposit affords valuable diagnostic aid to the physician, hence the importance of a correct analysis of these substances.

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THE GALENICAL PREPARATIONS OF THE BRITISH PHARMACOPŒIA.

The preparation of Confections, Decoctions, Enemas, Extracts, Glycerines, Infusions, Inhalations, Juices, Liniments, Lozenges, Mixtures, Fixed and Volatile Oils, Ointments, Pills, Plasters, Poultices, Powders, Spirits, Suppositories, Syrups, Tinctures, Waters, and Wines, includes a number of mechanical rather than chemical operations, and belong to the domain of pure Pharmacy. The medical or pharmaceutical student will doubtless have had ample opportunity of practically studying these compounds before working at experimental chemistry, and will probably have prepared many of them according to the directions of the Pharmacopœia; if not, he is referred to the pages of the last edition of that work for details.

Among the extracts, however, there are five (namely, those of Aconite, Belladonna, Hemlock, Henbane, and Lettuce) which are not simply evaporated infusions, decoctions, or tinctures, like most others, but are evaporated juices from which vegetable albumen, the supposed source of fermentation and decay, has been removed, and chlorophyll (the green colouring-matter of plant-juice) retained practically unimpaired in tint. In order that attention may be concentrated on the process by which these are prepared, rather than on the extracts themselves, it is advisable to make an extract of some ordinary green vegetable, such as cabbage or turnip-tops. Bruise the green leaves of a good-sized cabbage in a mortar, and press out the juice; heat it gradually to 130°, and remove the green flocks of chlorophyll which separate, by filtration through calico. When the liquor

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has all passed through the filter, set the chlorophyll aside for a time, heat the strained liquor to 200° to coagulate albumen; remove the latter by filtration and throw away; evaporate the filtrate by a water-bath to the consistence of thin syrup; then add to it the chlorophyll, and, stirring the whole together assiduously, continue the evaporation at a temperature not exceeding 140°, until the extract is of a suitable consistence for forming pills. A higher temperature than that indicated would cause the alteration of the chlorophyll to a dark-brown substance, the extract no longer having the green tint which custom and the Pharmacopœia demand.

The process by which volatile oils are usually obtained from herbs, flowers, fruits, or seeds, may be imitated on the small scale by placing the material (bruised cloves or caraways for instance) in a tubulated retort, adapting the retort to a Liebig's condenser, and passing steam, generated in a Florence flask, through a glass tube to the bottom of the retort. The steam in its passage upward through the substance will carry the oil over the neck of the retort into the condenser, and thence, liquefied and cooled, into the receiving vessel, where the oil will be found floating on the water. It may be collected by running off the distillate through a glass funnel, having a stopcock in the neck; or by letting the water from the condenser run into an old test-tube which has a small hole in the bottom, or any similar tube placed in a larger vessel, the water and oil being subsequently separately run off from the tube as from a pipette. The water will in most cases be the ordinary officinal medicated water (*Aqua Carui, Aqua Cinnamomi*) of the material operated on. Many volatile oils rapidly absorb oxygen from the air and yield stearoptens or camphor-like bodies; hence they must be kept in well-closed bottles.

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THE CHEMICAL PREPARATIONS OF THE BRITISH PHARMACOPŒIA.

The process by which every officinal chemical substance is prepared has already been described, and the strict chemical character of the processes illustrated by experiments and explained by aid of equations. Should the student, in addition, desire an intimate acquaintance with those details of manipulation on which the successful and economic manufacture of chemical substances depends, he is advised to prepare a few ounces of each of the salts mentioned in the British Pharmacopœia or commonly used in Pharmacy. His guide in these operations should be the Pharmacopœia itself, as well as any chemical works that may be at his disposal.

The production of many chemical and galenical substances on a commercial scale can only be successfully carried on in manufacturing-laboratories and with some knowledge of the circumstances of supply, demand, value of raw material, and of by-products, &c. These are points which, during pupilage, may be regarded as of secondary importance, the acquirement of chemical principles being considered of highest necessity.

The next subjects of experimental study will be determined by the nature of the student's future pursuits. In most cases the operations of quantitative analysis will engage his attention. These should be of a volumetric and gravimetric character; for details concerning them he is referred to the following pages.

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QUANTITATIVE ANALYSIS.

INTRODUCTORY REMARKS.

The proportions in which chemical substances unite with each other in forming compounds are definite and invariable. Quantitative analysis is based on this law. When, for example, aqueous solutions of a salt of silver and a chloride are mixed, a white curdy precipitate is produced containing chlorine and silver in atomic proportions, that is, 35·5 parts of chlorine to 108 of silver. No matter what the chloride or what the salt of silver, the resulting chloride of silver is invariable in composition. The formula AgCl is a convenient picture of this compound in these proportions. The weight of a definite compound being given, therefore, the proportional amounts of its constituents can be ascertained by simple calculation. Thus, for instance, 8·53 parts of chloride of silver contain 2·11 parts of chlorine and 6·42 of silver; for if 143·5 (the molecular weight) of chloride of silver contain 35·5 of chlorine, 8·53 of chloride of silver will be found to contain 2·11 of chlorine:—

$$143{\cdot}5 : 35{\cdot}5 :: 8{\cdot}53 : x$$

$$8{\cdot}53$$

$$1{\cdot}065$$
$$17{\cdot}75$$
$$284{\cdot}0$$

$$143{\cdot}5)302{\cdot}815(2{\cdot}11$$
$$287{\cdot}0$$

$$15{\cdot}81$$
$$14{\cdot}35$$

$$1{\cdot}465$$
$$1{\cdot}435$$

$$x = 2{\cdot}11.$$

And if 143·5 of chloride of silver contain 108 of silver, 8·53 of chloride of silver will contain 6·42 of silver. To ascertain, for example, the amount of silver in a substance, all that is neces-

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sary is to take a weighed quantity of the substance, dissolve it, precipitate the whole of the silver by adding hydrochloric acid or other chloride till no more chloride of silver falls, collect the precipitate on a filter, wash, dry, and weigh. The amount of silver in the dried chloride, ascertained by calculation, is the amount of silver in the quantity of substance on which the operation was conducted; a rule-of-three sum gives the quantity per cent.—the form in which the results of quantitative analysis are usually stated. Occasionally a constituent of a substance admits of being isolated and weighed in the uncombined state. Thus the amount of mercury in a substance may be determined by separating and weighing the mercury in the metallic condition; if occurring as calomel (Hg_2Cl_2) or corrosive sublimate ($HgCl_2$), the proportion of chlorine may then be ascertained by calculation (Hg=200; Cl=35·5).

So, then, a body may be isolated and weighed alone in a balance and its quantity thus ascertained; or it may be separated and weighed in combination with another body whose combining proportion is well known; this is quantitative analysis by the *gravimetric* method.

Quantitative analysis by the *volumetric* method consists in noting the volume of a liquid required to be added to the substance under examination before a given effect is produced. Thus, for instance, a solution of nitrate of silver of known strength may be used in experimentally ascertaining an unknown amount of a chloride in any substance. The silver solution is added to a solution of a definite quantity of the substance until flocks of chloride of silver cease to be precipitated: every 108 parts of silver added (or 170 of nitrate of silver: Ag=108, N=14, O_3=48; total 170) indicate the presence of 35·5 of chlorine, or an equivalent quantity of any chloride. The preparation of standard solutions, such as that of the nitrate of silver, to which allusion is here made, requires considerable care; but when made, certain analyses can be executed with far more rapidity and ease than by gravimetric processes.

The quantitative analysis of solids and liquids often involves determinations of temperature and specific gravity. These processes will now be explained, after which an outline of volumetric and gravimetric quantitative analysis will be given. The scope of this work precludes any attempt to describe all the little mechanical details observed by quantitative analysts; essential operations, however, are so fully treated that expert manipulators will meet with little difficulty.

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The analysis of gases and vapours also involves determinations of the varying pressure of the atmosphere, as indicated by the *barometer* (from βάρος, *baros*, weight, and μέτρον, *metron*, measure), a glass tube 33 or 34 inches long, closed at one end, filled with mercury, and inverted in a cup of mercury. The mercury remains in the tube owing to the weight or pressure of the atmosphere on the exposed surface of the liquid, the average height of the column being nearly 30 inches. In the popular form of the instrument, the wheel-barometer, the cistern is formed by a recurvature of the tube; on the exposed surface of the mercury a float is placed, from which a thread passes over a pulley and moves an index whenever the column of mercury rises or falls. For further information concerning the influence of pressure on the volume of a gas or vapour, and for descriptions of the methods of analyzing gases, refer to Ganot's 'Physics' (translated by Atkinson), Miller's 'Chemical Physics,' and "Analysis of Gases" in Watts's 'Dictionary of Chemistry.'

MEASUREMENT OF TEMPERATURE.

As a rule, all bodies expand on the addition, and contract on the abstraction of heat, the alteration in volume being constant and regular for equal increments or decrements of temperature. The extent of this alteration in a given substance, expressed in parts or degrees, constitutes the usual method of intelligibly stating, with accuracy, precision, and minuteness, a particular condition of warmth or temperature—that is, of sensible heat. The substance commonly employed for this purpose is mercury, the chief advantages of which are that it will bear a high temperature without boiling, a low temperature without freezing, does not adhere to glass to a sufficient extent to "wet" the sides of any tube in which it may be enclosed, and from its good conducting-power for heat responds rapidly to changes of temperature. Platinum, earthenware, alcohol, and air, are also occasionally used for thermometric purposes.

The construction of an accurate thermometer is a matter of great difficulty; but the following are the leading steps in the operation. Select a piece of glass tubing having a fine capillary bore, and about a foot long; heat one extremity in the blowpipe-flame until the orifice closes, and the glass is sufficiently soft to admit of a bulb being blown; heat the bulb to expel air, imme-

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diately plunging the open extremity of the tube into mercury; the bulb having cooled, and some mercury having entered and taken the place of expelled air, again heat the bulb and tube until the mercury boils and its vapour escapes at the open end of the tube; again plunge the extremity under mercury, which will probably now completely fill the bulb and tube. When cold the bulb is placed in melting ice. The top of the column of mercury in the capillary tube should then be within an inch or two of the bulb; if higher, some of the mercury must be expelled by heat; if lower, more metal must be introduced as before. The tube is now heated near the open end and a portion drawn out, until the diameter is reduced to about one-tenth. The bulb is next warmed until the mercurial column rises above the constricted part of the tube, which is then rapidly fused in the blowpipe-flame, and the extremity of the tube removed. The instrument is now ready for graduation. The bulb is placed in boiling water (a medium having, *cæteris paribus*, an invariable temperature), and, when the position of the top of the mercurial column is constant, a mark is made on the tube by a scratching diamond or a file. This operation is repeated with melting ice (a medium also having an invariable temperature). The space between these two marks is divided into a certain number of intervals termed *degrees*. Unfortunately this number is not uniform in all countries: in England it is 180, as proposed by Fahrenheit; in France 100, as proposed by Celsius (the Centigrade scale), a number generally adopted by scientific men: in some parts of the Continent the divisions are 80 for the same interval, as suggested by Reaumur. Whichever be the number selected, the markings should be continued above the boiling-point and below the freezing-point as far as the length of the stem admits.

On the Centigrade and Reaumur scales the freezing-point of water is made zero, and the boiling-point 100 and 80 respec-

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tively; on the Fahrenheit scale the zero is placed 32 degrees below the congealing-point of water, the boiling-point of which becomes, consequently, 212. Even on the Fahrenheit system temperatures below the freezing-point of water are often spoken of as "degrees of frost;" thus 19° as marked on the thermometer would be regarded as "13 degrees of frost." It is to be regretted that the freezing-point of water is not universally regarded as the zero-point, and the number of intervals between that and the boiling-point of water everywhere the same. The Centigrade scale, however, is being slowly adopted, and will doubtless, sooner or later, supersede the others.

The degrees of one scale are easily converted into those of another, if their relations be remembered, namely:—180 (F.), 100 (C.), 80 (R.), or 18, 10, and 8; or, best, 9, 5, and 4.

Formulæ for the conversion of degrees of one thermometric scale into those of another.

F = Fahrenheit. C = Centigrade.
R = Reaumur. D = The observed degree.

If above the freezing-point of water
(32° F; 0° C; 0° R),

F into C	(D−32) ÷ 9 × 5.
F „ R	(D−32) ÷ 9 × 4.
C „ F	D ÷ 5 × 9 + 32.
R „ F	D ÷ 4 × 9 + 32.

If below freezing, but above 0° F
(−17°·77 C; −14°·22 R),

F into C	(32−D) ÷ 9 × 5.
F „ R	(32−D) ÷ 9 × 4.
C „ F	32−(D ÷ 5 × 9).
R „ F	32−(D ÷ 4 × 9).

If below 0° F
(−17°·77 C; −14°·22 R),

F into C	(D+32) ÷ 9 × 5.
F „ R	(D+32) ÷ 9 × 4.
C „ F	D ÷ 5 × 9 + 32.
R „ F	D ÷ 4 × 9 + 32.

For all degrees:—

C into R	D ÷ 5 × 4.
R „ C	D ÷ 4 × 5.

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In ascertaining the temperature of a liquid, the bulb of a thermometer is simply inserted and the degree noted. In determining the boiling-point, the bulb is also inserted in the liquid, if a pure substance. In taking the boiling-point of a liquid which is being distilled from a mixture, the bulb of the thermometer should be near to, but not beneath the surface.

The following are the boiling-points of a few substances met with in pharmacy :—

	Centigrade.	Fahrenheit.
Alcohol, absolute	78·3	173
„ 84 per cent.	79·5	175
„ 49 per cent. (proof spirit)	81·4	178·5
„ amylic	132·2	270
Benzol	80·6	177
Bromine	47·2	117
Benzoic acid	239·0	462
Carbolic acid	187·8	370
Chloroform	142·	61
Ether (B P.) (below)	40·5	105
„ pure	35	95
Mercury *in vacuo* (as in a thermometer)	304	580
„ in air (barom. at 30 inches)	350	662
Water (barom. at 29·92 inches)	100	212
„ („ 29·33 „)	99·5	211
„ („ 28·74 „)	99	210
Saturated solutions of :—		
Cream of tartar	101	214
Common salt	106·6	224
Sal-ammoniac	113·3	236
Nitrate of sodium	119	246
Acetate of sodium	124·4	256
Chloride of calcium	179·4	355

To determine melting-points of fats &c.—Heat a fragment of the substance (spermaceti or wax for example) till it liquefies, and then draw up a small portion into a thin glass tube, about the size of a knitting-needle. Immerse the tube in cold water

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contained in a beaker, and slowly heat the vessel till the thin opaque cylinder of solid fat melts and becomes transparent: a delicate thermometer placed in the water indicates the point of change to the fifth of a degree. Remove the source of heat, and note the congealing-point of the substance; it will be identical with or close to the melting-point.

The following melting-points of officinal substances are given in the British Pharmacopœia:—

	In degrees Centigrade.	In degrees Fahrenheit.
Acetic acid, glacial	8·9	48
„ „ congeals at	1·1	34
Benzoic acid	120	248
Carbolic acid	35	95
Oil of theobroma	50	122
Phosphorus	43·3	110
Prepared lard (about)	38	100
Spermaceti	38	100
White wax (not under)	65·5	150
Yellow wax „	60	140

The order of fusibility of a few of the metals is as follows:—

	In degrees Fahrenheit.	In degrees Centigrade.
Mercury	− 39	− 39·4
Potassium	+144·5	+ 62·5
Sodium	207·7	97·6
Tin	442	227·8
Bismuth	507	264
Lead	617	325
Zinc	773	411·6
Antimony	1150	621
Silver	1873	1023
Copper	1996	1091
Gold	2016	1102
Cast iron	2786	1530

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SPECIFIC GRAVITY.

All bodies attract each other, the amount of attraction being in direct proportion to the quantity of matter of which they consist, and in inverse proportion to the square of their distances. This is *gravitation*. *Weight* is the effect of gravity, being the excess of the attraction which the earth has for a body over that which a body has for the earth. *Specific* weight is the definite or precise weight of a body in relation to its bulk; it is more usually termed *specific gravity* *. The comparative heaviness of solids and liquids is conventionally expressed in relation to water: they are considered as being so much lighter or heavier than water. Thus, water being regarded as unity = 1, the relative weight, or specific gravity, of ether is represented by the figures ·720 (it is nearly three-fourths, ·750 the weight of water), oil of vitriol by 1·843 (it is nearly twice, 2·000 as heavy as water). The standard of comparison for gases is usually air, but sometimes hydrogen.

Specific Gravity of Liquids.

Procure any small bottle holding from 100 to 1000 grains, and having a narrow neck; counterpoise it in a delicate balance; fill it to about halfway up the neck with pure distilled water having a temperature of 60° F.; ascertain the weight of the water, and add or subtract a drop or two, so that the weight shall be a round number of grains; mark the neck by a diamond or file-point at the part cut by the lower edge of the curved surface of the water. Consecutively fill up the bottle to the neck-mark with several other liquids, cooled or warmed to 60° F., first rinsing out the bottle once or twice with a small quantity of each liquid, and note the weights; the respective figures will represent the relative weights of equal bulks of the liquids. If the capacity of the

* *Density* is sometimes improperly regarded as synonymous with *specific gravity*. It is true that the density of a body is in exact proportion to its specific gravity; but the former is more correctly the comparative bulk of equal weights, while specific gravity is the comparative weight of equal bulks.

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bottle is 10, 100, or 1000 grains, the resulting weights will, without calculation, show the specific gravities of the liquids; if any other number, a rule-of-three sum must be worked out to ascertain the weight of the liquids as compared with 1 (or 1·000) of water. Bottles conveniently adjusted to contain 250, 500, or 1000 grains, or 100 or 500 grammes of water, when filled to the top of their perforated stopper, and other forms of the instrument, are sold by all chemical-apparatus makers.

The Balance.—The balance used in the foregoing and other quantitative operations must be accurate and sensitive. The points of suspension of the beam and pans should be polished steel knife-edges, working on agate planes. It should turn easily and quickly, without too much oscillation, to $\frac{1}{500}$ or $\frac{1}{600}$ of a grain, or $\frac{1}{10}$ of a milligramme, when 1000 grains, or 50 or 60 grammes, are placed in each scale. The beam should be light but strong, capable of supporting a load of 1500 grains or 100 grammes; its oscillations are observed by help of a long index attached to its centre, and continued downwards for some distance in front of the supporting pillar of the balance. The instrument should be provided with screws for purposes of adjustment, a mechanical contrivance for supporting the beam above its bearings when not in use or during the removal or addition of weights, spirit levels to enable the operator to give it a horizontal position, and be enclosed in a glass case to protect it from dust. It should be placed in a room the atmosphere of which is not liable to be contaminated by acid fumes, in a situation free from vibration, and a vessel containing lumps of quicklime should be placed in the case to keep the enclosed air dry and prevent the formation of rust on the steel knife-edges or other parts. During weighing the doors of the balance should be shut, in order that currents of air may not unequally influence the pans.

The Weights.—These should be preserved in a box having a separate compartment for each. They must not be lifted directly with the fingers, but by a small pair of forceps. If grain-weights, they should range from 1000 gr. to $\frac{1}{10}$ gr., a $\frac{1}{10}$ weight being fashioned of gold wire to act as a "rider" on the divided beam, and thus indicate by its position 100ths and 1000ths of a grain. From $\frac{1}{10}$ to 10 grs. the weights may be of platinum; thence upwards to 1000 grs., of brass. The relation of the weights to

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each other should be decimal. Metric decimal weights may range from 100 grammes to 1 gramme, of brass, and thence downwards to 1 centigramme, of platinum; a gold centigramme rider being employed to indicate milligrammes and tenths of a milligramme. The metric system of weights is greatly to be preferred to the British, the relation of the metric weights of all denominations to measures of length, capacity, and surface being so simple as to be within the comprehension of the merest child; while under the British plan, the weights have no such relation, either with each other or with the various measures. Moreover the metric system is in perfect harmony with the universal method of counting; it is a decimal system.

It is perhaps impossible to realize, much more express, the advantages we enjoy from the fact that in every country of the world the system of numeration is identical. That system is the decimal. Whatever language a man speaks, his method of numbering is decimal; his talk concerning number is decimal; his written or printed signs signifying number are decimal. With the figures 1, 2, 3, 4, 5, 6, 7, 8, 9, 0 he represents all possible variation in number, the position of a figure in reference to its companions alone determining its value, a figure on the left hand of any other figure in an allocation of numeral symbols (for example, 1867) having ten times the value of that figure, while the figure on the right hand of any other has a tenth of the value of that other. When the youngest apprentice is asked how many units there are in 1867, he smiles at the simplicity of the question, and says 1867. How many tens? 186, and 7 over. How many hundreds? 18, and 67 over. How many thousands? 1, and 867 over. But if he is asked how many scruples there are in 1867 grains, how many drachms, how many ounces—he brings out his slate and pencil. And so with the pints or gallons in 1867 fluid ounces, or the feet and yards in 1867 inches, or the pence, shillings, and pounds in 1867 farthings; to say nothing of cross questions, such as the value of 1867 articles at 9*s.* 6*d.* per dozen, or of the perplexity caused by the varying values of several individual weights or of measures of length, capacity, and surface in different parts of the country. What is desired is, that there should be an equally simple decimal relation among weights and measures and coins as already universally exists among numbers. This condition of things having already been introduced into other countries, there is no good reason why it should not be accomplished in this.

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WEIGHTS AND MEASURES OF THE METRICAL SYSTEM.

(From the British Pharmacopœia of 1867.)

WEIGHTS.

1 Milligramme	=the thousandth part of one	grm. or	0·001 grm.
1 Centigramme	=the hundredth ,,		0·01 ,,
1 Decigramme	=the tenth ,,		0·1 ,,
1 Gramme	=weight of a cubic centimetre of water at 40° C.		1·0 ,,
1 Decagramme	=ten grammes		10·0 ,,
1 Hectogramme	=one hundred grammes		100·0 ,,
1 Kilogramme	=one thousand grammes		1000·0 ,,

MEASURES OF CAPACITY.

1 Millilitre =	1	cub. centim.	or the mea. of	1	gram. of water.
1 Centilitre =	10	,,	,,	10	,, ,,
1 Decilitre =	100	,,	,,	100	,, ,,
1 Litre =	1000	,,	,,	1000	,, (1 kilo.).

MEASURES OF LENGTH.

1 Millimetre	=the thousandth part of one	metre or	0·001 metre.
1 Centimetre	=the hundredth ,,		0·01 ,,
1 Decimetre	=the tenth ,,		0·1 ,,
1 Metre	=the ten-millionth part of a quarter of the meridian of the earth.		

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The following Tables, from the British Pharmacopœia and the Diary of Messrs. De La Rue, will be found useful for reference:—

WEIGHTS AND MEASURES OF THE BRITISH PHARMACOPŒIA OF 1867.

WEIGHTS.

1 Grain	gr.			
1 Ounce	oz.		=	437·5 grains.
1 Pound	lb.	= 16 ounces	=	7000 „

MEASURES OF CAPACITY.

1 Minim	min.		
1 Fluid Drachm	fl. drm.	=	60 minims.
1 Fluid Ounce	fl. oz.	=	8 fluid drachms.
1 Pint	O.	=	20 fluid ounces.
1 Gallon	C.	=	8 pints.

MEASURES OF LENGTH.

1 line = $\frac{1}{12}$ inch.

1 inch = $\frac{1}{39{\cdot}1393}$ seconds-pendulum.

12 „ = 1 foot.

36 „ = 3 „ = 1 yard.

Length of pendulum vibrating seconds of mean time in the latitude of London, in a vacuum at the level of the sea ..... } 39·1393 inches.

RELATION OF MEASURES TO WEIGHTS.

1 Minim is the measure of			0·91	grain of water.
1 Fluid Drachm	„		54·68	grains of water.
1 Fluid Ounce	„	1 ounce or	437·5	„
1 Pint	„	1·25 pound or	8750·0	„
1 Gallon	„	10 pounds or	70,000·0	„

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Metrical Measures of Length.

	In English inches.	In English feet =12 inches.	In English yards =3 feet.	In English fathoms =6 feet.	In English miles =1760 yards.
Millimètre	0·03937	0·003281	0·0010936	0·0005468	0·0000006
Centimètre	0·39371	0·032809	0·0109363	0·0054682	0·0000062
Décimètre	3·93708	0·328090	0·1093633	0·0546816	0·0000621
Mètre	39·37079	3·280899	1·0936331	0·5468165	0·0006214
Décamètre	393·70790	32·808992	10·9363310	5·4681655	0·0062138
Hectomètre	3937·07900	328·089920	109·3633100	54·6816550	0·0621382
Kilomètre	39370·79000	3280·899200	1093·6331000	546·8165500	0·6213824
Myriomètre	393707·90000	32808·992000	10936·3310000	5468·1655000	6·2138244

1 inch = 2·539954 centimètres. 1 yard = 0·9143835 mètre.
1 foot = 3·0479449 décimètres. 1 mile = 1·6093149 kilomètre.

Metrical Measures of Surface.

	In English square feet.	In English sq. yards =9 square feet.	In English poles= 272·25 square feet.	In English roods= 10890 square feet.	In English acres= 43560 square feet.
Centiare or square mètre	10·764299	1·196033	0·0395383	0·0009885	0·0002471
Are or 100 square mètres	1076·429934	119·603326	3·9538290	0·0988457	0·0247114
Hectare or 10,000 sq. mètres	107642·993418	11960·332602	395·3828959	9·8845724	2·4711431

1 square inch = 6·4513669 square centimètres. 1 square yard = 0·83609715 square mètre or centiare.
1 square foot = 9·2899683 square décimètres. 1 acre = 0·40467102 hectare.

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Metrical Measures of Capacity.

	In cubic inches.	In cubic feet = 1728 cubic inches.	In pints = 34·65923 cubic inches.	In gallons = 8 pints = 277·27384 cubic inches.	In bushels = 8 gallons = 2218·19075 cubic inches.
Millilitre, or cubic centimètre	0·06103	0·000035	0·00176	0·0002201	0·0000275
Centilitre, or 10 cubic centimètres	0·61027	0·000353	0·01761	0·0022010	0·0002751
Décilitre, or 100 cubic centimètres	6·10271	0·003532	0·17608	0·0220097	0·0027512
Litre, or cubic décimètre	61·02705	0·035317	1·76077	0·2200967	0·0275121
Décalitre, or centistère	610·27052	0·353166	17·60773	2·2009668	0·2751208
Hectolitre, or décistère	6102·70515	3·531658	176·07734	22·0096677	2·7512085
Kilolitre, or stère, or cubic mètre	61027·05152	35·316581	1760·77341	220·0966767	27·5120846
Myriolitre, or décastère	610270·51519	353·165807	17607·73414	2200·9667675	275·1208459

1 cubic inch = 16·386176 cubic centimètres. 1 cubic foot = 28·315312 cubic décimètres. 1 gallon = 4·543358 litres.

Metrical Measures of Weight.

	In English grains.	In troy ounces = 480 grains.	In avoirdupois lbs. = 7000 grains.	In cwts. = 112 lbs. = 784000 grains.	Tons = 20 cwts. = 15680000 grains.
Milligramme	0·01543	0·000032	0·0000022	0·0000000	0·0000000
Centigramme	0·15432	0·000322	0·0000220	0·0000002	0·0000000
Décigramme	1·54323	0·003215	0·0002205	0·0000020	0·0000001
Gramme	15·43235	0·032151	0·0022046	0·0000197	0·0000010
Décagramme	154·32349	0·321507	0·0220462	0·0001968	0·0000098
Hectogramme	1543·23488	3·215073	0·2204621	0·0019684	0·0000984
Kilogramme	15432·34880	32·150727	2·2046213	0·0196841	0·0009842
Myriogramme	154323·48800	321·507267	22·0462126	0·1968412	0·0098421

grain = 0·064799 gramme. 1 troy oz. = 31·103496 grams. 1 lb. avd. = 0·453593 kilogr. 1 cwt. = 50·802377 kilogrs.

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The following are the stated specific gravities of officinal liquids:—

Acid, acetic	1·044
„ „ diluted	1·006
„ „ glacial	1·065 to 1·066
„ carbolic	1·065
„ hydrochloric	1·160
„ „ diluted	1·052
„ hydrocyanic	0·997
„ nitric	1·420
„ „ diluted	1·101
„ nitro-hydrochloric	1·074
„ phosphoric, diluted	1·080
„ sulphuric	1·843
„ „ aromatic	0·927
„ „ diluted	1·094
„ sulphurous, solution of	1·040
Alcohol, absolute	0·795
„ (rectified spirit, 84 per cent.)	0·838
„ (proof spirit, 49 per cent.)	0·920
„ amylic	0·818
Ammonia, aromatic spirit of	0·870
„ solution of	0·959
„ strong solution of	0·891
Antimony, solution of chloride of	1·470
Arsenic, hydrochloric solution of	1·009
Arsenical solution (*Liquor Arsenicalis*)	1·009
Benzol	0·850
Bismuth and ammonia, sol. of citrate of	1·122
Bromine	2·966
Chlorine, solution of	1·003
Chloroform	1·490
„ spirit of	0·871
Cinchona, liquid ext. of yellow (about)	1·100
Creasote	1·071
Ether	0·735
„ pure	0·720
Glycerin	1·250
Iron, solution of pernitrate of	1·107
„ „ persulphate of	1·441
„ strong solution of perchloride of	1·338
„ tincture of perchloride of	0·992
Lead, solution of subacetate of	1·260

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Lime, saccharated solution of.....	1·052
„ solution of chlorinated	1·035
Mercury, acid solution of nitrate of ..	2·246
Nitre, sweet spirit of.....	0·845
Potash, solution of.....	1·058
Soda, „	1·047
„ „ chlorinated	1·103
Squill, oxymel of	1·320
Syrup.....	1·330
„ of buckthorn.....	1·320
„ of ginger	
„ of hemidesmus.....	1·335
„ of iodide of iron	1·385
„ of lemons.....	1·340
„ of mulberries	1·330
„ of orange-flower	1·330
„ of „ peel	
„ of phosphate of iron.....	
„ of poppies.....	1·320
„ of red poppy.....	1·330
„ of „ roses	1·335
„ of rhubarb	
„ of senna	1·310
„ of squill	
„ of tolu	1·330
Treacle .....(about)	1·400

Hydrometers.—The specific gravity of liquids may be ascertained, without scales and weights, by means of an *hydrometer*; an instrument usually of glass, having a graduated stem and a bulb or bulbs at the lower part. The specific gravity of a liquid is indicated by the depth to which the hydrometer sinks in the liquid, the zero of the scale marking the depth to which it sinks in pure water. Hydrometers constructed for special purposes are known under the names of saccharometer, galactometer, elæometer, urinometer, alcohometer. Hydrometers require a considerable quantity of liquid to fairly float them, and specific gravities observed with them are less delicate and trustworthy than those obtained by the balance.

Specific Gravity of Solids in Mass.

Weigh a piece (50 to 250 grains) of any solid substance heavier than water in the usual manner. Then weigh it in water, by

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suspending it from a shortened balance-pan by a fine thread or hair and immersing in a vessel of water. The buoyant properties of the water will cause the solid to apparently lose weight: *this loss in weight is the exact weight of an equal bulk of water.* The weight of the substance and the weight of an equal bulk of water being thus ascertained, a rule-of-three sum shows the proportional weight of the substance to 1·000 of water. To express the same thing by rule, divide the weight in air by the loss of weight in water, the resulting number is the specific gravity in relation to 1 part of water, the conventional standard of comparison.

Verify some of the following specific gravities:—

Aluminium	2·56
Antimony	6·71
Bismuth	9·83
Coins, English, gold	17·69
„ „ silver	10·30
„ „ bronze	8·70
Copper	8·95
Gold	19·34
Iron	7·84
Lead	11·36
Magnesium	1·74
Marble	2·70
Phosphorus	1·77
Platinum	21·53
Silver	10·53
Sulphur	2·05
Tin	7·29
Zinc	7·14

Specific gravities of solid substances should be taken in water having a temperature of about 60° F. The body should be immersed about half an inch below the surface of the water; adhering air-bubbles must be carefully removed; the body must be quite insoluble in water. The true weight of a body is its weight in air plus the weight of an equal bulk of air, or, in other words, its weight *in vacuo*, uninfluenced by the buoyancy of the air; but such a correction of the ordinary weight of a body is seldom necessary, or, indeed, desirable.

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Specific Gravity of Solids in Powder or small Fragments.

Weigh the particles; place them in a counterpoised specific-gravity bottle of known capacity, and fill up with water, taking care that the substance is thoroughly wetted; again weigh. From the combined weights of water and substance subtract the amount due to the substance; the residue is the weight of the water. Subtract this weight of water from the quantity which the bottle normally contains; the residue is the amount of water displaced by the substance. Having thus obtained the weights of equal bulks of water and substance, a rule-of-three sum shows the relation of the weight of the substance to 1 part of water—the specific gravity.

Or, suspend a cup, short glass tube, or bucket from a shortened balance-pan; immerse in water; counterpoise; place the weighed powder in the cup, and proceed as directed for taking the specific gravity of a solid in mass.

This operation may be conducted on fragments of any of the metals &c. the specific gravities of which are given in the foregoing Table, or on the powdered piece of marble the specific gravity of which has been taken in mass. The specific gravity of one piece of glass, first in mass then in powder, may be ascertained; the result should be identical. The specific gravity of shot is about 11·350; of sand, 2·600.

Specific Gravity of Solids Soluble in Water.

Weigh a piece of sugar or other substance soluble in water; suspend it from a balance in the usual manner, and weigh it in turpentine, benzol, or petroleum, the specific gravity of which is known or has been previously determined; the loss in weight is the weight of an equal bulk of the turpentine. Ascertain the weight of an equal bulk of water by calculation:—

Sp. gr. of turpentine	:	sp. gr. of water	::	observed bulk of turp.	:	equal bulk of water.

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The weights of equal bulks of sugar and water being thus obtained, the weight of a bulk of sugar corresponding to one of water is shown by a rule-of-three sum; in other words, divide the weight of sugar by that of the equal bulk of water, the product is the specific gravity of sugar.

Specific Gravity of Solids lighter than Water.

This is obtained in a manner similar to that for solids heavier than water; but the light body is sunk by help of a piece of heavy metal, the bulk of water which the latter displaces being deducted from the bulk displaced by both; the product is the weight of a bulk of water equal to the bulk of the light body. For instance, a piece of wood weighing 12 grammes (or grains) is tied to a piece of metal weighing 22 grammes, the loss of weight of the metal in water having been previously found to be 3 grammes. The two, weighing 34 grammes, are now immersed, and the loss in weight found to be 26 grammes. But of this loss 3 grammes have been proved to be due to the buoyant action of the water on the lead; the remaining 23, therefore, represent the same effect on the wood; 23 and 12, therefore, represent the weights of equal bulks of water and wood. As 23 are to 12 so is 1 to ·5217. Or, shortly, as before, divide the weight in air by the weight of an equal bulk of water; ·5217 is the specific gravity of the wood. Another specimen of wood may be found to be three-fourths (·750) the weight of water, and others still heavier. Cork varies from ·100 to ·300.

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VOLUMETRIC ANALYSIS.

APPARATUS.

The only special vessels necessary in volumetric quantitative operations are:—1. *A litre flask*, which, when filled to a mark on the neck, contains one litre (1000 cubic centimetres, *i. e.* 1000 grammes of water *); it serves for preparing solutions in quantities of one litre. 2. A tall cylindrical *graduated litre jar* divided into 100 equal parts; it serves for the measurement and admixture of decimal or centesimal parts of a litre. 3. A graduated tube or *burette*, which, when filled to 0, holds 100 cubic centimetres (a decilitre), and is divided into 100 equal parts; it is used for accurately measuring small volumes of liquids.

The best form of burette is Mohr's (with Erdmann's float). It consists of a glass tube about the width of a little finger and the length of an arm from the elbow, contracted at the lower extremity and graduated. To the contracted portion is fitted a small piece of vulcanized caoutchouc tubing, into the other end of which a small spout made of narrow glass tube is tightly inserted. A strong wire clamp effectually prevents any liquid from passing out of the burette unless the knobs of the clamp are pressed by the finger and thumb of the operator, when a stream or drops flow at will. The accurate reading of the height of a solution in the burette is a matter of great importance. For this purpose a hollow glass float or bulb is used, of such a width that it can move freely in the tube without undue friction, and so adjusted in weight that it shall sink to not less than half its length in any ordinary liquid. A fine line is scratched round the centre of the float; this line must be always regarded as marking the height of the fluid in the burette. In charging the burette, a solution is poured in, not until its surface is coincident with 0, but until the mark on the float is coincident with 0.

* A cubic centimetre is, strictly speaking, the volume occupied by one gramme of distilled water at its point of greatest density, namely, 4° C.; metrical measurements, however, are uniformly taken at 15°·55 C. (60° F.).

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ESTIMATION OF ALKALIES ETC.

An equation represents much more than the formation of certain substances from others. Thus

$$2AmHO + H_2C_2O_4, 2H_2O = Am_2C_2O_4, H_2O + 3H_2O$$

not only shows that oxalate of ammonium is produced when ammonia and crystallized oxalic acid are mixed together, but, among other facts, that 70 parts of ammonia and 126 of oxalic acid yield 142 of crystallized oxalate of ammonium and 54 of water. For formulæ represent molecules; the weight of a molecule is the sum of the weights of its atoms; and atomic weights are represented by definite invariable numbers (see the Table of atomic weights at the end of the volume).

As 126 parts (= 1 molecule) of oxalic acid combine with 70 parts (= 2 molecules) of ammonia, 63 of oxalic acid will unite with 35 (= 1 molecule) of ammonia; 63 parts of oxalic acid will also unite with 56 of caustic potash (KHO = 56), 40 of caustic soda (NaHO = 40), 100 of acid carbonate of potassium ($KHCO_3$, = 100), 69 of anhydrous carbonate of potassium (K_2CO_3 = 138), 84 of acid carbonate of sodium ($NaHCO_3$ = 84), 53 of anhydrous carbonate of sodium (Na_2CO_3 = 106), 143 of crystallized carbonate of sodium (Na_2CO_3, $10H_2O$ = 286), &c. And if 63 parts of oxalic acid be dissolved in 100 volumes of water, the stated weights of these various salts should be exactly neutralized by such a solution. 143 parts of crystallized carbonate of sodium, for instance, should, if pure, be exactly neutralized by the 100 volumes of oxalic acid solution; and if a less number of volumes is required, the salt is so much per cent. impure. 143 parts by weight of a commercial sample of carbonate of sodium (common washing-"soda") requiring only 97 of the standard oxalic acid solution is thus shown to contain 97 per cent. of pure carbonate of sodium, the remainder being impurities. Further, the strength of solutions of ammonia, soda, potash, and lime may be accurately determined by adding them gradually, from a burette, to a solution containing oxalic acid in known quantity, until exact neutralization is effected. If the quantity of oxalic acid be 53 parts by weight, then the parts by volume of the solutions added contain, of potash (KHO) 56 parts by weight, of soda (NaHO) 40, of ammonia (AmHO) 35 parts, of slaked lime (Ca2HO) 37, anhydrous lime (CaO) 28, &c. The strength of an alkaline solution (or, in other words, the proportion required to effect neutralization of 100 volumes of the acid solution) having once been determined

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and decided by authority (B. P. *e. g.*), that quantity may always be expected to take 100 volumes of the oxalic acid liquid; if less is required, the alkaline liquid is so much per cent. weak.

The exact point of neutralization of acid or alkaline liquids is experimentally ascertained by litmus paper, or, more generally, infusion of litmus, which is turned red by the slightest amount of free acid, and blue by alkali.

Standard Solution of Oxalic Acid.

(Crystallized Oxalic Acid, $H_2C_2O_4$, $2H_2O = 126$.)

On account of the bivalent character of the oxalic radical and the univalent character of most of the metals contained in the salts which are estimated by oxalic acid, it is convenient to take half the molecular weight of the acid for experiments, with the whole of the molecular weights of salts of univalent basylous radicals. The oxalic acid must be pure, leaving no ash when a gramme or so is heated to redness in a porcelain or platinum crucible; it must also be quite dry but not effloresced.

Place 63 grammes of the crystals in a litre flask, add distilled water and shake till dissolved, diluting until the solution, at about 60° F., has an exact volume of 1 litre. Preserve in a stoppered bottle.

100 cubic centimetres of this solution contain $\frac{1}{20}$ of the molecular weight of oxalic acid in grammes, and will neutralize $\frac{1}{20}$ of the molecular weight in grammes of a salt containing one atom of certain bivalent metals (Ca2HO &c.), or two atoms of univalent metals (Na_2CO_3 &c.), or $\frac{1}{10}$ of the molecular weight in grammes of salts containing one atom of univalent radicals ($KHCO_3$ &c.).

The following officinal substances are tested with this solution:—

	Grammes weight of substance.		C. c. of vol. sol.
Ammonia, solution of	17·00	=	100·0
„ strong solution of..	5·23	=	100·0
Ammonium, carbonate of	5·90	=	100·0

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	Grammes weight of substance.		C. c. of vol. sol.
Borax	19·10	=	100·0
Lead, acetate of	9·50	=	50·0
„ sol. of subacetate of	51·02	=	100·0
Lime, aqueous solution of	438·00	=	20·0
„ saccharated sol. of	45·30	=	25·0
Potash, caustic	5·60	=	90·0 to 100·0
„ solution of	48·02	=	50·0
Water, effervescing	292·00	=	10·0
Potassium, acid carbonate of	5·00	=	50·0
„ „ tartrate of	18·80	=	100·0
„ carbonate of	8·30	=	98·0 to 100·0
„ citrate of	10·20	=	100·0
„ tartrate of	11·30	=	100·0
Soda, caustic	4·00	=	90·0 to 100·0
„ solution of	48·72	=	50·0
Water, effervescing	246·07	=	10·0
Sodium, acid carbonate of	8·40	=	100·0
„ and potassium, tart. of	14·10	=	100·0
„ carbonate of	14·30	=	96·0 to 100·0

The solutions of ammonia require only the addition of a little litmus, and then the acid cautiously added until the last drop turns the liquid red. The amount of acid used previously to the addition of the portion that reddened the litmus indicates the proportional purity of the alkaline liquid. The quantity of ammonia (NH_4HO) or ammoniacal gas (NH_3) in the solutions is readily ascertained by calculation thus: 100 c. c. of the acid solution have been used; these contain $\frac{1}{20}$ of the molecular weight of oxalic acid in grammes = 6·3, and have neutralized $\frac{1}{10}$ of the molecular weight of ammonia in grammes = 3·5 (or 1·7 of NH_3); 5·23 parts, by weight, of strong solution of ammonia contain, therefore, 3·5 of ammonia (AmHO or 1·7 of ammoniacal gas

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(NH_3); hence 100 parts of strong solution of ammonia contain 67 of the hydrate or 32·5 of the gas.

The carbonate of ammonium should be dissolved in 30 or 40 c. c. of distilled water, infusion of litmus added, the standard oxalic acid solution allowed to flow in until the well-stirred liquid assumes a purple hue (due to the influence of carbonic acid on the litmus), the whole gently warmed to promote evolution of carbonic acid gas, more standard acid then dropped in until the liquid again becomes purple, heat once more applied, and the operation continued until the last drop of acid turns the solution red; the height of the column of liquid in the burette before the last drop escaped represents the true amount of standard solution used, and hence the percentage of real carbonate of ammonium in the specimen on which the experiment was performed. The solution must be heated with care, or ammonia will escape.

The borax should be dissolved in several ounces of distilled water.

The solutions of the acetates of lead in distilled water must be well stirred after each addition of acid. The action is complete when the last drop of acid produces no more precipitate (oxalate of lead). The solutions of lime require similar treatment.

Solid caustic potash or soda are never met with in a state of chemical purity, but should not contain less than 90 per cent. of the hydrates of potassium or sodium. The standard acid is added to an aqueous solution of the hydrate, the termination of the action between the alkali and acid being observed by aid of litmus.

If carbonic acid be present, the mixture must be gently boiled before a final reading of the amount of acid added is taken.

The alkaline carbonates are often moist, and include traces of sulphates, chlorides, and silicates, but are sufficiently pure if containing, in the case of carbonate of potassium, 98 per cent., and carbonate of sodium 96 per cent., of the respective crystalline

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salts. The volumetric manipulations with these salts are similar to those for carbonate of ammonium.

One molecule of tartrate of potassium, or two of the acid tartrate, yield one of carbonate when burnt, two molecules of citrate yielding three of carbonate under the same circumstances. A volumetric estimation of the amount of carbonate thus produced affords indirect means of quantitatively determining the purity of the original salts.

The foregoing processes are often spoken of as those of *alkalimetry* (the measurement of alkalies).

Solution of litmus is prepared by digesting the commercial fragments in about fifteen or twenty times their weight of water for a few hours, decanting, dividing into two equal portions, adding acid to one till it is faintly red, then pouring in the other, and mixing. The solution may be kept in a stoppered bottle, but occasionally exposed to the air. It should never be filtered, but gradually allowed to deposit.

Standard sulphuric acid may be used in the place of oxalic acid if the latter cannot readily be obtained in a state of purity, 100 c.c. of the liquid containing $\frac{1}{20}$ of the molecular weight of the pure acid in grammes. It is prepared by diluting oil of vitriol with from three to four times its bulk of distilled water, ascertaining how much of the acid liquid is required to exactly neutralize $\frac{1}{20}$ of the molecular weight of pure carbonate of sodium, taken in grammes (5·3), and adding water until the observed volume of acid is increased to 100 c. c. Pure anhydrous carbonate of sodium (Na_2CO_3) is obtained by heating the pure acid carbonate to dull redness in a platinum or porcelain crucible for about a quarter of an hour. The commercial acid carbonate should be tested for chlorides and sulphates, which are usually present in small quantities. Two or three hundred grammes may be purified by washing, first with a solution of acid carbonate of sodium and then

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cold distilled water until all trace of impurity has disappeared, drying over a water-bath, and then igniting to convert into carbonate.

Other quantities of salts than those stated in the foregoing and following Tables may be employed in volumetric determinations, calculation giving any desired form to the experimental results, the expert analyst thus saving much time and material. In the case of substances which are liable to alter by exposure to air, it is important that a selected quantity should be quickly weighed, rather than selected weights be accurately balanced by material, the former operation occupying much the shorter time.

Salts other than the officinal may be quantitatively analyzed by the volumetric solutions of the Pharmacopœia, slight modifications of manipulation even enabling the processes to be adapted to fresh classes of salts. Ample instructions for extending operations in this manner will be found in Sutton's 'Handbook of Volumetric Analysis.'

ESTIMATION OF ACIDS.

In the previous experiments a known amount of an acid has been used in determining unknown amounts of alkalies. In those about to be described a known amount of an alkali is employed in estimating unknown amounts of acids. The alkaline salt selected may be a hydrate or a carbonate; but the former is to be preferred; for the carbonic acid, set free when a strong acid is added to a carbonate, interferes to some extent with the indications of alkalinity, acidity, or neutrality afforded by litmus. The alkali most convenient for use is soda, a solution of which has probably already been made the subject of experiment in operations with the standard solution of oxalic acid.

Standard Solution of Soda.

(Hydrate of Sodium, $NaHO = 40$.)

100 c. c. of the standard solution of oxalic acid are placed in a beaker with a little litmus, the tube in which the acid was measured rinsed out, and the washings poured into the beaker. A strong solution of caustic soda is poured through the tube to remove water adhering to the tube and float, and the tube filled to 0 with the alkaline liquid. The solution of

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soda is cautiously allowed to flow into the beaker until exact neutrality is obtained, the quantity noted, and to every similar quantity of the whole bulk of the solution of soda water added until the liquid measures 100 parts. If, for example, 93 c. c. of solution of soda have neutralized the 100 c. c. of acid, then 7 c. c. of distilled water must be added to 93 c. c. of the soda solution, or 70 to 930 to make a litre. A sum of simple proportion will show to what extent any other quantity is to be diluted. Thus, if the bulk of soda solution remaining measures, say, 900 c. c., its volume must be augmented to 967·7 c. c.; for if 93 are to be diluted to 100, 900 must be diluted to 967·7.

100 c. c. of the soda solution contain $\frac{1}{10}$ of the molecular weight, taken in grammes (4·0), of pure hydrate of sodium, and will neutralize an equivalent quantity of any acid. That is, 100 c. c. will neutralize $\frac{1}{10}$ of the molecular weight in grammes of an acid containing one atom of any univalent acidulous radical, $\frac{1}{20}$ of the molecular weight in grammes of an acid containing one atom of any bivalent acidulous radical, or $\frac{1}{30}$ of the molecular weight in grammes of an acid containing one atom of any trivalent acidulous radical.

The following officinal acids are tested with this solution :—

	Grammes weight of substance.		C. c. of vol. sol.
Acid, acetic	18·20	=	100·0
„ „ diluted	70·29	=	50·0
„ „ glacial	6·00	=	99·0
„ citric	7·00	=	100·0
„ hydrochloric	11·48	=	100·0
„ „ diluted	34·50	=	100·0
„ nitric	9·00	=	100·0
„ „ diluted	36·13	=	100·0
„ nitro-hydrochloric, diluted	38·30	=	100·0
„ sulphuric	5·06	=	100·0
„ „ aromatic	36·65	=	100·0
„ „ diluted	35·90	=	100·0
„ tartaric	7·50	=	100·0

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In volumetrically estimating the strength of acids by an alkali, the indicator of neutrality is the same as that used in testing alkalies by an acid, namely litmus.

Pure acetates, citrates, tartrates, and some other organic salts have an alkaline action on litmus, but not to an important extent. If the soda solution be added to acetic, citric, or tartaric acids, containing litmus, until the liquid is fairly blue, the operator will obtain trustworthy results.

Six grammes of pure glacial acetic acid are neutralized by 100 c. c. of the standard solution of soda. But acid of this degree of purity is extremely difficult of preparation. The commercial acid contains only 1 per cent. of water, and is sufficiently pure for use in medicine.

The operations for the quantitative analysis or measurement of acids are often collectively spoken of under the name of *acidimetry*. They admit of considerable extension. (See the work previously cited.)

ESTIMATION OF ACIDULOUS RADICALS PRECIPITATED BY NITRATE OF SILVER.

The purity of many salts, and the strength of their solutions may be determined by this process; but at present only three officinal substances (namely diluted hydrocyanic acid, bromide of potassium, and arseniate of sodium) are quantitatively analyzed by standard solution of nitrate of silver. The reactions on which the success of the process depends are expressed in the following equations:—

$$\begin{cases} AgNO_3 + 2NaCy = NaCyAgCy + NaNO_3, \\ NaCyAgCy + AgNO_3 = 2AgCy + NaNO_3; \end{cases}$$

$$KBr + AgNO_3 = AgBr + KNO_3;$$

$$Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3.$$

Standard Solution of Nitrate of Silver.

(Nitrate of Silver, $AgNO_3 = 170$.)

Dissolve 17 grammes of crystals of pure nitrate of silver in

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1 litre of water. 100 c. c. of this solution contain $\frac{1}{100}$ of the molecular weight in grammes of nitrate of silver, and will decompose an equivalent quantity of a salt of any acidulous radical yielding silver compounds insoluble in water.

	Grammes weight of substance.		C. c. of vol. sol.
Acid, hydrocyanic, diluted	27·00	=	100·0
Potassium, bromide of.....	1·19	=	100·0
Sodium, arseniate of (dry)	·62	=	100·0

Diluted hydrocyanic acid is converted into cyanide of sodium by adding caustic soda until, after stirring, litmus shows that the liquid has an alkaline reaction. The nitrate-of-silver solution is then allowed to flow in gradually, until, after thorough agitation, a slight permanent turbidity remains. When this occurs, the quantity of nitrate of silver added represents exactly half the amount of real hydrocyanic acid present in the diluted preparation. Thus the 100 c. c. of standard solution contain $\frac{1}{100}$ of the molecular weight in grammes of nitrate of silver (=1·7); this would ordinarily correspond, in a case of complete decomposition, to $\frac{1}{100}$ of the molecular weight in grammes of hydrocyanic acid (= ·27); 27 grammes of the diluted acid, the quantity employed in the experiment, apparently contain therefore ·27 gramme of real acid, equal to 1 per cent. A glance at the equation shows that at the moment cyanide of silver begins to be precipitated, only half of the cyanogen has been converted into cyanide of silver; the quantity of acid indicated by the amount of nitrate added must therefore be doubled for the correct percentage (= 2).

Bromide of potassium is dissolved in distilled water in a beaker, and the standard solution added until, after agitation of the liquid and subsidence of the bromide of silver, a drop of the solution of nitrate of silver gives no more precipitate.

Arseniate of sodium ($Na_2HAsO_4,7H_2O$) must be dried at

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300° F. before weighing. It is thus reduced to a definite anhydrous salt (Na_2HAsO_4), losing, if pure, 40·38 per cent. of water. The weighed residue is dissolved in distilled water, and treated as described in the previous paragraph.

ESTIMATION OF SUBSTANCES READILY OXIDIZED.

Any substance which quickly absorbs a definite amount of oxygen may be quantitatively tested by ascertaining how much of an oxidizing agent of known power must be added to a given quantity before complete oxidation is effected. The oxidizing agents employed for this purpose in the British Pharmacopœia are iodine and the red chromate of potassium; permanganate of potassium is often used for the same purpose. Iodine acts indirectly, by taking hydrogen from water and liberating oxygen; the red chromate of potassium directly, by the facility with which it yields three-sevenths of its oxygen.

Standard Solution of Iodine.

(Iodine, I=127.)

Prepare pure iodine by mixing the commercial article with about a fourth of its weight of iodide of potassium and subliming. Sublimation may be effected by gently heating the mixture in a beaker, the mouth of which is closed by a funnel; the iodine vapour condenses on the funnel, while fixed impurities are left behind, and any chlorine which the iodine may contain is absorbed by the iodide of potassium, an equivalent quantity of iodine being liberated. Small quantities may be similarly treated between two watch-glasses, placed edge to edge. Any trace of moisture in the resublimed iodine is removed by exposure for a few hours under a glass shade near a vessel containing oil of vitriol.

Place 12·7 grammes of pure iodine and about 18 grammes of pure iodide of potassium (the best solvent of iodine) in a litre flask, add a small quantity of water, and agitate until the iodine is dissolved, dilute to 1 litre. 100 c. c. of this solution con-

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tain $\frac{1}{100}$ of the atomic weight of free iodine in grammes, and, water being present, will cause the oxidation of $\frac{1}{200}$ of the molecular weight of sulphurous acid (H_2SO_3) in grammes (=·41), or $\frac{1}{200}$ (=·32) of sulphurous acid gas (SO_2), sulphuric acid being formed. 100 c. c. will also oxidize $\frac{1}{200}$ of the molecular weight of arsenious acid (H_3AsO_3) in grammes, or $\frac{1}{400}$ of the molecular weight of common white arsenic (As_2O_3) in grammes (=·495), arsenic acid (H_3AsO_4) being produced. The reactions are expressed in the following equations:—

$$I_2 + H_2O + H_2SO_3 = 2HI + H_2SO_4.$$
$$I_2 + 2H_2O + SO_2 = 2HI + H_2SO_4.$$
$$I_2 + H_2O + H_3AsO_3 = 2HI + H_3AsO_4.$$
$$2I_2 + 5H_2O + As_2O_3 = 4HI + 2H_3AsO_4.$$

The following officinal substances are tested with the standard solution of iodine:

	Grammes weight of substance.		C. c. of vol. sol.
Acid, solution of sulphurous	3·47	=	100
Arsenic, in mass	0·495	=	100
„ in alkaline sol. (*Liquor Arsenicalis*)	54·64	=	100
„ in acid sol. (*Liq. Arsen. Hydrochl.*)	54·64	=	100

The solution of sulphurous acid is diluted with three-fourths of a litre of water, and the iodine solution added until a slight permanent brown tint is produced, showing the presence of free iodine. A better indication of the termination of the action is afforded by mucilage of starch, which gives a blue colour with the slightest trace of iodine. $\frac{1}{200}$ of the molecular weight of sulphurous acid (H_2SO_3) in grammes is 0·41; if 3·47 grammes of the solution contain 0·41 of the acid, 100 of the solution will be found to contain 11·8. By a similar calculation the officinal solution may be shown to contain, or, rather, yield 9·22 per cent. of sulphurous acid gas (SO_2).

If the sulphurous acid be diluted to a less degree than 0·5 per

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cent., some of the sulphuric acid formed will again be reduced to sulphurous acid, with liberation of iodine.

The arsenic is dissolved in boiling water by help of about two grammes of acid carbonate of sodium. When the liquid is quite cold, mucilage of starch is added, and the iodine solution allowed to flow in until, after well stirring, a permanent blue colour is produced.

The arsenical solution already containing carbonate of potassium requires only about one and a half gramme of acid carbonate of sodium for the neutralization of the arsenious acid. After boiling and cooling, starch and the iodine solution are added as before.

The solution of arsenic in dilute hydrochloric acid requires about three grammes of acid carbonate of sodium, if 54 or 55 grammes of solution be the quantity employed. After boiling for a few minutes and cooling, the starch and iodine are added.

These arsenical solutions contain ·9 per cent. of arsenic.

Standard Solution of Red Chromate of Potassium.

(Red Chromate of Potassium, K_2CrO_4, $CrO_3=295$.)

One molecule of red chromate of potassium in presence of an acid, under favourable circumstances, yields four atoms of oxygen to the hydrogen of the acid, leaving three available either for direct oxidation or for combination with the hydrogen of more acid, an equivalent proportion of acidulous radical being liberated for any required purpose.

When used as a volumetric agent, the red chromate always yields the whole of its oxygen to the hydrogen of the accompanying acid, a corresponding quantity of acidulous radical being set free—four-sevenths of this radical immediately combining with the potassium and chromium of the red chromate, three-sevenths becoming available. Ferrous may thus be converted into ferric salts with sufficient rapidity and exactitude to admit of the estimation of an unknown quantity of iron by a known quantity of the red chromate. As one atom of the liberated acidulous radical will convert two molecules of ferrous into one of ferric salt,

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one molecule of red chromate causes six of ferrous to become three of ferric, as shown in either of the following equations :—

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

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

These equations indicate that, in presence of excess of acid, 295 parts (the molecular weight) of red chromate of potassium will convert 1668 parts of crystallized ferrous sulphate, $6(FeSO_4, 7H_2O = 278)$, or an equivalent quantity of ferrous chloride ($6FeCl_2$), ferrous carbonate ($6FeCO_3$), ferrous arseniate ($2Fe_3As_2O_8$), ferrous phosphate ($2Fe_3P_2O_8$), or iron itself ($3Fe_2$), into ferric salt. If these parts be taken in grammes, $\frac{1}{200}$ of the stated amounts will be found to be convenient quantities for experiment.

Dissolve 14·75 grammes of red chromate of potassium in one litre of distilled water. 100 c. c. of this solution contain $\frac{1}{200}$ of the molecular weight of the salt in grammes, and will cause the conversion of $\frac{1}{200}$ of the weight of 6 atoms of iron in grammes, or an equivalent quantity of the lower salts of iron, from the ferrous to the ferric state.

The solution is used in determining the strength of the following officinal ferrous preparations. It is known that the whole of the ferrous has been converted to ferric salt when a small drop of the liquid placed in contact with a drop of a very dilute solution of ferridcyanide of potassium, on a white plate, ceases to strike a blue colour.

	Grammes weight of substance.		C. c. of vol. sol.
Iron, arseniate of	2·94	=	25
„ magnetic oxide of	2·41	=	10
„ phosphate of	2·00	=	25
„ saccharated carbonate of	3·82	=	50

The several compounds are dissolved in excess of hydrochloric acid diluted with water, and the standard solution then dropped

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in. It will be found that the proportion of carbonate of iron in the saccharated compound, as indicated by the above numbers, is 45·5 in 100. This is the percentage that would be present if the compound were anhydrous and unoxidized, conditions never obtained in practice.

The use of these volumetric solutions in quantitative analysis admits of great extension.

ESTIMATION OF SUBSTANCES READILY DEOXIDIZED.

Any substance which quickly yields a definite amount of oxygen may be quantitatively tested by ascertaining how much of a deoxidizing agent of known power must be added to a given quantity before complete deoxidation is effected. The compounds which may be used as absorbers of oxygen—deoxidizers or reducing agents, as they are commonly termed—are, hyposulphite of sodium, sulphurous acid, ferrous sulphate, oxalic acid, arsenious acid, &c. The first-named is officinally employed; it is only used in the estimation of free iodine, and, indirectly, of chlorine and chlorinated compounds. Iodine and chlorine are regarded as oxidizing agents, because their great affinity for hydrogen enable them to become powerful indirect oxidizers in presence of water.

Standard Solution of Hyposulphite of Sodium.

(Crystallized Hyposulphite of Sodium, $Na_2S_2O_3, 5H_2O=248$.)

Dissolve about 30 grammes of hyposulphite of sodium in a litre or less of water. Fill a burette with this solution and allow it to flow into a beaker, containing exactly 100 c. c. of the volumetric solution of iodine until the brown colour of the iodine is just discharged—or, starch being added, until the blue iodide of starch is decolorized. Note the number of c. c. of hyposulphite solution required, and to the bulk of the solution add water, so that 2·48 grammes of hyposulphite of sodium shall be contained in every 100 c. c.

When iodine and hyposulphite of sodium react, two atoms of iodine remove two of sodium from two molecules of the hypo-

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sulphite, tetrathionate of sodium being formed, as indicated in the following equation:—

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

As, therefore, 100 c. c. of the iodine solution contain $\frac{1}{100}$ of the atomic weight of iodine in grammes, 100 c. c. of the standard solution of hyposulphite of sodium will contain $\frac{1}{100}$ of the molecular weight of the salt in grammes, and will show the existence of $\frac{1}{100}$ of the atomic weight of iodine in grammes in any quantity of a liquid normally containing free iodine, or iodine liberated by an equivalent quantity of free chlorine.

This solution is employed in the British Pharmacopœia for quantitatively testing the following substances:—

	Grammes weight of substance.		C. c. of vol. sol.
Chlorine, solution of	29·26	=	50
Iodine	1·27	=	100
Lime, chlorinated.....	1·17	=	100
„ solution of chlorinated	6·00	=	50
Soda, solution of chlorinated	7·00	=	50

Owing to the volatility of chlorine and iodine, and the readiness with which they attack the metals of which balances are made, it is not desirable to experiment on stated weights of substances containing these elements. A small stoppered bottle or tube containing the material may be counterpoised, and a convenient quantity removed for analysis, the precise amount taken being ascertained by again weighing the bottle.

The iodine may be dissolved in water containing about a gramme and a half of iodide of potassium, a salt giving no reaction with hyposulphite of sodium.

The solution of chlorine is added to water containing excess of iodide of potassium (about a gramme and a third); a quantity of iodine, equivalent to the amount of chlorine present, is thus liberated. The hyposulphite solution is then dropped in.

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The chlorinated lime is mixed with about a fifth of a litre of water containing excess of iodide of potassium (3·5 grms.) and acidulated with hydrochloric acid. The available oxygen of the chlorinated lime liberates chlorine from an equivalent quantity of hydrochloric acid; and this, with the available chlorine of the chlorinated lime, sets free an equivalent amount of iodine from the iodide of potassium. The hyposulphite and iodine reacting show the direct and indirect oxidizing power of the chlorinated lime; it should correspond to 30 per cent. of chlorine.

The solution of chlorinated lime is mixed with about a fifth of a litre of water containing a couple of grammes of iodide of potassium, and ten or twelve c. c. of hydrochloric acid. The hyposulphite solution is then added from a burette until the colour of the liberated iodine is just discharged. The solution of chlorinated soda is similarly treated.

In these experiments the blue colour formed on the addition of mucilage of starch to the liquids will be found to be a more delicate indicator of the termination of reactions than the brown tint of the iodine.

Standard solutions used in volumetric analysis are often described as normal, decinormal, and centinormal. A normal solution (N) contains in every litre a molecule of the salt in grammes, a decinormal solution is one tenth ($\frac{N}{10}$), and a centinormal ($\frac{N}{100}$) one hundredth the strength of a normal solution.

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GRAVIMETRIC ANALYSIS.

ESTIMATION OF METALS.

POTASSIUM.

This element is usually estimated in the form of double chloride of potassium and platinum. Qualitative analysis having proved the presence of potassium and other elements in a substance, a small quantity of the material is accurately weighed, dissolved, and the other elements removed by appropriate reagents; the precipitates are well washed, in order that no trace of the potassium salt shall be lost, the resulting liquid concentrated over a water-bath to avoid loss that would occur mechanically during ebullition, hydrochloric acid added if necessary, solution of perchloride of platinum poured in, and evaporation continued to dryness; excess of the perchloride is then dissolved by adding spirit of wine containing half its bulk of ether (a liquid in which the double chloride is insoluble), the mixture carefully poured on to a tared and dried filter, washed with the spirit till every trace of free perchloride of platinum is removed, the whole dried and weighed; from the resulting amount the proportion of potassium, or equivalent quantity of a salt of potassium, is ascertained by calculation.

From this short description it will be seen, first, that the chemistry of quantitative is the same as that of qualitative analysis; and second, that the principle of gravimetric is the same as that of volumetric quantitative analysis; namely, the combining proportions of substances being known, unknown quantities of elements may be ascertained by calculation from known quantities of their compounds.

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Filtering-paper should be of the kind known as *Swedish*, the texture of which is of the requisite degree of closeness, and its ash small in amount. A large number of circular pieces of one size, six to eight centimetres in diameter, should be cut ready for use. In delicate experiments, where a precipitate on a filter has to be heated and the paper consequently burnt, the weight of the ash of the filter must be deducted from the weight of the residue. The ash is estimated by burning ten or twenty of the cut filters. These are folded into a small compass, a portion of a piece of platinum wire twisted a few times round the packet, so as to form a cage, the whole held by the free end of the wire over a weighed porcelain crucible placed in the centre of a sheet of glazed paper, the bundle ignited by a spirit-lamp or smokeless gas-flame, the flame allowed to impinge against the charred mass till it falls into the crucible below, any stray fragments on the sheet carefully shaken into the crucible, the latter placed over a flame till carbon has all burnt off and nothing but ash remains, the whole cooled, weighed, and the weight of the crucible deductcd; the weight of the residue divided by the number of pieces used gives the average amount of ash in each filter.

A pair of Weighing-tubes, for holding dried filters during operations at the balance, may be made from two test-tubes, one fitting closely within the other. About five centimetres of the closed end of the outer and seven of the inner are cut off, by leading a crack round the tube with a pencil of incandescent charcoal, and the sharp edges fused in the blowpipe-flame. A filter, or filter and precipitate, after drying, is quickly folded and placed in the narrower tube, the mouth of which is then closed by the wider tube.

The Washing-bottle, holding the alcohol and ether, is simply a common bottle, through the cork of which a small tube passes. The outer end of the tube should be sufficiently narrowed to enable it to deliver a very fine stream of the liquid. The bottle

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being inverted, the warmth of the hand expands the air and vapour to a sufficient extent to force out the liquid.

The ordinary washing-bottle for quantitative operations should be formed of a flask in which water may be boiled. Two tubes pass through holes in the cork, the one reaching to the bottom of the flask within, externally bent to a slightly acute angle, and its outer extremity drawn to a capillary opening, the other bent to a slightly obtuse angle, the inner arm terminating just within the bottle. Air blown into the bottle through the short tube by the lungs forces water out at the capillary orifice.

A Water-oven is the best form of drying apparatus. It is a small square copper vessel, jacketed on five sides and having a door on the sixth; water is poured into the space between the inner and outer casing, and the whole placed over a gas-lamp or other source of heat, moist air and steam escaping by appropriate apertures. Higher temperatures than the boiling-point of water may be obtained by using oil or paraffin instead of water, inserting a thermometer in the fat. The apparatus may be purchased of any maker of chemical instruments.

Pure distilled water must be used in all quantitative determinations.

Note.—In practising the operations of quantitative analysis, experiments should at first be conducted on definite salts of known composition. The accuracy of results may then be tested by calculation.

Select two or three crystals of pure nitrate of potassium, powder them in a clean mortar, dry the powder by gently heating in a porcelain crucible over a flame for a few seconds, place about a couple of decigrammes (0·2 gr.) of the powder in a counterpoised watch-glass, accurately weigh the selected quantity, transfer to a small dish, letting water from a wash-bottle flow over the watch-glass and run into the dish, warm the dish till the nitrate is dissolved, acidulate with hydrochloric acid, add

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excess of aqueous solution of perchloride of platinum (a quantity containing about 0·4 of solid salt), evaporate to dryness over a water-bath. While evaporation is going on place a filter and the weighing tubes in the water-oven, exposing them to a temperature of 212° F. for about half an hour; fold the filter and insert it in the tubes, place them on a plate under a glass shade, and when cold accurately note their weight. Arrange the weighed filter in a funnel over a beaker. Transfer the dried and cooled platinum salt from the dish to the filter by moistening the residue with the mixture of alcohol and ether and, when the salt is loosened, pouring the contents of the dish into the paper cone. Any salt still adhering may be freed by the finger, which, together with the dish, should be washed in the stream of spirit, the rinsings at once flowing into the filter. The filtrate should have a yellowish-brown colour, due to the excess of perchloride of platinum. If it is colourless, an insufficient amount of perchloride has been added, and the whole operation must be repeated. The washed precipitate and filter are finally dried in the water-oven, folded and placed in the weighing-tubes, the drying continued until the whole, when cold, ceases to lose weight, and the weight noted.

Analytical memoranda in the note-book may have the following form:—

Watch-glass and substance	
Watch-glass	
Substance..	

Weighing-tubes, filter, and pt. salt	
Weighing-tubes and filter	
$PtCl_4, 2KCl$..	

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The calculations in this instance are simple:—

$$\text{If} \left\{ \begin{matrix} 2KNO_3 \\ =202 \end{matrix} \right\} \text{produce} \left\{ \begin{matrix} PtCl_4, 2KCl \\ =489 \end{matrix} \right\}$$

$$\text{then} \left\{ \begin{matrix} \text{the weight of} \\ KNO_3 \\ \text{taken} \end{matrix} \right\} \text{will produce} \left\{ \begin{matrix} x = \text{weight of} \\ PtCl_4, 2KCl \\ \text{obtained.} \end{matrix} \right\}$$

The results of calculation and experiment should be identical. A table of atomic weights, from which to find molecular weights, is given at the end of the volume.

A Water-bath for the evaporation of liquids at temperatures below 212° F. is an iron, tin, or earthenware pan, the mouth of which can be narrowed by iron or tin diaphragms of various sizes, and having orifices adapted to the diameters of the evaporating-dishes.

Platinum residues &c. should be preserved, and the metal recovered from them from time to time (*vide* p. 158).

Hot alcohol decomposes perchloride of platinum, the metal being thrown out of solution in a finely divided form, known as *platinum black*; hence only aqueous solutions of the salt must be used where heat is employed. Hence, also, in washing out excess of perchloride of platinum from the double chloride of platinum and potassium by spirit, the application of heat must be avoided.

SODIUM.

Sodium is usually estimated as sulphate. Accurately counterpoise, and take the weight of a porcelain crucible and lid, place within about ·3 of pure rock-salt, again noting the weight. Add rather more strong sulphuric acid than may be considered sufficient to convert the chloride into acid sulphate of sodium. Heat the crucible gradually, the flame being first directed against the side of the crucible to avoid violent ebullition, until fumes of sulphuric acid cease to be evolved, towards the end of the operation dropping in one or two fragments of carbonate of ammonium to facilitate complete decomposition. When cold, weigh

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the crucible and contents. The weight of the crucible having been deducted, the amount of sulphate obtained should be the exact equivalent of the quantity of chloride of sodium employed.

$$\underbrace{2NaCl}_{117} + H_2SO_4 = \underbrace{Na_2SO_4}_{152} + 2HCl.$$

AMMONIUM.

Salts of ammonium are, for purposes of quantitative analysis, generally converted into the double chloride of ammonium and platinum ($PtCl_4 2NH_4Cl$), the details of manipulation being the same as those observed in the case of potassium. About 0·15 grm. of pure, white, dry chloride of ammonium may be taken for experiment.

COMPOSITION OF THE PLATINUM SALT.

	In 1 molecule.		In 100 parts.
Pt	198	.... 198	44·30
Cl_6	35·5 × 6	.... 213	47·64
N_2	14·0 × 2	.... 28	6·27
H_8	1·0 × 8	.... 8	1·79
		447	100·00
$PtCl_4$	340	.... 340	76·06
$2NH_4Cl$ ..	53·5 × 2	.... 107	23·94
		447	100·00

The proportion of nitrogen, ammonium, or chloride of ammonium in the double chloride may also be ascertained from the weight of platinum left on igniting the double chloride; for this purpose heat must be applied slowly, or platinum would be mechanically carried off with the gaseous products of decomposition.

BARIUM.

Barium is estimated in the form of anhydrous sulphate of barium ($BaSO_4$).

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Dissolve 0·3 or 0·4 of pure crystallized and dried chloride or nitrate of barium in about half a litre of water in a beaker, heating to incipient ebullition, and slightly acidulating with hydrochloric or nitric acid. Add diluted sulphuric acid (prepared some days previously, so that sulphate of lead may have deposited) so long as a precipitate forms, keep the mixture hot for some time, set aside for half an hour, pass the supernatant liquid through a filter, gently boil the residue two or three times with more water; finally collect the precipitate on the filter, removing adherent particles from the beaker by the finger, and cleansing by a stream of hot water from the wash-bottle. The precipitate must be washed with hot water until the filtrate ceases to turn litmus-paper red, or give any cloudiness when tested with chloride of barium. The filter and sulphate of barium having thoroughly drained is dried in a warm place, commonly by supporting the funnel in an inverted bottomless beaker over a sand-bath or hot plate.

The sulphate of barium is now removed from the filter, heated to drive off every trace of moisture, and weighed. This is accomplished by placing a weighed porcelain crucible (and cover) on a sheet of glazed paper, holding the filter over it, and carefully transferring the precipitate; the sides of the filter are then gently rubbed together and detached powder dropped into the crucible, the paper folded, encased in two or three coils of one end of a platinum wire and burnt, ash and any particles in the sheet of paper added to the sulphate of barium, the crucible exposed over a flame till its contents are quite white, covered, cooled, and weighed.

	Formulæ.	Molecular weights.
Chloride of barium	$BaCl_2$	208
Nitrate of barium	$Ba2NO_3$	261
Sulphate of barium	$BaSO_4$	233

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Composition of Sulphate of Barium.

		In one molecule.	In 100 parts.
Ba	137	137	58·80
S	32	32	13·73
O_4	16×4	64	27·47
		233	100·00

In these experiments it is unnecessary to take filter-ash into account. Faults of manipulation cause far greater errors.

CALCIUM.

Calcium is usually thrown out of solution in the form of oxalate, the precipitate ignited, and the resulting carbonate weighed.

Dissolve 0·3 or 0·4 of dried colourless crystals of calc-spar in about a third of a litre of water acidulated with hydrochloric acid, heat the solution to near the boiling-point, add excess of solution of oxalate of ammonium, then ammonia until, after stirring, the liquid smells strongly ammoniacal; set aside in a warm place for twelve hours. Carefully pour off the supernatant liquid, passing it through a filter; add hot water to the precipitate, set aside for half an hour, again decant, and, after once more washing, transfer the precipitate to the filter, allowing all contained fluid to pass through before a fresh portion is added. Wash the precipitate with hot water, avoiding a rapid stream, or the precipitate may be driven through the pores of the paper. Dry, transfer to a weighed crucible, and incinerate, as described for sulphate of barium, and slowly heat the precipitate till the bottom of the crucible is just visibly red in a dark room. As soon as the residue is white, or only faintly grey, remove the lamp, cool, and weigh.

The resulting carbonate of calcium should have the same

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weight as the calc-spar from which it was obtained. If loss has occurred, carbonic acid gas has probably escaped. In that case moisten the residue with water, and after a few minutes test the liquid with red litmus or turmeric paper; if an alkaline reaction is noticed, it is due to the presence of caustic lime. Add a small lump of carbonate of ammonium, evaporate to dryness over a water-bath, and again ignite, this time being careful not to go beyond the prescribed temperature. The treatment may, if necessary, be repeated.

MAGNESIUM.

The light or heavy carbonate of magnesium of pharmacy may be estimated by heating a weighed quantity to redness in a porcelain crucible. If it has the composition indicated by the formula given in the British Pharmacopœia ($3MgCO_3$, Mg2HO, $4H_2O$), it will yield 42 per cent. of magnesia. According to that work, the purity of even sulphate of magnesium ($MgSO_4$, $7H_2O$) may be determined by boiling a weighed quantity with excess of carbonate of sodium, collecting the precipitate, washing, drying, igniting, and weighing the resulting magnesia (MgO). The crystallized sulphate should yield 16·26 per cent. of oxide.

The general form in which magnesium is precipitated is as phosphate of ammonium and magnesium ($MgNH_4PO_4$, $6H_2O$); this, by heat, is converted into pyrophosphate of magnesium ($Mg_2P_2O_7$).

Accurately weigh a small quantity (0·4 to 0·5) of pure dry crystals of sulphate of magnesium, dissolve in two to three hundred cubic centimetres of cold water in a beaker, add chloride of ammonium, ammonia, and phosphate of sodium or ammonium, agitate with a glass rod (without touching the sides of the vessel, or crystals will firmly adhere to the rubbed portions), and set aside for twelve hours. Collect on a filter, wash the precipitate

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with water containing a tenth of its volume of the strongest solution of ammonia, until the filtrate ceases to give a precipitate with an acid solution of nitrate of silver. Dry, transfer to a crucible, burn the filter in the usual way, heat slowly to redness, cool, and weigh.

Proportional weights of equivalent quantities of magnesium salts.

Pyrophosphate	$Mg_2P_2O_7$ 222
Sulphate	$2(MgSO_4, 7H_2O)$ 246
Oxide	$2(MgO)$ 80
Officinal carbonate	$(3MgCO_3, Mg2HO, 4H_2O) \div 2$ .. 191

ZINC.

Zinc is usually estimated as oxide (ZnO); occasionally as sulphide (ZnS).

Dissolve a weighed quantity (0·5 to 0·6) of sulphate of zinc in about half a litre of water in a beaker, heat to near the boiling-point, add carbonate of sodium in slight excess, boil, set aside for a short time; pass the supernatant liquid through a filter, gently boil the precipitate with more water, again decant; repeat the ebullition &c. two o rthree times; collect the precipitate on the filter, wash, dry, transfer to a crucible, incinerate, ignite, cool, and weigh. 287 (=molec. weight) of sulphate should yield 81 (=molec. weight) of oxide.

ALUMINIUM.

Aluminium is always precipitated as hydrate (Al_26HO) and weighed as oxide (Al_2O_3).

Dissolve about two grammes of pure dry ammonium-alum in half a litre of water, heat the solution, add chloride of ammonium and a slight excess of ammonia, boil gently till the odour of ammonia has nearly disappeared, set aside for the hydrate

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to deposit, pass the supernatant liquid through a filter, wash the precipitate three or four times by decantation, transfer to the filter, finish the washing, dry, burn the filter, ignite in a covered crucible, and weigh.

$Al_2 3SO_4$, Am_2SO_4, $24H_2O$	907
Al_2O_3	103
Per cent. of Al_2O_3 yielded by ammonium-alum	11·356

IRON.

Iron and its salts are gravimetrically estimated in the form of ferric oxide (Fe_2O_3).

Compounds containing organic acidulous radicals are simply incinerated, and the resulting oxide weighed. Thus 1 gramme of the officinal citrate of iron and ammonium (*Ferri et Ammoniæ Citras*, B. P.) incinerated, with exposure to air, leaves not less than ·27 of ferric oxide. A small quantity of the salt is weighed in a tared covered porcelain crucible, flame cautiously applied until vapours cease to be evolved, the lid then removed, the crucible slightly inclined and exposed to a red heat until all carbonaceous matter has disappeared. The residual ferric oxide is then weighed. The tartrate of potassium and iron (*Ferrum Tartaratum*, B. P.) is treated in the same manner, except that the ash must be washed and again heated before weighing, in order to remove carbonate of potassium produced during incineration; 5 grammes should yield 1·5 gramme of ferric oxide.

From other compounds of iron, soluble in water or acid, the metal is precipitated in the form of hydrate ($Fe_2 6HO$) by solution of ammonia, and converted into oxide (Fe_2O_3) by ignition. Dissolve a piece (about 0·2) of the purest iron obtainable (piano-wire), accurately weighed, in water acidulated with hydrochloric acid; add a few drops of nitric acid and gently boil; pour in excess of ammonia, stir, set aside till the ferric hydrate has

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deposited, pass the supernatant liquid through a filter, treat the precipitate three or four times with boiling water; transfer to the filter, wash till the filtrate yields no traces of chlorine (for chloride of ammonium will decompose ignited ferric oxide, with volatilization of ferric chloride), dry, and ignite as usual, and weigh. Iron in the officinal solutions (*Liquor Ferri Perchloridi Fortior*, *Liquor Ferri Pernitratis*, and *Liquor Ferri Persulphatis*) is estimated by this general process.

The proportion of metallic iron in a mixture of iron and oxides of iron may be determined by digestion in a strong solution of iodine in iodide of potassium, which attacks the metal only. The reduced iron of pharmacy (*Ferrum Redactum*, B. P.) is in good condition so long as it contains, as shown by this method, half its weight of free metal.

Proportional weights of equivalent quantities of iron and its salts.

Metal	Fe_2	112
Ferric oxide	Fe_2O_3	160
Ferric hydrate	Fe_26HO	214
Ferric chloride	Fe_2Cl_6	325
Ferric sulphate	Fe_23SO_4	400
Ferrous sulphate ..	$2(FeSO_4, 7H_2O)$.....	556

ARSENICUM.

Arsenic (As_2O_3) is usually estimated volumetrically (*vide* p. 337). With certain precautions arsenicum may also be precipitated and weighed as sulphide (As_2S_3).

The pure, white, massive arsenic (about 0·2) is dissolved in a flask in a small quantity of water containing acid carbonate of sodium or potassium, the liquid being heated. A slight excess of hydrochloric acid is then added, and sulphuretted hydrogen gas passed through the solution so long as a precipitate falls, the

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mouth of the flask being stopped by a plug of cotton-wool (to prevent undue access of air and consequent decomposition of the gas resulting in precipitation of sulphur). Warm the mixture in the flask and pass carbonic acid gas through it until the odour of sulphuretted hydrogen has nearly disappeared. Collect the precipitate on a tared filter, wash as quickly as possible with hot water containing a little sulphuretted hydrogen, dry in a water-oven and weigh. 198 parts of arsenic should yield 246 of sulphide of arsenicum.

ANTIMONY.

The metal is precipitated in the form of sulphide (Sb_2S_3), with the precautions observed in estimating arsenicum, a small quantity of tartaric acid, as well as hydrochloric, being added to prevent the precipitation of an oxysalt. The experiment may be performed on about half a gramme of pure tartar-emetic: this salt should yield nearly half its weight (49·56 per cent.) of sulphide. According to Fresenius, the sulphide dried at 100° C. still contains 2 per cent. of water, and must be heated, in a current of carbonic acid gas, until it turns from an orange to a black colour, before all moisture is expelled. In the British Pharmacopœia the purity of tartar-emetic (*Antimonium Tartaratum*), and the strength of solution of chloride of antimony (*Liquor Antimonii Chloridi*), is determined by this process.

COPPER.

Copper is precipitated from its solutions and weighed either as (1) metal (Cu_2), or as (2) oxide (CuO).

1. Dissolve about half a gramme of dry crystallized sulphate of copper in a small quantity of water, in a tared porcelain crucible or beaker, acidulate with hydrochloric acid, introduce a fragment or two of pure zinc, cover the vessel with a watch-glass, and set aside till evolution of hydrogen has ceased, and the

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still acid liquid is colourless. The copper is then washed with hot water by decantation until no trace of acid remains, the precipitate drained, rinsed with strong spirit of wine, dried in the water-oven, and weighed.

2. About three-fourths of a gramme of sulphate of copper is accurately weighed, dissolved in half a litre of water, the liquid boiled; dilute solution of potash or soda is then added till no more precipitate falls, ebullition continued for a short time, and the beaker set aside; the supernatant liquid is decanted, the precipitate boiled with water twice or thrice, collected on a filter, washed, dried, transferred to a crucible, the filter incinerated, and its ash moistened with a drop of nitric acid; the whole is finally heated strongly, cooled, and weighed.

249·5 parts of sulphate of copper yield 79·5 of oxide, or 63·5 of metal.

BISMUTH.

Dissolve 0·3 or 0·4 of pure oxycarbonate of bismuth ($2Bi_2O_2CO_3$, H_2O) (*Bismuthi Carbonas*, B. P.) in a small quantity of hydrochloric acid, dilute with water slightly acidulated by hydrochloric acid, pass excess of sulphuretted hydrogen through the liquid, collect the precipitate on a tared filter, wash, dry at 100° C., and weigh. The sulphide must not be exposed too long in the water-oven, or it will increase in weight owing to absorption of oxygen; hence it should be tested in the balance every half-hour during desiccation. 517 of oxycarbonate should yield 512 of sulphide (Bi_2S_3). The strength of the officinal solution of citrate of bismuth and ammonium (*Liquor Bismuthi et Ammoniæ Citratis*, B. P.) is determined by this process. "Three fluid drachms of the solution, mixed with an ounce of distilled water, and treated with sulphuretted hydrogen in excess, yield a black precipitate, which, collected, washed, and dried, weighs 9·92 grains. One fluid drachm contains three grains of oxide of bismuth."

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MERCURY.

This element may be isolated and estimated in the form of (1) metal, or precipitated and weighed as (2) mercurous chloride, or (3) mercuric sulphide.

1. The process by which the metal itself is separated is one of distillation, into a bulb surrounded by water. About half a metre of the difficultly fusible German glass known as *combustion-tubing*, is sealed at one end after the manner of a test-tube; a mixture of acid carbonate of sodium and dry chalk is then dropped into the tube to the height of two or three centimetres, and, next, several small fragments of quicklime so as to occupy another centimetre; a mixture of about a gramme of pure calomel or corrosive sublimate with enough powdered quicklime to occupy 10 or 12 centimetres of the tube is added, then the lime-rinsings of the mixing-mortar, a layer of a few centimetres of powdered quicklime, and, finally, a plug of *asbestos* (a fibrous mineral unaffected by heat). The whole powder should occupy two-thirds of the length of the tube. The part of the tube just above the asbestos is now softened in the blowpipe-flame and drawn out about a decimetre to the diameter of a narrow quill; it is again drawn out to the same extent at a point about two or three centimetres nearer the mouth, and any excess of tubing cut off. The bulb thus formed may be enlarged by softening and blowing. The tube is next softened at a point close to but anterior to the asbestos, and bent nearly to a right angle; the tube is then softened close to the bulb and slightly bent so that the bulb may be parallel with the large tube; then softened on the other side of the bulb, and the narrow terminal tube bent to a right angle, so that, the tube being held in a horizontal position, the bulb may be sunk in water, and the terminal tube point upwards. The long tube is now laid in the gas-furnace found in most laboratories, a basin so placed that the bulb of the

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apparatus may be cooled by being surrounded by water, the part of the tube occupied by asbestos heated to redness, and the flame slowly lengthened until the whole tube is red-hot. Under these circumstances the mercurial compound volatilizes, is decomposed by the lime, and its acidulous radical fixed, the mercury carried in vapour to and condensed in the bulb, the carbonic acid gas evolved from the acid carbonate of sodium and chalk washing out the last portions of mercury-vapour from the tube. When the distillation is considered to be complete, the dish of water is removed, the bulb dried, and then detached by help of a file at a point beyond any sublimate of mercury. The bulb is lastly weighed, mercury shaken or dissolved out, and the tube again dried and weighed.

2. The process by which mercury is separated in the form of calomel, consists in adding hydrochloric and phosphorous acids (*vide* p. 120) to an aqueous or even acid solution of a weighed quantity of the mercurial compound, setting the mixture aside for twelve hours, collecting the precipitate on a tared filter, washing, drying at 100° C., and weighing (Rose). The experiment may be tried on half a gramme to a gramme of corrosive sublimate.

3. Two or three decigrammes of corrosive sublimate are dissolved in water, the solution acidulated with hydrochloric acid, excess of sulphuretted hydrogen passed, the precipitate collected on a tared filter, washed with cold water, dried at 100° C., and weighed.

Proportional weights of equivalent quantities of mercury and its salts.

Metal	Hg_2	400
Mercurous chloride	Hg_2Cl_2	471
Mercuric chloride	$2HgCl_2$	542
Mercuric sulphide	$2HgS$	464

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LEAD.

Lead may be estimated as (1) oxide, (2) sulphate, (3) chromate &c.

1. Weigh out one or two grammes of pure acetate of lead in a covered crucible, previously tared, and heat slowly until no more vapours are evolved. Remove the lid, stir down the carbonaceous mass with a clean iron wire, and keep the crucible in the flame so long as any carbon remains unconsumed. Introduce some fragments of fused nitrate of ammonium, and again ignite until no metallic lead remains, and all excess of the nitrate has been decomposed. Cool and weigh the resulting oxide.

2. Dissolve 0·4 to 0·5 of a gramme of acetate of lead in a small quantity of water, drop in diluted sulphuric acid, add to the mixture twice its bulk of methylated spirit of wine, and set aside. Decant the supernatant liquid, collect the sulphate on a filter, wash with spirit, dry, transfer to a crucible, removing as much of the sulphate as possible from the paper, incinerate, ignite, cool, and weigh.

3. About half a gramme of acetate of lead is dissolved in two or three hundred c. c. of water, acetic acid added, and then solution of red chromate of potassium. Collect the precipitate on a tared filter, wash, dry at 100° C., and weigh.

Molecular weights of salts of lead.

Acetate ..	$Pb2C_2H_3O_2, 3H_2O$ ...	379
Oxide	PbO	223
Sulphate ..	$PbSO_4$	303
Chromate..	$PbCrO_4$	323·5

SILVER.

Compounds of silver which are readily decomposed by heat

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are estimated in the form of (1) metal, others usually as (2) chloride (AgCl), but sometimes as (3) cyanide (AgNC).

1. Heat about a gramme of oxide of silver (Ag_2O) in a tared crucible, cool, and weigh. 232 of oxide yield 216 of metal. "29 grains heated to redness yield 27 grains of metallic silver." —*Brit. Pharm.*

2. Dissolve 0·4 to 0·5 of pure dry crystals of nitrate of silver in water, acidulate with two or three drops of nitric acid, slowly add hydrochloric acid, stirring rapidly, until no more precipitate falls. Pour off the supernatant liquid through a filter, wash the chloride of silver once or twice with hot water, transfer to the filter, complete the washing, and dry. After removing as much as possible of the precipitate, burn the filter, letting its ash fall on the inverted lid of the crucible, moisten with a drop of nitric acid, warm, add a drop of hydrochloric acid, evaporate to dryness, replace the lid on the crucible, ignite the whole until the edges of the mass of chloride begin to fuse; cool, and weigh. 170 of nitrate yield 143·5 of chloride.

3. Cyanide of silver may be collected on a tared filter and dried at 100° C. 170 of nitrate yield 134 of cyanide.

Silver and its salts may be volumetrically estimated by a standard solution of chloride of sodium.

Cupellation.—The amount of silver in an alloy may be also determined by a dry method. The metal is folded in a piece of thin sheet lead, placed on a *cupel* (*cupella*, little cup) made of compressed bone-earth and heated in a furnace, the cupel being protected from the direct action of flame by a muff-shaped, or, rather oven-shaped case, termed a muffle. The metals melt, the lead becoming oxidized to litharge, which dissolves other oxides; the latter are absorbed by the porous cupel, a button of pure silver remaining.

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ESTIMATION OF SALTS OF ACIDULOUS RADICALS ETC.

CHLORIDES.

Free chlorine (chlorine-water) and compounds which by action of acids yield free chlorine (Chlorinated Lime, Chlorinated Soda, and their officinal Solutions) are estimated volumetrically by a standard solution of hyposulphite of sodium (*vide* p. 342). The amount of combined chlorine in pure chlorides (HCl, NaCl, &c.) may also be determined by volumetric analysis with a standard solution of nitrate of silver.

Combined chlorine is gravimetrically estimated in the form of chloride of silver, the operation being identical with that just described for silver salts; 58·5 parts of pure, colourless, crystallized chloride of sodium (rock-salt) yield 143·5 of chloride of silver.

IODIDES.

Free iodine is estimated volumetrically by solution of hyposulphite of sodium (*vide* p. 342). Combined iodine is determined gravimetrically in the form of iodide of silver, the operations being conducted as with chloride of silver. Iodide of potassium may be used for an experimental determination: KI=166 should yield AgI=235. Of the officinal iodide of cadmium (*Cadmii Iodidum*, B. P.) it is stated that "ten grains dissolved in water, and nitrate of silver added in excess, give a precipitate which, when washed with water and afterwards with half an ounce of solution of ammonia, and dried, weighs 12·5 grains."

In presence of chlorides and bromides the iodine in iodides may be precipitated and weighed as iodide of palladium.

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BROMIDES.

Free bromine may be estimated by shaking with excess of solution of iodide of potassium, and then determining the equivalent quantity of liberated iodine by a standard solution of hyposulphite of sodium.

The bromine in bromides may be precipitated and weighed as bromide of silver, the manipulations being the same as those for chloride of silver: 0·2 to 0·3 of pure bromide of potassium may be used for an experimental analysis.

CYANIDES.

The hydrogen cyanide (hydrocyanic acid) is usually estimated volumetrically (*vide* p. 336). From all soluble cyanides, cyanogen may be precipitated by nitrate of silver, after acidulating with nitric acid, the cyanide of silver collected on a tared filter, and dried at 100° C.

Cyanide of Silver.

		In 1 molecule.	In 100 parts.
Silver	Ag	107·93	80·59
Cyanogen ..	CN	26·00	19·41
		133·93	100·00

NITRATES.

Nitrates cannot be estimated by direct gravimetric analysis, none of the basylous radicals yielding a definite nitrate insoluble in water. With some difficulty they may be determined by indirect volumetric methods.

One process by Harcourt will be found in the Journal of the Chemical Society, page 384; it is founded on the fact that the nitrogen of nitrates is eliminated as ammonia when the salt is heated with a strong caustic alkali and a mixture of zinc and iron filings.

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Another good process is by Pugh, and is based on the observation that under pressure at a temperature of 160° F., stannous is converted into stannic chloride in the presence of nitric and hydrochloric acids:—

$$2HNO_3 + 8SnCl_2 + 18HCl = 2NH_4Cl + 8SnCl_4 + 6H_2O.$$

The nitrate and a measured excess of an acid solution of stannous chloride of known strength is introduced into a third of a metre of combustion tubing sealed at one end, air in the tube displaced by the carbonic acid gas evolved when a small fragment of marble is dropped into the mixture, the tube closed at the blowpipe and heated to 160° C. in an air-bath for twenty minutes, cooled, opened, and the residual stannous chloride estimated by a standard solution of iodine. The experiment may be made on two or three decigrammes of pure nitrate of potassium: the solution of stannous chloride should be tolerably strong. The product of the action is neutralized by acid carbonate of sodium, a quantity of the double tartrate of potassium and sodium being previously added to keep the liquid clear; mucilage of starch is then poured in, and the standard solution of iodine delivered from a burette until the blue iodide of starch appears. Each molecule of stannous is converted into one of stannic by the influence of two atoms of iodine.

SULPHIDES.

Soluble sulphides (H_2S, NaHS, &c.) may be determined volumetrically by adding to the aqueous liquid a measured excess of an alkaline solution of arsenic of known strength, neutralizing by hydrochloric acid, diluting to any given volume, filtering off the sulphide of arsenicum precipitated, taking a portion of the filtrate equal to half or a third of the original volume, and, after neutralizing by acid carbonate of sodium, estimating the residual arsenic by the standard iodine solution (*vide* p. 338). The pro-

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cess may be tried on a measured volume of sulphuretted hydrogen (the weight of which is easily calculated—1 litre of hydrogen = 0·0896 gramme) absorbed by a strong solution of soda or potash.

Sulphur and sulphides may also be quantitatively analyzed by oxidizing to sulphuric acid and precipitating in the form of sulphate of barium. A couple of decigrammes of a pure metallic sulphide may be decomposed by careful deflagration with a mixture of chlorate of potassium and carbonate of sodium, the product dissolved in water, acidulated with hydrochloric acid, solution of chloride of barium added, and the precipitated sulphate of barium purified and collected as described in connexion with the estimation of barium (p. 350). Many sulphides may be oxidized in a flask by chlorate of potassium and hydrochloric acid, and then precipitated by chloride of barium. Experimental determinations may also be made on a weighed fragment of sulphur, about 0·1, cautiously fused with a solid caustic alkali, and the product oxidized while hot by the slow addition of powdered chlorate of potassium, or, when cold, by treatment with chlorate of potassium and hydrochloric acid, and subsequent precipitation by chloride of barium.

Soluble sulphides may also be treated with excess of an alkaline arsenite, sulphide of arsenicum be then precipitated by the addition of hydrochloric acid, and the precipitate collected and weighed with the usual precautions (*vide* p. 355).

Weights of equivalent quantities of sulphur and its compounds.

Sulphur	S	32
Sulphuretted hydrogen	H_2S	34
Sulphate of barium	$BaSO_4$	233
Sulphide of arsenicum	$(As_2S_3) \div 3$	82
Iron pyrites	$(FeS_2) \div 2$	60
Galena	PbS	239

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SULPHITES.

Sulphites are usually estimated volumetrically by a standard solution of iodine (*vide* p. 338). Sulphites insoluble in water are diffused in that menstruum, hydrochloric acid added, and the iodine solution then dropped in.

If necessary, sulphites may be estimated gravimetrically by oxidation and precipitation in the form of sulphate of barium.

SULPHATES.

These salts are always precipitated and weighed as sulphate of barium, the manipulations being identical with those performed in the determination of barium by means of sulphates (*vide* p. 350). The purity of Sulphate of Sodium (*Sodæ Sulphas*, B.P.), and the presence of not more than a given amount of sulphuric acid in Vinegar (*Acetum*, B.P.), are directed, in the British Pharmacopœia, to be ascertained by this process.

CARBONATES.

Carbonates are usually estimated by the loss in weight they undergo on the addition of a strong acid.

A small light flask is selected—of such a size that it can be conveniently weighed in a delicate balance. Two narrow glass tubes are fitted to the flask by a cork; the one straight, extending from about two or three centimetres above the cork to the bottom of the flask; the other cut off close to the cork on the inside and curved outwards so as to carry a thin drying-tube horizontally above the flask. The drying-tube may be a short narrow test-tube, the bottom of which is constricted so as to form a narrow tube open at the end; it is nearly filled with small pieces of chloride of calcium, a plug of cotton-wool preventing escape of any fragments at either end, and is attached by a

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pierced cork to the free extremity of the curved tube of the flask. A weighed quantity of any pure soluble carbonate is placed in the flask, a little water added, a miniature test-tube containing sulphuric acid lowered into the flask by a thread and supported so that the acid may not flow out, the cork inserted, the outer end of the piece of straight glass tubing closed by a fragment of cork or wax, and the whole weighed. The apparatus is then inclined so that the oil of vitriol and carbonate may slowly react; carbonic acid gas is evolved and escapes through the horizontal tube, any moisture being retained by the chloride of calcium. When effervescence has ceased, the gas still remaining in the vessel is sucked out; this is accomplished by adapting a piece of india-rubber tubing to the end of the drying-tube, removing the small plug from the straight tube, and aspirating slowly with the mouth for a few minutes. If the heat educed by the action of the oil of vitriol and solution is considered insufficient to expel all the carbonic acid from the liquid, the plug is again inserted in the tube and the contents of the flask gently boiled for some seconds. When the apparatus is cold, air is again drawn through it, and the whole finally weighed. The loss is due to carbonic acid gas (CO_2), from the weight of which that of any carbonate is ascertained by calculation. Carbonates insoluble in water may be attacked by hydrochloric instead of sulphuric acid; granulated mixtures of carbonates and powdered tartaric or citric acids by enclosing the preparation in the inner tube and placing water in the flask, or *vice versâ*. The apparatus may also be modified in many ways to suit the requirements, convenience, or taste of the operator.

Carbonates from which carbonic acid gas is evolved by heat may be estimated by the loss they experience on ignition. Free carbonic acid gas may be absorbed by a solid stick of potash or a strong alkaline solution.

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Weights of equivalent quantities of carbonic acid gas and certain carbonates.

Carbonic acid gas	CO_2	44
Carbonic acid	H_2CO_3	62
Anhydrous carbonate of sodium	Na_2CO_3	106
Anhydrous carbonate of potassium	K_2CO_3	138
Carbonate of calcium	$CaCO_3$	100

OXALATES.

The oxalic radical is usually precipitated in the form of oxalate of calcium, and weighed as carbonate, the manipulations being identical with those observed in the estimation of calcium (*vide* p. 351). The experiment may be performed on 0·3 or 0·4 of pure crystallized oxalic acid, 126 parts of which should yield 100 of carbonate of calcium.

Oxalates may also be determined by conversion of their acidulous radical into carbonic acid gas, and observation of the weight of the latter. The oxalate, water, and excess of black oxide of manganese are placed in the carbonic-acid apparatus, a tube full of oil of vitriol lowered into the flask, the whole weighed, and the operation completed as for carbonates. From the following equation it will be seen that every 88 parts of carbonic acid gas evolved indicates the presence of 126 parts of crystallized oxalic acid or an equivalent quantity of any oxalate:—

$$Na_2C_2O_4 + MnO_2 + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + 2CO_2.$$

The black oxide of manganese used in this experiment must be free from carbonates. The amount of materials employed must be regulated by the size of the vessels.

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PHOSPHATES.

The phosphoric radical may be precipitated and weighed in the form of pyrophosphate of magnesium, the details of manipulation being similar to those observed in estimating magnesium (*vide* p. 352). Half a gramme or rather more of pure dry crystallized phosphate of sodium may be employed in experimental determinations. The officinal phosphate of ammonium (*Ammoniæ Phosphas*, B.P.) is quantitatively analyzed by this method. "If twenty grains of this salt be dissolved in water, and solution of ammonio-sulphate of magnesia added, a crystalline precipitate falls, which, when well washed upon a filter with solution of ammonia diluted with an equal volume of water, dried, and heated to redness, leaves 16·8 grains." Half a gramme, or less, is a more convenient quantity if the operations be conducted with care. Solution of ammonio-sulphate of magnesium is prepared by dissolving 2 parts of sulphate of magnesium, 1 of chloride of ammonium, and 1 of solution of ammonia (20·6 per cent. AmHO) in 18 or 20 of distilled water; such a solution is of considerable use if several phosphoric determinations are about to be made.

Free phosphoric acid is most readily determined as phosphate of lead ($Pb_3 2PO_4$). Of the officinal solution of phosphoric acid, it is stated that "355 grains by weight poured upon 180 grains of oxide of lead in fine powder leave, by evaporation, a residue (principally phosphate of lead), which, after it has been heated to dull redness, weighs 215·5 grains." One-tenth of these quantities may be used for experimental purposes; one to two grammes will give good results. The oxide of lead must be quite pure; it should be prepared by digesting red lead in warm dilute nitric acid, washing, drying, and heating the resulting puce-coloured plumbic oxide in a covered porcelain crucible. The increase in weight obtained on evaporating a given amount

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of solution of phosphoric acid with a known weight of oxide of lead may be regarded as entirely due to phosphoric anhydride,

$$3PbO + P_2O_5 = Pb_3 2PO_4,$$

the actual reaction being,

$$3PbO + 2H_3PO_4 = Pb_3 2PO_4 + 3H_2O.$$

From these equations, and the table of atomic weights, the percentage of phosphoric acid (H_3PO_4) in any specimen of its solution may be easily calculated.

The strength of solution of phosphoric acid may also be determined by its specific gravity at 15°·5 C.

TABLE OF THE PERCENTAGE OF PHOSPHORIC ANHYDRIDE IN SOLUTIONS OF PHOSPHORIC ACID OF VARIOUS STRENGTHS (J. Watts).

Specific Gravity.	Per-centage.	Specific Gravity.	Per-centage.	Specific Gravity.	Per-centage.	Specific Gravity.	Per-centage.
1·508	49·60	1·369	39·21	1·247	28·24	1·113	14·33
1·492	48·41	1·356	38·00	1·236	27·30	1·109	13·25
1·476	47·10	1·347	37·37	1·226	26·36	1·095	12·18
1·464	45·63	1·339	36·74	1·211	24·79	1·081	10·44
1·453	45·38	1·328	36·15	1·197	23·23	1·073	9·53
1·442	44·13	1·315	34·82	1·185	22·07	1·066	8·62
1·434	43·95	1·302	33·49	1·173	20·91	1·056	7·39
1·426	43·28	1·293	32·71	1·162	19·73	1·047	6·17
1·418	42·61	1·285	31·94	1·153	18·81	1·031	4·15
1·401	41·60	1·276	31·03	1·144	17·89	1·022	3·03
1·392	40·86	1·268	30·13	1·136	16·95	1·014	1·91
1·384	40·12	1·257	29·16	1·124	15·64	1·006	·79
1·376	39·66						

Relative weights of equivalent quantities of phosphoric compounds.

Phosphoric acid	H_3PO_4	98
Pyrophosphate of magnesium	$(Mg_2P_2O_7=222)\div 2=$	111
Phosphate of lead	$(Pb_3 2PO_4=811)\div 2=$	405·5
Phosphoric anhydride	$(P_2O_5=142)\div 2=$	71

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SILICATES.

Silica (SiO_2) may be separated from alkaline silicates, or from silicates decomposable by hydrochloric acid, by digesting the substance in hydrochloric acid at a temperature of 70° or 80° C., until completely disintegrated, evaporating to dryness, heating in an air-bath, again moistening with acid, diluting with hot water, filtering, washing, drying, igniting, and weighing.

ESTIMATION OF WATER OF CRYSTALLIZATION ETC.

Water being readily volatile, it is most usually estimated by the loss in weight which a substance undergoes on being heated to a proper temperature. Thus, in the British Pharmacopœia, crystalline gallic acid ($H_3C_7H_3O_5, H_2O$) is stated to lose 9·5 per cent. of its weight at a temperature of 100° C., oxalate of cerium ($CeC_2O_4, 3H_2O$) 52 per cent. on incineration, carbonate of potassium about 16 per cent. on exposure to a red heat, sulphate of quinine ($2C_{20}H_{24}N_2O_2, H_2SO_4, 7H_2O$) 14·4 per cent. at 100° C., arseniate of sodium ($Na_2HAsO_4, 7H_2O$) 40·38 per cent. at 149° C., carbonate of sodium ($Na_2CO_310H_2O$) 63 per cent., phosphate of sodium ($Na_2HPO_4, 12H_2O$) 63 per cent., and sulphate of sodium 55·9 per cent. at a low red heat.

One or two grammes of substance is sufficient in experiments on desiccation, the material being placed in a watch-glass, covered or uncovered porcelain crucible, or other vessel, according to the temperature to which it is to be exposed. Rapid desiccation at an exact temperature may be effected by introducing the powder &c. into a tube having somewhat the shape of the letter U, sinking the lower part of the tube into a liquid kept at a definite temperature by aid of a thermometer, and drawing or forcing a current of dry air slowly through the apparatus. Substances liable to oxidation may be dehydrated

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in a current of dried carbonic acid gas. The weights of the U-tube before and after the introduction of the salt, and after desiccation, give the amount of water sought. In all cases the material must be heated until it ceases to lose weight. Occasionally it is desirable to estimate water directly by conveying its vapour in a current of air through a weighed tube containing chloride of calcium.

Highly dried substances rapidly absorb moisture from the air; they must therefore be weighed quickly, enclosed, if possible, in a tube, a pair of clamped watch-glasses, or a crucible having a tightly-fitting lid.

CARBON, HYDROGEN, OXYGEN, NITROGEN.

The quantitative analysis of animal and vegetable substances is either *proximate* or *ultimate*. Proximate analysis includes the estimation of water, oil, albumen, starch, cellulose, gum, resin, alkaloids, acids, glucosides, ash, &c. It requires the application of much theoretical knowledge and manipulative skill, and cannot well be studied except under the guidance of a tutor. The best published work on the subject is by Rochleder, a translation of whose monograph will be found in the Pharmaceutical Journal, vol. i. 2nd ser. pp. 562, 610; vol. ii. 2nd ser. pp. 24, 129, 160, 215, 274, 420, 478.

Ultimate organic analysis can only be successfully accomplished with the appliances of a well-appointed laboratory—a good balance, a gas-furnace giving a smokeless flame (7 or 8 centimetres wide and 70 or 80 centimetres long), special forms of glass apparatus, &c. The theory of the operation is simple: a weighed quantity of a substance is burnt to carbonic acid gas ($CO_2=44$) and water ($H_2O=18$), and these products collected and weighed; 12 parts in every 44 of carbonic acid gas ($=\frac{3}{11}$) are carbon, 2 in every 18 of water ($=\frac{1}{9}$) are hydrogen; nitrogen if present escapes as gas. If nitrogen be a constituent, more of the substance is strongly heated with a mixture of the hydrates of sodium and calcium; these bodies then split up into oxides, oxygen, and hydrogen; the oxygen burns the carbon of the substance to carbonic acid gas, its hydrogen and nitrogen appearing as water and ammonia respectively; the carbonic acid

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and water are disregarded, the ammonia collected and weighed in the form of double chloride of platinum and ammonium ($PtCl_4 2NH_4Cl = 447$), of which 28 parts in every 447 ($= \frac{1}{16}$) are nitrogen. The difference between the sum of the weights of hydrogen and carbon, and the weight of substance taken, is the proportion of oxygen in the body, supposing nitrogen to be absent. If nitrogen is present, the difference between the sum of the percentages of carbon, hydrogen, and nitrogen and 100, is the percentage of oxygen. Shortly, carbon is estimated in the form of carbonic acid gas, hydrogen as water, nitrogen as ammonia, and oxygen by loss.

The following is an outline of the necessary manipulations. The source of the oxygen for the combustion of carbon and hydrogen is black oxide of copper in coarse powder. 200 or 300 grammes of this material are heated to low redness for a short time to expel every trace of moisture; then transferred to tubes resembling test-tubes, half a metre long, and having a slightly narrowed mouth, the tube being held in a cloth to protect the hand; as soon as the well-corked tube is cool, the oxide is poured into a similar tube (the combustion-tube), somewhat longer, drawn out to a quill at one end, not constricted at the mouth, and containing a few decigrammes of fused chlorate of potassium. After ten or fifteen centimetres of oxide have been poured in, about a decigramme of the prepared substance is dropped down the tube, then a few grammes of oxide, then another decigramme of substance, then more oxide, until three or four decigrammes of the body under examination have been added. The fifteen or twenty centimetres of alternate layers are now thoroughly mixed by a long copper wire having a short helix, more oxide is introduced, the wire cleansed by twisting the helix about in the pure oxide, and a plug of asbestos finally placed on the top of the oxide at about five centimetres from the mouth of the tube; the tube is then securely corked and set aside. The substance operated on may be pure white sugar, powdered and dried; the tube in which it is contained is

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weighed before and after the removal of a portion for combustion, the loss is the quantity employed in the experiment. If the combustion-furnace is powerful, or the combustion-tube not of the hardest glass, the tube should be enclosed in wire gauze the elasticity of which has been destroyed by heating to redness. In the combustion of substances containing nitrogen, the plug of asbestos must be displaced by one of copper turnings, which serve to reduce any oxides of nitrogen, and thus ensure the escape of the nitrogen itself. The water, produced when the prepared tube is heated, is collected in a small U-tube containing pieces of chloride of calcium, or pumicestone moistened with sulphuric acid; the carbonic gas in a series of bulbs containing solution of potash (sp. gr. about 1·27). These bulbs may be purchased at any apparatus-shop. The chloride-of-calcium tube is fitted by a good cork to the combustion-tube, the potash-bulbs by a short piece of india-rubber tubing to the chloride-of-calcium tube. The potash bulbs may carry a short light tube containing a rod of caustic potash three or four centimetres long; this serves to arrest any moisture that might be carried away from the solution of potash by the dried expanded air which escapes during the operation. The combustion-tube having been placed in the furnace, and the drying-tube and potash-bulbs weighed and attached, the gas is lit under the asbestos, and when the tube is red-hot, the flame slowly extended until nearly the whole tube is at the same temperature, the operation being conducted at such a rate that bubbles of gas escape through the bulbs at about the rate of one per second. When no more gas passes, the extremity of the tube containing the chlorate of potassium is gently heated until oxygen ceases to be evolved; the quilled extremity of the combustion-tube is then broken, and air drawn through the apparatus by suction through an india-rubber tube fixed on the free end of the potash-bulbs, perfect combustion of carbon and removal of all carbonic acid

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gas is thus ensured. The drying-tubes and bulbs are disconnected and weighed; the increase in weight due to carbonic acid gas and water respectively noted, and the percentages of carbon, hydrogen, and (by loss) oxygen calculated. This method is that of Liebig, with modifications by Bunsen; one of the best combustion-furnaces is that known as Hofmann's.

The general manipulations for substances containing nitrogen resemble the foregoing so far as the use of a combustion-tube and furnace and collection of the ammoniacal gas are concerned. The combustion-tube must be quilled at one end, and about a third of a metre long. The soda-lime is made by slaking quicklime with a solution of soda, of such a strength that about two parts of quicklime shall be mixed with one of hydrate of sodium, drying the product, heating to bright redness, and finely powdering; it should be preserved in a well-closed bottle. Some of the soda-lime is introduced into the tube, then layers of substance and soda-lime, mixture effected by a wire, more soda-lime added, and lastly, a plug of asbestos. Bulbs, known as those of Will and Varrentrapp (the originators of the method), containing hydrochloric acid of about 25 per cent., are then fitted by a cork, and the tube heated in the furnace. When gas ceases to pass, the quill is broken, and aspiration continued until ammoniacal gas may be considered to have been all removed. The bulbs are disconnected, their contents and rinsings poured into a small dish, solution of perchloride of platinum added, and the operation completed as in the estimation of ammonium and potassium salts (*vide* pages 349 and 347).

Liquids are analyzed by a similar method to that adopted for solids, volatile liquids being enclosed in small bulbs having a long quill. These bulbs are weighed previously to and after the introduction of the liquid; just before being dropped into the combustion-tube the quill is broken.

From the percentage composition of an organic substance an

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empirical formula may be deduced by dividing the weight of each constituent by its atomic weight, and converting the product into the simplest whole numbers; a rational formula by ascertaining the proportion in which the substance unites with a body having a known combining proportion.

QUININE.

The following process for the estimation of the quality of yellow cinchona bark is from the pages of the British Pharmacopœia:—

Boil 100 grains (or 6 to 7 grammes) of the bark reduced to very fine powder for a quarter of an hour in a fluid ounce of distilled water acidulated with ten minims of hydrochloric acid, and allow it to macerate for twenty-four hours. Transfer the whole to a small percolator, and, after the fluid has ceased to drop, add at intervals about an ounce and a half of similarly acidulated water, or until the fluid which passes through is free from colour. Add to the percolated fluid solution of subacetate of lead, until nearly the whole of the colouring-matter has been removed, taking care that the fluid remains acid in reaction. Filter and wash with a little distilled water. To the filtrate add about thirty-five grains of caustic potash, or as much as will cause the precipitate which is at first formed to be nearly redissolved, and afterwards six fluid drachms of pure ether. Then shake briskly, and, having removed the ether, repeat the process twice with three fluid drachms of ether, or until a drop of the ether employed leaves on evaporation scarcely any perceptible residue. Lastly, evaporate the mixed ethereal solutions in a capsule. The residue, which consists of nearly pure quinine, when dry, should weigh not less than 2 grains (2 per cent.), and should be readily soluble in diluted sulphuric acid. 200 grains of pale cinchona bark treated in the same manner, with the

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substitution of chloroform for ether, should yield not less than 1 grain of alkaloids, and 100 of red cinchona bark 1·5 grain of alkaloids.

A quantitative determination of the purity of commercial sulphate of quinine may be made by De Vry's process: 2 grammes of the salt are dissolved in 12 c. c. of distilled water and 1·6 c. c. of diluted sulphuric acid (B. P.). 8 c. c. of solution of hydrate of sodium (1 to 12) and 30 c. c. of pure dry ether are added, the whole well shaken and laid aside for twelve hours. The ethereal solution decanted and evaporated gives the quinine. The aqueous solution carefully neutralized by acetic acid and strong solution of iodide of potassium (1 in 4) added, gives a precipitate of hydriodate of quinidine, the mother-liquor containing any cinchonine and cinchonidine that may be present. The precipitate is collected on a tared filter, washed, dried, and weighed; it contains 71·68 per cent. of pure quinidine. The filtrate and washings are rendered alkaline by solution of soda; cinchonine and cinchonidine are precipitated, and may be collected, washed, dried, and weighed.

MORPHINE.

The officinal process for the estimation of this alkaloid in opium is conducted in the following manner:—

Take of opium 100 grains, slaked lime 100 grains, distilled water 4 ounces. Break down the opium, and steep it in an ounce of the water for twenty-four hours, stirring the mixture frequently. Transfer it to a displacement-apparatus, and pour on the remainder of the water in successive portions, so as to exhaust the opium by percolation. To the infusion thus obtained, placed in a flask, add the lime, boil for ten minutes, place the undissolved matter on a filter, and wash it with an ounce of boiling water. Acidulate the filtered fluid slightly with diluted hydrochloric acid, evaporate it to the bulk of half

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an ounce, and let it cool. Neutralize cautiously with solution of ammonia, carefully avoiding an excess; remove by filtration the brown matter which separates, wash it with an ounce of hot water, mix the washings with the filtrate, concentrate the whole to the bulk of half an ounce, and add now solution of ammonia in slight excess. After twenty-four hours collect the precipitated morphia on a weighed filter, wash it with cold water, and dry it at 212° F. It ought to weigh at least from six to eight grains.

Of hydrochlorate of morphine it is stated that "twenty grains of the salt dissolved in half an ounce of warm water, with ammonia added in the slightest possible excess, give on cooling a crystalline precipitate, which, when washed with a little cold water and dried by exposure to the air, weighs 15·18 grains.

SUGAR.

The qualitative test for sugar, by means of an alkaline copper solution (*vide* p. 268), may be applied in the estimation of sugar. 34·64 grammes of pure dry crystals of sulphate of copper are dissolved in about 250 c. c. of distilled water. 173 grammes of pure crystals of the double tartrate of potassium and sodium are dissolved in 480 c. c. of solution of caustic soda of sp. gr. 1·14. The solutions are mixed and water added to 1 litre. 100 c. c. of this solution represent 3·464 grammes of sulphate of copper, and correspond to 0·5 of a gramme of pure anhydrous grape-sugar, 0·475 of cane-sugar, or 0·45 of starch. It must be preserved in a well-stoppered bottle to prevent absorption of carbonic acid, and be kept in a dark place. If it gives a precipitate on boiling, a little solution of soda may be added in making experiments.

Dissolve 0·475 of pure dry powdered cane-sugar in about 50 c. c. of water, convert into grape-sugar by acidulating with sulphu-

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ric acid, and boiling for an hour or two, neutralize with carbonate of sodium, and dilute to 100 c. c. Place 10 c. c. of the copper solution in a small flask, dilute with three or four times its bulk of water, and gently boil. Into the boiling liquid drop the solution of sugar from a burette, one cubic centimetre, or less, at a time, until, after standing for the precipitate to subside, the supernatant liquid has just lost its blue colour; 10 c. c. of the solution of sugar should be required to produce this effect, =0·475 of cane-sugar or 0·5 of grape-sugar. Experiments on pure cane-sugar must be practised until accuracy is attained; syrups, diabetic urine, and saccharated substances containing unknown quantities of sugar may then be analyzed.

Starch may be converted into grape-sugar by ebullition with dilute acid for eight or ten hours, the solution being finally diluted so that one part of starch, or rather sugar, shall be contained in about 150 of water.

ALCOHOL.

Mulder's process for the determination of the amount of alcohol in wines, beer, tinctures, and other alcoholic liquids containing vegetable matter is as follows:—Take the specific gravity and temperature of the liquid, and measure off a certain quantity (100 cubic centimetres); evaporate to one half or less, avoiding ebullition in order that particles of the material may not be carried away by the steam. Dilute with water to the original bulk, and take the specific gravity at the same temperature as before. Of the figures representing this latter specific gravity, all over 1000 show to what extent dissolved solid matter affected the original specific gravity of the wine. Thus, the specific gravity of a sample of wine at 15°·5 C. is 0·9951; evaporated till all alcohol is removed and diluted with water to the original bulk, the specific gravity at 15°·5 C. is 1·0081 : 0·0081 represents the gravitating effect of the solid matter in the 0·9951 part of original wine. 0·0081

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subtracted from 0·9951 leaves 0·987, which is the specific gravity of the water and alcohol of the wine. On referring to a Table of the strengths of diluted alcohol of different specific gravities, 0·987 is found to indicate a spirit containing 8 per cent. of real alcohol. If the foregoing operation be conducted in a retort, the liquid being boiled and the steam carefully condensed, the distillate, diluted with water to the original bulk of wine operated on, will still more accurately represent the amount of water and alcohol in the wine; its specific gravity showing the percentage of real alcohol present.

Detailed instructions for the quantitative analysis of potable water, articles of food, general technical products, minerals, ashes, soils, manures, urine, alloys, illuminating agents (including solid fats, oils, spirits, petroleum, and gas), dyes, and tanning-materials, would scarcely be in place in 'An Introduction to Pharmaceutical Chemistry.'

The course of experimental study through which the student has been conducted will, it is hoped, have taught him the principles of the science of chemistry, and given him special knowledge concerning the applications of that science to pharmacy, as well as imparted sufficient manipulative skill to enable him to manufacture or analyze when necessary. The author would venture to suggest that this knowledge be utilized, not only in the way of personal advantage, but in experimental researches on subjects connected with pharmacy. The discovery and publication of a new truth, however small, is the best means whereby to aid in advancing the calling in which we may be engaged, to benefit our fellow creatures, and glorify the Creator of all things.

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APPENDIX.

DIALYSIS.

DIALYSIS (διά, *dia*, through, and λύσις, *lusis*, a loosing or resolving) is a term applied by Mr. Graham to a process of analysis by diffusion through a septum. The apparatus used in the process is called a *dialyzer*, and is constructed and employed in the following manner. The most convenient septum is the commercial article known as *parchment paper*, made by immersing unsized paper for a short time in sulphuric acid; it is sold by most dealers in chemical apparatus. A piece of this material is stretched over a gutta-percha hoop, and secured by a second external hoop. Dialyzers of useful size are one or two inches deep and five to ten inches wide. Liquids to be dialyzed are poured into the dialyzer, which is then floated in a flat dish containing distilled water.

The practical value of dialysis depends upon the fact that certain substances will diffuse through a given septum far more rapidly than others. Uncrystallizable bodies diffuse very slowly. Of such matters as starch, gum, albumen, and gelatin, the last named is perhaps least diffusive; hence substances of this class are termed *colloids*, or bodies like *collin*, which is the soluble form of gelatin. Substances which diffuse rapidly are mostly crystalline; hence bodies of this class are termed *crystalloids*.

Aqueous solutions of two parts of the following named substances in 100 parts of water, were dialyzed by Mr. Graham for twenty-four hours. The amounts of each substance which passed through the septum bore the following relations to one another:—

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Chloride of sodium	1000
Ammonia	847
Theine	703
Salicin	503
Cane-sugar	472
Amygdalin	311
Extract of logwood	168
Catechu	159
Extract of cochineal	51
Gallo-tannic acid	30
Extract of litmus	19
Purified caramel	5

Ten-per-cent. solutions, under similar circumstances, gave the following results:—

Gum Arabic	4
Starch-sugar	266
Cane-sugar	214
Glycerine	440
Alcohol	476
Chloride of sodium	1000

The phenomena of dialysis show that crystalloids are superior to colloids in affinity for water. If a solution of chloride of sodium be placed at the bottom of a jar, and covered by a hot solution of gelatine of sufficient strength to solidify on cooling, the chloride of sodium will diffuse up into the solid jelly, because the water of the solid jelly has a greater affinity for the salt than it has for the gelatin. The solid jelly may obviously be reduced in thickness, and saline liquids placed above it; indeed the conditions would then be still more favourable for diffusion. Replace the stratum of jelly by a permanent colloid, such as parchment paper; the result is the same, but the permanent character of the septum admits of its practical application.

Further researches on dialysis will probably throw much light on several important points in connexion with physiological chemistry, for there is little doubt that alimentary matter passes through the cell-walls of animals and plants by this process.

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TABLES.

TABLE OF THE QUANTITY OF REAL SULPHURIC ACID AND OF SULPHURIC ANHYDRIDE, IN 100 PARTS OF DILUTE SULPHURIC ACID OF DIFFERENT DENSITIES (URE).

Real acid in 100 parts of liquid.	Specific gravity.	Anhydride in 100 parts of liquid.	Real acid in 100 parts of liquid.	Specific gravity.	Anhydride in 100 parts of liquid.
100	1·8485	81·54	64	1·5280	52·18
99	1·8475	80·72	63	1·5170	51·37
98	1·8460	79·90	62	1·5066	50·55
97	1·8439	79·09	61	1·4960	49·74
96	1·8410	78·28	60	1·4860	48·92
95	1·8376	77·46	59	1·4760	48·11
94	1·8336	76·65	58	1·4660	47·29
93	1·8290	75·83	57	1·4560	46·48
92	1·8233	75·02	56	1·4460	45·66
91	1·8179	74·20	55	1·4360	44·85
90	1·8115	73·39	54	1·4265	44·03
89	1·8043	72·57	53	1·4170	43·22
88	1·7962	71·75	52	1·4073	42·40
87	1·7870	70·94	51	1·3977	41·58
86	1·7774	70·12	50	1·3884	40·77
85	1·7673	69·31	49	1·3788	39·95
84	1·7570	68·49	48	1·3697	39·14
83	1·7465	67·68	47	1·3612	38·32
82	1·7360	66·86	46	1·3530	37·51
81	1·7245	66·05	45	1·3440	36·69
80	1·7120	65·23	44	1·3345	35·88
79	1·6993	64·42	43	1·3255	35·06
78	1·6870	63·60	42	1·3165	34·25
77	1·6750	62·78	41	1·3080	33·43
76	1·6630	61·97	40	1·2999	32·61
75	1·6520	61·15	39	1·2913	31·80
74	1·6415	60·34	38	1·2826	30·98
73	1·6321	59·52	37	1·2740	30·17
72	1·6204	58·71	36	1·2654	29·35
71	1·6090	57·89	35	1·2572	28·54
70	1·5975	57·08	34	1·2490	27·72
69	1·5868	56·26	33	1·2409	26·91
68	1·5760	55·45	32	1·2334	26·09
67	1·5648	54·63	31	1·2260	25·28
66	1·5503	53·82	30	1·2184	24·46
65	1·5390	53·00	29	1·2108	23·65

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TABLE (*continued*).

Real acid in 100 parts of liquid.	Specific gravity.	Anhydride in 100 parts of liquid.	Real acid in 100 parts of liquid.	Specific gravity.	Anhydride in 100 parts of liquid.
28	1·2032	22·83	14	1·0953	11·41
27	1·1956	22·01	13	1·0887	10·60
26	1·1876	21·20	12	1·0809	9·78
25	1·1792	20·38	11	1·0743	8·97
24	1·1706	19·57	10	1·0682	8·15
23	1·1626	18·75	9	1·0614	7·34
22	1·1549	17·94	8	1·0544	6·52
21	1·1480	17·12	7	1·0477	5·71
20	1·1410	16·31	6	1·0405	4·89
19	1·1330	15·49	5	1·0336	4·08
18	1·1246	14·68	4	1·0268	3·26
17	1·1165	13·86	3	1·0206	2·446
16	1·1090	13·05	2	1·0140	1·63
15	1·1019	12·23	1	1·0074	0·8154

$SO_3 = 80$; $SO_4 = 96$; $H_2SO_4 = 98$.

TABLE OF THE QUANTITY OF NITRIC ANHYDRIDE IN 100 PARTS OF LIQUID ACID OF DIFFERENT DENSITIES (URE).

Specific gravity.	Anhydride in 100 parts of the liquid.	Specific gravity.	Anhydride in 100 parts of the liquid.
1·5000	79·700	1·4228	60·572
1·4980	78·903	1·4189	59·775
1·4960	78·106	1·4147	58·978
1·4940	77·309	1·4107	58·181
1·4910	76·512	1·4065	57·384
1·4880	75·715	1·4023	56·587
1·4850	74·918	1·3978	55·790
1·4820	74·121	1·3945	54·993
1·4790	73·324	1·3882	54·196
1·4760	72·527	1·3833	53·399
1·4730	71·730	1·3783	52·602
1·4700	70·933	1·3732	51·805
1·4670	70·136	1·3681	51·068
1·4640	69·339	1·3630	50·211
1·4600	68·542	1·3579	49·414
1·4570	67·745	1·3529	48·617
1·4530	66·948	1·3477	47·820
1·4500	66·155	1·3427	47·023
1·4460	65·354	1·3376	46·226
1·4424	64·557	1·3323	45·429
1·4385	63·760	1·3270	44·632
1·4346	62·963	1·3216	43·835
1·4306	62·166	1·3163	43·038
1·4269	61·369	1·3110	42·241

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TABLE (*continued*).

Specific gravity.	Anhydride in 100 parts of the liquid.	Specific gravity.	Anhydride in 100 parts of the liquid.
1·3056	41·447	1·1465	20·722
1·3001	40·440	1·1403	19·925
1·2947	39·685	1·1345	19·128
1·2887	39·053	1·1286	18·331
1·2826	38·256	1·1227	17·534
1·2765	37·459	1·1168	16·737
1·2705	36·662	1·1109	15·940
1·2644	35·865	1·1051	15·143
1·2583	35·068	1·0993	14·346
1·2523	34·271	1·0935	13·549
1·2462	33·474	1·0878	12·752
1·2402	32·677	1·0821	11·955
1·2341	31·880	1·0764	11·158
1·2277	31·083	1·0708	10·361
1·2212	30·286	1·0651	9·564
1·2148	29·489	1·0595	8·767
1·2084	28·692	1·0540	7·970
1·2019	27·895	1·0485	7·173
1·1958	27·098	1·0430	6·376
1·1895	26·301	1·0375	5·579
1·1833	25·504	1·0320	4·782
1·1770	24·707	1·0267	3·985
1·1709	23·910	1·0212	3·188
1·1648	23·113	1·0159	2·391
1·1587	22·316	1·0106	1·594
1·1526	21·519	1·0053	0·797

$N_2O_5 \div 2 = 54$; $NO_3 = 62$; $HNO_3 = 63$.

TABLE OF THE QUANTITY OF HYDROCHLORIC ACID IN THE LIQUID ACID OF DIFFERENT SPECIFIC GRAVITIES (URE).

Acid of 1·2 in 100.	Specific gravity.	Chlorine.	Hydrochloric gas.
100	1·2000	39·675	40·777
99	1·1982	39·278	40·369
98	1·1964	38·882	39·961
97	1·1946	38·485	39·554
96	1·1928	38·089	39·146
95	1·1910	37·692	38·738
94	1·1893	37·296	38·330
93	1·1875	36·900	37·923
92	1·1857	36·503	37·516
91	1·1846	36·107	37·108
90	1·1822	35·707	36·700
89	1·1802	35·310	36·292

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TABLE (*continued*).

Acid of 1·2 in 100.	Specific gravity.	Chlorine.	Hydrochloric gas.
88	1·1782	34·913	35·884
87	1·1762	34·517	35·476
86	1·1741	34·121	35·068
85	1·1721	33·724	34·660
84	1·1701	33·328	34·252
83	1·1681	32·931	33·845
82	1·1661	32·535	33·437
81	1·1641	32·136	33·029
80	1·1620	31·743	32·621
79	1·1599	31·343	32·213
78	1·1578	30·946	31·805
77	1·1557	30·550	31·398
76	1·1536	30·153	30·990
75	1·1515	29·757	30·582
74	1·1494	29·361	30·174
73	1·1473	28·964	29·767
72	1·1452	28·567	29·359
71	1·1431	28·171	28·951
70	1·1410	27·772	28·544
69	1·1389	27·376	28·136
68	1·1369	26·979	27·728
67	1·1349	26·583	27·321
66	1·1328	26·186	26·913
65	1·1308	25·789	26·505
64	1·1287	25·392	26·098
63	1·1267	24·996	25·690
62	1·1247	24·599	25·282
61	1·1226	24·202	24·874
60	1·1206	23·805	24·466
59	1·1185	23·408	24·058
58	1·1164	23·012	23·650
57	1·1143	22·615	23·242
56	1·1123	22·218	22·834
55	1·1102	21·822	22·426
54	1·1082	21·425	22·019
53	1·1061	21·028	21·611
52	1·1041	20·632	21·203
51	1·1020	20·235	20·796
50	1·1000	19·837	20·388
49	1·0980	19·440	19·980
48	1·0960	19·044	19·572
47	1·0939	18·647	19·165
46	1·0919	18·250	18·757
45	1·0899	17·854	18·349
44	1·0879	17·457	17·941
43	1·0859	17·060	17·534
42	1·0838	16·664	17·126

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TABLE (*continued*).

Acid of 1·2 in 100.	Specific gravity.	Chlorine.	Hydrochloric gas
41	1·0818	16·267	16·718
40	1·0798	15·870	16·310
39	1·0778	15·474	15·902
38	1·0758	15·077	15·494
37	1·0738	14·680	15·087
36	1·0718	14·284	14·679
35	1·0697	13·887	14·271
34	1·0677	13·490	13·863
33	1·0657	13·094	13·456
32	1·0637	12·597	13·049
31	1·0617	12·300	12·641
30	1·0597	11·903	12·233
29	1·0577	11·506	11·825
28	1·0557	11·109	11·418
27	1·0537	10·712	11·010
26	1·0517	10·316	10·602
25	1·0497	9·919	10·194
24	1·0477	9·522	9·786
23	1·0457	9·126	9·379
22	1·0437	8·729	8·971
21	1·0417	8·332	8·563
20	1·0397	7·935	8·155
19	1·0377	7·538	7·747
18	1·0357	7·141	7·340
17	1·0337	6·745	6·932
16	1·0318	6·348	6·524
15	1·0298	5·951	6·116
14	1·0279	5·554	5·709
13	1·0259	5·158	5·301
12	1·0239	4·762	4·893
11	1·0220	4·365	4·486
10	1·0200	3·998	4·078
9	1·0180	3·571	3·670
8	1·0160	3·174	3·262
7	1·0140	2·778	2·854
6	1·0120	2·381	2·447
5	1·0110	1·984	2·039
4	1·0080	1·588	1·631
3	1·0060	1·191	1·224
2	1·0040	0·795	0·816
1	1·0020	0·397	0·408

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THE PROPORTION BY WEIGHT OF ABSOLUTE OR REAL ALCOHOL (C_2H_5HO) IN 100 PARTS OF SPIRITS OF DIFFERENT SPECIFIC GRAVITIES (FOWNES).

Sp. gr. at 60° (15°·5 C.).	Percentage of real alcohol.	Sp. gr. at 60° (15°·5 C.).	Percentage of real alcohol.	Sp. gr. at 60° (15°·5 C.).	Percentage of real alcohol.
0·9991	0·5	0·9511	34	0·8769	68
0·9981	1	0·9490	35	0·8745	69
0·9965	2	0·9470	36	0·8721	70
0·9947	3	0·9452	37	0·8696	71
0·9930	4	0·9434	38	0·8672	72
0·9914	5	0·9416	39	0·8649	73
0·9898	6	0·9396	40	0·8625	74
0·9884	7	0·9376	41	0·8603	75
0·9869	8	0·9356	42	0·8581	76
0·9855	9	0·9335	43	0·8557	77
0·9841	10	0·9314	44	0·8533	78
0·9828	11	0·9292	45	0·8508	79
0·9815	12	0·9270	46	0·8483	80
0·9802	13	0·9249	47	0·8459	81
0·9789	14	0·9228	48	0·8434	82
0·9778	15	0·9206	49	0·8408	83
0·9766	16	0·9184	50	0·8382	84
0·9753	17	0·9160	51	0·8357	85
0·9741	18	0·9135	52	0·8331	86
0·9728	19	0·9113	53	0·8305	87
0·9716	20	0·9090	54	0·8279	88
0·9704	21	0·9069	55	0·8254	89
0·9691	22	0·9047	56	0·8228	90
0·9678	23	0·9025	57	0·8199	91
0·9665	24	0·9001	58	0·8172	92
0·9652	25	0·8979	59	0·8145	93
3·9638	26	0·8956	60	0·8118	94
0·9623	27	0·8932	61	0·8089	95
0·9609	28	0·8908	62	0·8061	96
0·9593	29	0·8886	63	0·8031	97
0·9578	30	0·8863	64	0·8001	98
0·9560	31	0·8840	65	0·7969	99
0·9544	32	0·8816	66	0·7938	100
0·9528	33	0·8793	67		

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CENTESIMAL AMOUNTS OF OXIDE OF POTASSIUM (K_2O) IN SOLUTIONS OF POTASH OF DIFFERENT SPECIFIC GRAVITIES (DALTON).

Specific gravity.	K_2O per cent.	Boiling-point.	Specific gravity.	K_2O per cent.	Boiling-point.
1·63	51·2	329°	1·33	26·3	229°
1·60	46·7	290	1·28	23·4	224
1·52	42·9	276	1·23	19·5	220
1·47	39·6	265	1·19	16·2	218
1·44	36·8	255	1·15	13·0	215
1·42	34·4	246	1·11	9·5	214
1·39	32·4	240	1·06	4·7	213
1·36	29·4	234			

$K_2O \div 2 = 47$; $KHO = 56$.

CENTESIMAL AMOUNTS OF OXIDE OF SODIUM (Na_2O) IN SOLUTIONS OF SODA OF DIFFERENT SPECIFIC GRAVITIES (DALTON).

Specific gravity.	Na_2O per cent.	Boiling-point.	Specific gravity.	Na_2O per cent.	Boiling-point.
2·00	77·8	—°	1·40	29·0	242°
1·85	63·6	600	1·36	26·0	235
1·72	53·8	400	1·32	22·0	228
1·63	46·6	300	1·29	19·0	224
1·56	41·2	280	1·23	16·0	220
1·50	36·8	265	1·18	13·0	217
1·47	34·0	255	1·12	9·8	214
1·44	31·0	248	1·06	4·7	213

$Na_2O \div 2 = 31$; $NaHO = 40$.

PERCENTAGE OF AMMONIACAL GAS IN SOLUTIONS OF AMMONIA OF VARIOUS STRENGTHS.

Sp. gr. of solution at 57° F.	Ammonia in 100 parts, by weight.	Sp. gr. of solution at 57° F.	Ammonia in 100 parts, by weight.	Sp. gr. of solution at 57° F.	Ammonia in 100 parts, by weight.
0·8844	36	0·9133	24	0·9520	12
0·8864	35	0·9162	23	0·9556	11
0·8885	34	0·9191	22	0·9593	10
0·8907	33	0·9221	21	0·9631	9
0·8929	32	0·9251	20	0·9670	8
0·8953	31	0·9283	19	0·9709	7
0·8976	30	0·9314	18	0·9749	6
0·9001	29	0·9347	17	0·9790	5
0·9026	28	0·9380	16	0·9831	4
0·9052	27	0·9414	15	0·9873	3
0·9078	26	0·9449	14	0·9915	2
0·9106	25	0·9484	13	0·9959	1

$NH_3 = 17$; $NH_4HO = 35$.

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THE ELEMENTS.

	Symbol and atomic value.	Atomic weight.
Aluminium ($^{II}Al_2^{VI}$)	Al^{IV}	27·5
Antimony ($^{II}Sb^{III}$)	Sb^{V}	122
Arsenicum ($^{II}As^{III}$)	As^{V}	75
Barium	Ba^{II}	137
Bismuth ($^{II}Bi^{III}$)	Bi^{V}	208
Boron	B^{III}	11
Bromine	Br^{I}	80
Cadmium	Cd^{II}	112
Cæsium	Cs^{I}	133
Calcium	Ca^{II}	40
Carbon	C^{IV}	12
Cerium	Ce^{VI}	92
Chlorine (35·457, Stas)	Cl^{I}	35·5
Chromium ($^{VI}Cr_2^{I}$)	Cr^{VI}	52·5
Cobalt ($^{IV}Co^{II}$)	Co^{VI}	58·8
Copper	Cu^{II}	63·5
Didymium	D^{II}	96
Fluorine	F^{I}	19
Glucinum	G^{II}	14
Gold	Au^{II}	196·7
Hydrogen	H^{I}	1
Indium	In	74
Iodine (126·85, Stas)	I^{I}	127
Iridium	Ir^{VI}	198
Iron ($^{IV}Fe^{II}$ & $^{VI}Fe_2^{VI}$)	Fe^{VI}	56
Lanthanium	L^{II}	92
Lead ($^{II}Pb^{II}$)	Pb^{IV}	207
Lithium	Li^{I}	7
Magnesium	Mg^{II}	24
Manganese ($^{IV}Mn^{II}$ & $^{II}Mn^{IV}$)	Mn^{VI}	55
Mercury	Hg^{II}	200
Molybdenum	Mo^{VI}	92
Nickel ($^{IV}Ni^{II}$)	Ni^{VI}	58·8
Niobium	Nb^{IV}	97·6
Nitrogen ($^{IV}N^{I}$ & $^{II}N^{III}$)	N^{V}	14

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THE ELEMENTS (*continued*).

	Symbol and atomic value.	Atomic weight.
Osmium	Os^{VI}	199
Oxygen	O^{II}	16
Palladium	Pd^{IV}	106·5
Phosphorus ($^{II}P^{III}$)	P^{V}	31
Platinum (197·88, Andrews)	Pt^{IV}	198
Potassium (39·137, Stas)	K^{I}	39
Rhodium	Rh^{VI}	104
Rubidium	Rb^{I}	85·5
Ruthenium	Ru^{VI}	104
Selenium	Se^{VI}	79
Silicon	Si^{IV}	28·5
Silver (107·93, Stas)	Ag^{I}	108
Sodium	Na^{I}	23
Strontium	Sr^{II}	87·5
Sulphur ($^{IV}S^{II}$ & $^{II}S^{IV}$)	S^{VI}	32
Tantalum	Ta^{IV}	137·5
Tellurium	Te^{VI}	128
Thallium (203, Crookes)	Tl^{I}	204
Thorium	Tr^{IV}	231·5
Tin ($^{II}Sn^{II}$)	Sn^{IV}	118
Titanium	Ti^{IV}	50
Tungsten	W^{VI}	184
Uranium	U^{VI}	120
Vanadium	V^{VI}	137
Yttrium	Y^{II}	68
Zinc	Zn^{II}	65
Zirconium	Zr^{IV}	90
Total.....62.		

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QUESTIONS AND EXERCISES.

1. Of how many elements is terrestrial matter composed?

2. In what state do the elements occur in nature?

3. State the difference between the *art* and the *science* of chemistry.

4. Define *Pharmaceutical Chemistry.*

5. Enumerate the chief non-metallic elements.

6. Describe a process for the preparation of oxygen.

7. How are gases usually stored?

8. Give a method for the elimination of hydrogen from water.

9. State the properties of hydrogen.

10. Why is a mixture of hydrogen and air explosive?

11. Explain the effects producible by the ignition of large quantities of coal-gas and air.

12. To what extent is hydrogen lighter than oxygen?

13. Why does phosphorus burn in air?

14. What remains when ignited phosphorus has removed all the oxygen from a confined portion of air?

15. Give the specific gravity of nitrogen.

16. How is chlorine prepared?

17. Enumerate the properties of chlorine.

18. State the prominent characters of sulphur, carbon, and iodine.

19. Give the derivations of the names of some of the elements.

20. Adduce familiar examples of the manifestation of chemical action.

21. What are the characteristics of the chemical force? how

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is it distinguished from those of gravitation, heat, light, electricity, and magnetism?

22. How may the results of chemical reactions be shortly expressed on paper?

23. Illustrate the difference between chemical symbols and formulæ.

24. Define the terms *atom* and *molecule*.

25. In what does an atom differ from a molecule of oxygen?

26. Describe the method of producing ammoniacal gas.

27. How many pints of their constituents are represented by one quart of hydrochloric acid gas, steam, and ammoniacal gas respectively?

28. What is *atomic weight*?

29. Admitting the existence of atoms, and assigning the weight 1 to that of hydrogen, what are the atomic weights of oxygen, chlorine, nitrogen, and carbon? Give reasons for considering the stated weights to be correct.

30. What is to be understood by quantivalence? Give examples of univalent, bivalent, trivalent, and quadrivalent atoms.

31. How is the quantivalence of an element expressed in its atomic symbol?

32. Name the sources of potassium.

33. Construct an equation or a diagram expressive of the reaction between carbonate of potassium and slaked lime.

34. What is the composition of Acetate of Potassium, and what its relation to other acetates?

35. Give a general process for the conversion of carbonates into other salts.

36. What is the difference between Carbonate and Acid Carbonate of Potassium? How is the latter prepared?

37. What is the relation between salts whose specific names end in the syllable "*ate*," and acids ending in "*ic*"?

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38. Draw out equations descriptive of the formation of Tartrate of Potassium from the Acid Tartrate, and Citrate from the Carbonate of Potassium.

39. How is Iodide of Potassium made?

40. Give a method for the detection of iodate in iodide of potassium. Explain the reaction.

41. Has the syllable "*ide*" any general signification in chemical nomenclature?

42. What is the difference between sulphides, sulphites, and sulphates?

43. Describe the formation of Permanganate of Potassium.

44. Enumerate the tests for potassium.

45. What is the natural source of the sodium salts?

46. How is the officinal Solution of Soda prepared?

47. State the difference between Anhydrous and Crystallized Carbonate of Sodium.

48. What is the relation of Rochelle Salt to Cream of Tartar?

49. Give the mode of preparation and composition of the officinal Solution of Chlorinated Soda.

50. How is the granular effervescing Citro-tartrate of Sodium prepared?

51. What is the general relation of potassium salts to those of sodium?

52. How are sodium salts analytically distinguished from those of potassium?

53. Why are ammoniacal salts classed with those of potassium and sodium?

54. Adduce evidence of the existence of ammonium.

55. How are the officinal Solutions of Ammonia prepared?

56. How is the officinal Solution of Acetate of Ammonium prepared?

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57. What is the composition of commercial Carbonate of Ammonium?

58. Give equations illustrating the formation of Citrate, Phosphate, and Benzoate of Ammonium.

59. Show how hydrate of ammonium may be converted into sulphydrate.

60. Describe the preparation of Sulphuretted Hydrogen gas.

61. Enumerate and explain the tests for ammonium.

62. How is potassium detected in the presence of ammonium?

63. Describe the analysis of an aqueous liquid containing salts of potassium, sodium, and ammonium.

64. Write down the formulæ of oxide, hydrate, chloride, nitrate, carbonate, and sulphate of barium.

65. Which of the tests for barium is most characteristic?

66. Name the antidote in cases of poisoning by soluble barium salts, and explain its action.

67. Enumerate some of the common natural compounds of calcium.

68. Explain the action of hydrochloric acid on marble.

69. Why is chloride of calcium used as a desiccator for gases?

70. How would you purify Chloride of Calcium which has been made from ferruginous marble

71. Write a few lines on the chemistry of the lime-kiln.

72. In what sense is the conversion of chalk into lime an analytical action?

73. What occurs when lime is slaked? Explain the simultaneous production of steam.

74. To what extent is lime soluble in water? to what in syrup?

75. Describe the preparation of pure Precipitated Carbonate of Calcium; in what does it differ from Prepared Chalk?

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76. How is "Bone-earth" purified for use in medicine?

77. Explain the action of hydrochloric acid on Animal Charcoal.

78. Give equations showing the conversion of Phosphate of Calcium into Phosphate of Sodium.

79. Write a short article on the manufacture, composition, and uses of "bleaching-powder."

80. How may calcium be detected in Gum-Arabic?

81. Can calcium be precipitated from an aqueous solution containing barium?

82. Barium being absent, what reagents may be used for the detection of calcium?

83. Name the natural sources of the various salts of magnesium.

84. Explain the evolution of heat and light during the combustion of metallic magnesium.

85. Give a process for the preparation of Epsom salt.

86. Show by an equation the process for the preparation of the officinal Carbonate of Magnesium.

87. What circumstances determine the two different states of aggregation of the officinal Carbonate of Magnesium?

88. Is magnesia soluble in water?

89. Can magnesium be detected in presence of barium and calcium?

90. Describe the analysis of an aqueous liquid containing salts of barium, calcium, and magnesium.

91. How may magnesium be precipitated from solutions containing ammoniacal salts?

92. In what respects do barium, calcium, and magnesium resemble, and in what differ, from potassium, sodium, and ammonium?

93. Give the sources and uses of metallic zinc.

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94. What occurs when zinc is dissolved in dilute sulphuric acid?

95. How may solutions of Chloride or Sulphate of Zinc be purified from salts of iron? Give equations descriptive of the reactions.

96. What is the formula of the officinal Carbonate of Zinc?

97. In what respect does Oxide of Zinc, resulting from the ignition of the carbonate, differ from that produced during the combustion of the metal?

98. How is Valerianate of Zinc prepared?

99. Name the more important tests for zinc.

100. What is there remarkable about the quantivalence of aluminium?

101. Enumerate the chief natural compounds of aluminium.

102. Write down a formula which shall represent either of the Alums.

103. Why are aluminium compounds used in dyeing?

104. How are salts of aluminium analytically distinguished from those of zinc?

105. Name the chief ores of iron.

106. Illustrate by formulæ the difference between ferrous and ferric salts.

107. Under what different circumstances may the atom of iron be considered to exert bivalent, trivalent, quadrivalent, and sexivalent activity?

108. In what respects do the officinal Sulphate of Iron, Granulated Sulphate of Iron, and Dried Sulphate of Iron differ?

109. Describe the action of atmospheric oxygen on Ferrous Carbonate: can the effect be prevented?

110. Write out an equation illustrative of the formation of the officinal Phosphate of Iron.

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111. What compounds of iron may be formed by the direct union of their elements?

112. Give four methods for the preparation of Ferric Chloride.

113. Explain the action of nitric acid on a hot solution of ferrous chloride containing hydrochloric acid.

114. How may Ferrous be converted into Ferric Sulphate?

115. Express, by formulæ, the difference between *Ferri Peroxidum Humidum*, B. P., and *Ferri Peroxidum Hydratum*, B. P., and cite a case in which their chemical action is different.

116. What are the general characters and mode of production of the medicinal scale-preparations of iron?

117. Give equations illustrating the chief steps in the artificial production of Magnetic Oxide of Iron.

118. How much anhydrous ferric oxide can be obtained, theoretically, from one hundredweight of iron?

119. Give the characteristic tests for iron, distinguishing between ferrous and ferric reactions.

120. Describe the action of ammonia on salts of iron, aluminium, and zinc respectively.

121. What precautions must be used in testing for calcium in the presence of iron?

122. How is magnesium detected in the presence of zinc?

123. To what extent does aluminium interfere with the tests for magnesium?

124. Draw a scheme for the analysis of an aqueous liquid containing salts of iron, barium, and potassium.

125. In what form does arsenicum occur in nature?

126. Name the officinal preparations of arsenicum, and their strength.

127. By what method may arsenic be reduced to arsenicum?

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128. Give the formulæ of arsenious and arsenic acids.

129. Explain the reactions which occur in converting arsenic into Arseniate of Sodium by the process of the Pharmacopœia.

130. In the preparation of Arseniate of Iron from ferrous sulphate and arseniate of sodium, why is acetate of sodium included?

131. Describe the manipulations necessary in distinguishing arsenic by its crystalline form.

132. How is Reinsch's test for arsenicum applied? under what circumstances may its indications be fallacious?

133. Give the details of Marsh's test for arsenicum, and the precautions which must be observed in its performance.

134. What peculiar value has Fleitmann's test for arsenicum?

135. Describe the conditions under which sulphuretted hydrogen becomes a trustworthy test for arsenicum.

136. How are salts of copper and silver applied as reagents for the detection of arsenicum?

137. How are arsenites distinguished from arseniates?

138. Mention the best antidote in cases of poisoning by arsenic, explain the process by which it may be most quickly prepared, and describe its action.

139. What is the composition and what the source of the *Black Antimony* of pharmacy?

140. How is "Butter of Antimony" prepared?

141. Write out equations expressive of the reactions which occur in converting sulphide of antimony into Tartar-Emetic.

142. Explain the officinal process for the preparation of Oxysulphide of Antimony (*Antimonium Sulphuratum*, B. P.).

143. Give a comparative statement of the tests for arsenicum and antimony.

144. How is antimony detected in the presence of arsenicum?

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145. To what extent does antimony mask the analytical reactions of arsenicum?

146. How may arsenicum and iron be distinguished analytically?

147. Describe a method by which antimony, magnesium, and iron may be separated from each other.

148. Draw out an analytical chart for the examination of an aqueous liquid containing salts of arsenicum, zinc, calcium, and ammonium.

149. Name the sources of copper.

150. How much Crystallized Sulphate of Copper may be obtained from 100 parts of sulphide?

151. Name a good clinical test for copper.

152. What is the analytical position of copper?

153. How may copper be separated from arsenicum?

154. Why is finely divided iron an effective antidote in cases of poisoning by copper?

155. Name the chief ore of mercury, and describe a process for the extraction of the metal.

156. In what state does mercury exist in "Grey Powder?"

157. Give the chemical and physical points of difference between Calomel and Corrosive sublimate.

158. How may a small quantity of corrosive sublimate in calomel be detected?

159. State the composition and mode of preparation of the two Iodides of Mercury.

160. Under what circumstances does mercuric iodide assume two different colours?

161. Write down the formulæ of Mercurous and Mercuric Nitrates and Sulphates.

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162. Describe the processes necessary for the conversion of mercury into Calomel and Corrosive Sublimate.

163. How much mercury will be required in the manufacture of one ton of Calomel?

164. Mention the officinal preparations of the chlorides of mercury.

165. Give the formulæ and mode of formation of the Yellow, Red, and Black Oxides of Mercury.

166. Explain the action of the chief test for mercury.

167. How are mercurous and mercuric salts analytically distinguished?

168. Give a probable view of the constitution of *Hydrargyrum Ammoniatum*, B. P.

169. Why is the formula of calomel Hg_2Cl_2 and not HgCl?

170. Write down equations descriptive of the smelting of galena.

171. Mention some of the alloys of lead.

172. In what respect does white lead differ from red lead?

173. Describe the preparation and composition of *Liquor Plumbi Subacetatis*, B. P.

174. What is the action of nitric acid on red lead, litharge, and metallic lead?

175. How is the officinal Iodide of Lead prepared?

176. Describe the reaction between oxide of lead, water, and olive-oil, at the temperature of boiling water, and give chemical formulæ explanatory of the constitution of the products.

177. Mention the chief tests for lead.

178. State a method whereby lead, barium, and silver may be separated.

179. Name the best antidote in cases of poisoning by salts of lead.

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180. By what process is silver obtained from argentiferous galena?

181. What weight of English silver coin will yield one pound of pure nitrate of silver?

182. How may the metal be recovered from an impure mixture of silver salts?

183. Describe the reaction of lime-water and nitrate of silver.

184. Mention the chief test for silver, and the precautions to be observed in order that it may be distinguished from lead and mercury.

185. Name the antidote for silver.

186. Give processes for the qualitative analysis of liquids containing the following substances:—

a. Antimony and Mercurous salt.
b. Lead and Calcium.
c. Silver and Mercurous salt.
d. Lead and Mercuric salt.
e. Copper and Arsenicum.
f. Arsenicum and Antimony.
g. Aluminium and Zinc.
h. Iron and Copper.
i. Magnesium, Calcium, and Potassium.
j. Silver, Antimony, Zinc, Barium, and Ammonium.

187. Name the sources and officinal compounds of lithium.

188. Write a paragraph on strontium, its natural compounds, technical applications, and tests.

189. Give an equation descriptive of the reaction of black oxide of manganese with hydrochloric acid.

190. What are the tests for manganese?

191. How are salts of cobalt analytically distinguished from those of nickel?

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192. State the method of preparation of red chromate of potassium.

193. Mention the chief tests for the chromic radical.

194. Describe the action of sulphuretted hydrogen on acidified solutions of chromates.

195. Define the terms stream tin, block tin, grain tin, tin-plate.

196. What is the difference between stannic acid and metastannic acid?

197. Name the chief tests for stannous and stannic salts.

198. How much pure gold is contained in English coin, and in jewellers' gold?

199. What effect is produced on gold by hydrochloric, nitric, and nitrohydrochloric acids respectively?

200. Whence is platinum obtained?

201. How is perchloride of platinum prepared?

202. Describe an experiment demonstrative of the large amount of attraction for gases possessed by metallic platinum.

203. By what process may Iodide of Cadmium be prepared, and in what form is it used in medicine?

204. Write down equations descriptive of the action of nitric acid on bismuth, and water on nitrate of bismuth.

205. How may pure salts be prepared from arsenical bismuth?

206. Give formulæ showing the accordance of the officinal Subnitrate and Carbonate with the other salts of Bismuth.

207. Give processes for the qualitative analysis of liquids containing the following substances:—

a. Arsenicum and Cadmium.

b. Bismuth and Antimony.

c. Ferrous and Ferric salts.

d. Aluminium, Iron, and Chromium.

e. Arsenicum, Antimony, and Tin.

f. Lead and Strontium.

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g. Iron and Phosphate of Calcium.
h. Mercury, Manganese, and Magnesium.
i. Zinc, Manganese, Nickel, and Cobalt.
j. Barium, Strontium, and Calcium.

208. Mention the basylous radical of acids.

209. Give illustrations of univalent, bivalent, and trivalent acidulous radicals, and monobasylous, dibasylous, and tribasylous salts.

210. What is the difference between an elementary and a compound acidulous radical?

211. Name the grounds on which salts may be assumed to contain radicals.

212. What is the specific gravity of hydrochloric acid gas, hydrogen being taken as unity?

213. The officinal Hydrochloric Acid contains 31·8 per cent. by weight of gas, and its specific gravity is 1·16; what volume of it will be required, theoretically, to make one gallon of chlorine-water, one fluid ounce of which contains 2·66 grains of chlorine?

214. Why does hydrochloric acid gas give visible fumes on coming into contact with air?

215. How much chloride of sodium will be required to furnish one pound of chlorine?

216. Give the analytical reactions of chlorides.

217. State the method by which Bromine is obtained from its natural compounds.

218. How may the Bromides of Potassium and Ammonium be made?

219. By what reagents may bromides be distinguished from chlorides?

220. Whence is Iodine obtained?

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221. Give the analytical reactions of iodides.

222. Describe a method by which iodides may be removed from a solution containing chlorides and bromides.

223. Mention the source of the cyanogen of all cyanides.

224. How is Ferrocyanide of Potassium prepared?

225. Write an equation expressive of the reaction which ensues when ferrocyanide and carbonate of potassium are brought together at a high temperature.

226. What are the properties of cyanogen? How may it be obtained in a pure condition?

227. How much real hydrocyanic acid is contained in the officinal liquid?

228. Give details of the preparation of hydrocyanic acid, and an equation of the reaction.

229. State the proportion of water that must be added to an aqueous solution containing 15 per cent. of hydrocyanic acid to reduce the strength to 2 per cent.

230. What are the characters of pure hydrocyanic acid? How may it be obtained?

231. Enumerate the tests for cyanogen, giving equations.

232. Explain the action of the best antidote in cases of poisoning by hydrocyanic acid or cyanide of potassium.

233. Trace the origin of nitrates to their elements.

234. In what does cubic nitre differ, chemically, from prismatic nitre?

235. Describe a process by which nitrate of potassium may be obtained artificially.

236. What group of elements is characteristic of all nitrates? and what claim has this group to the title of radical?

237. How is the officinal Nitric Acid prepared? What its specific gravity and centesimal strength?

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238. What reactions occur when strong nitric and hydrochloric acids are mixed?

239. Enumerate and explain the tests for nitrates.

240. How is nitric acid distinguished from other nitrates?

241. What quantity of cubic nitre will be required to produce ten carboys of officinal nitric acid, each containing 114 pounds?

242. Give details of the preparation of chlorate of potassium.

243. What decompositions occur when chlorate of potassium is heated?

244. How may the presence of chlorine in chlorates be demonstrated?

245. Mention the tests for chlorates.

246. One hundred cubic inches of oxygen, at 60° F. and barometer at 30 inches, weighing 34·203 grains, and 1 gallon containing 277¼ cubic inches, what weight of chlorate of potassium will be required, under similar conditions, to yield 10 gallons of the gas?

247. State the source, chemical name, and composition of borax.

248. Give an equation descriptive of the action of sulphuric acid on a hot dilute solution of borax.

249. Mention the chief analytical reactions of borates.

250. What is the molecular weight of acetic acid?

251. Name the sources of acetic acid.

252. From what compound is the acetic acid of vinegar immediately derived?

253. How much real acid is contained in officinal vinegar?

254. Write the formulæ of several acetates.

255. How may acetic acid be obtained from acetate of sodium?

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256. Give three or more views of the constitution of acetates, illustrating each by formulæ.

257. Enumerate the tests for acetates.

258. In what forms does sulphur occur in nature?

259. State the modes of preparation of the three chief commercial varieties of sulphur.

260. What are the characters of pure precipitated sulphur?

261. Give equations explanatory of the reactions which occur in precipitating sulphur according to the officinal process.

262. Define sulphides and sulphydrates.

263. Describe the preparation of sulphuretted hydrogen.

264. Mention the tests for sulphides, and the character by which sulphuretted hydrogen is distinguished from other sulphides.

265. What are the differences between sulphurous acid and sulphurous acid gas, sulphites and acid sulphites?

266. How is the officinal Sulphurous Acid prepared?

267. By what test may sulphurous acid be recognized in acetic acid?

268. Give a method by which sulphites may be detected in presence of sulphides and sulphates.

269. Write a short article on the manufacture and uses of sulphuric acid.

270. How may nitrous compounds be detected in, and eliminated from, sulphuric acid?

271. What percentage of real acid is contained in commercial oil of vitriol?

272. By what process is sulphuric anhydride obtained from Nordhausen sulphuric acid?

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273. Explain the reactions which occur in testing for sulphates.

274. Ascertain by calculation the weight of oil of vitriol necessary for the production of one ton of sulphate of ammonium.

275. Name the chief natural carbonates.

276. Adduce evidence of the existence of true carbonic acid.

277. Trace the steps by which the carbonic constituents of chalk are transferred to sodium by the process usually adopted in alkali-works.

278. Carbonic acid gas is constantly exhaled from the lungs of animals; why does it not accumulate in the atmosphere?

279. What is the effect of pressure on carbonic acid gas?

280. By what processes may carbonic acid gas be obtained for experimental and manufacturing purposes?

281. Describe the action of carbonic acid gas on the carbonates of potassium or sodium.

282. What quantity of chalk will be required to furnish the carbonic acid necessary to convert one ton of carbonate of potassium into acid carbonate, supposing no gas to be wasted?

283. Define "hardness" in water.

284. How may the presence of carbonates be demonstrated?

285. Explain the constitution of oxalates, and state how they are obtained.

286. Mention the chief test for oxalic acid and other soluble oxalates.

287. By what reactions are insoluble oxalates recognized?

288. State the origin of tartaric acid and other tartrates.

289. Give equations illustrative of the production of tartaric acid from cream of tartar.

290. Write formulæ of normal, acid, and double tartrates,

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tartar-emetic being treated as an oxytartrate of antimony with tartrate of potassium.

291. By what general process may normal or double tartrates be obtained from acid tartrate of potassium?

292. Enumerate the tests for tartrates.

293. Mention a process by which tartrates can be separated from citrates.

294. Describe the method by which citric acid is prepared.

295. Illustrate by formulæ the various classes of tartrates and citrates.

296. What are the tests for citrates?

297. Whence is phosphorus obtained?

298. Give equations explanatory of the isolation of phosphorus from its natural compounds.

299. What is the composition of farmers' "superphosphate," and how prepared?

300. How is the officinal Diluted Phosphoric Acid made?

301. Write formulæ illustrative of all classes of orthophosphates.

302. Mention the chief tests for soluble and insoluble phosphates.

303. By what reactions may phosphates be distinguished from arseniates?

304. Give the preparation, composition, uses, and tests of benzoic acid.

305. How is cyanate of potassium prepared, how converted into an ammonium salt, and what the relations of the latter to urea?

306. Describe the artificial production of formic acid.

307. What are the respective reactions of ferrocyanide of potassium with strong and weak sulphuric acid?

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308. Write equations illustrative of the changes effected on ferrocyanide of potassium during its conversion into ferridcyanide.

309. By what reactions may the presence of a mixture of ferrocyanide and ferridcyanide of potassium in a solution be demonstrated?

310. Describe the source, mode of preparation, and chief use of hydrofluoric acid.

311. Under what circumstances is hypochlorous acid formed? what are its relations to common bleaching-powder?

312. Describe the preparation and composition of hyposulphite of sodium.

313. Mention the uses and characteristic reactions of hyposulphite of sodium.

314. Define, by formulæ, metaphosphates, pyrophosphates, orthophosphates, phosphites, and hypophosphites.

315. Describe the preparation of phosphorous acid.

316. Give the mode of manufacture of hypophosphites.

317. How are pyrophosphates prepared?

318. By what ready method may metaphosphoric acid be obtained for experimental purposes?

319. Mention the tests by which meta-, pyro-, and orthophosphates are analytically distinguished.

320. Name the reactions by which hypophosphites and phosphites are detected.

321. Offer two views of the constitution of pyrophosphates.

322. State the conditions under which lactates are formed, and the method by which lactic acid is obtained.

323. Name the sources and tests for malates.

324. What is the constitution of nitrites?

325. Mention a test for nitrites in potable waters.

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326. Give the names of some natural and artificial silicates.

327. What is "soluble glass?"

328. How are silicates detected?

329. State the mode of manufacture and tests of sulphocyanates.

330. Describe the officinal process for the preparation of Tannic Acid.

331. Explain the chemistry of "tanning."

332. Enumerate the tests for tannic acid.

333. What is the assumed constitution of tannic acid?

334. How is gallic acid prepared?

335. By what reaction is gallic distinguished from tannic acid?

336. Mention the characteristic properties of pyrogallic acid.

337. Explain the murexid test for uric acid.

338. Describe the artificial preparation of valerianic acid and other valerianates.

339. Give a sketch of the method by which to analyze an aqueous liquid for the acidulous radicals of salts. In what stage of the process would the following salts be detected?

Carbonates and Sulphates.
Oxalates.
Tartrates and Nitrates.
Acetates and Sulphites.
Bromides and Cyanides.
Borates.
Iodides and Phosphates.

h. Chlorates, Oxalates, and Acetates.

i. Chlorides and Iodides.

j. Sulphites.

k. Sulphides, Carbonates, and Nitrates.

340. Nitrate of silver gives no precipitate in an aqueous solution; what salts may be present?

341. Chloride of barium gives no precipitate in a neutral solu-

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tion, but nitrate of silver a white; what acidulous radicals are indicated?

342. Ferric chloride produces a deep red colour in a solution, chloride of calcium yielding no precipitate; what salt is present?

343. Ferric chloride gives a black precipitate in a solution in which sulphuric acid developes no odour; to what is the effect due?

344. Describe the preliminary treatment to which a salt is subjected prior to systematic analysis.

345. Give examples of salts which are identified by appearance, weight, colour, crystalline form, &c.; by their behaviour when heated; by their reaction with strong sulphuric acid; by their comportment in the blowpipe-flame, with or without borax or microcosmic salt.

346. What are the solvents usually employed in endeavouring to obtain a substance in a state of solution? and what the order of their application?

347. Sketch out a method for the complete analysis of a liquid suspected to be an aqueous solution of neutral salts.

348. How can earthy phosphates and oxalates with ferric oxide be separated?

349. By what process may substances insoluble in water or acids be analyzed?

350. Write general formulæ of artificial alkaloids.

351. Name the substances represented by the following formulæ:—

$$\left.\begin{matrix} C_3H_7 \\ H \\ H \end{matrix}\right\} N, \qquad \left.\begin{matrix} C_3H_7 \\ C_3H_7 \\ H \end{matrix}\right\} N, \qquad \left.\begin{matrix} CH_3 \\ C_2H_5 \\ C_5H_{11} \end{matrix}\right\} N.$$

352. Give the officinal process for the preparation of Hydrochlorate of Morphine.

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353. Mention the analytical reactions of morphine.

354. By what method is Disulphate of Quinine obtained?

355. Describe the tests for quinine.

356. How is the adulteration of disulphate of quinine by salicin detected?

357. Show how the sulphates of quinidine or cinchonine may be proved to be present in commercial quinine.

358. Enumerate the tests for strychnine, and describe their mode of application.

359. By what reagent is brucine distinguished from strychnine?

360. How is Aconitine prepared?

361. Give the strengths of the officinal preparations of Atropine.

362. Mention Pharmacopœial substances containing beberine and berberine respectively.

363. By what process is Conine educed?

364. Name the alkaloid of tobacco.

365. Whence is theine obtained?

366. Describe the preparation of Veratrine.

367. How is wheat-starch or potato-starch isolated?

368. Define gluten and glutin.

369. Is starch soluble in water?

370. Which is the best chemical test for starch?

371. Distinguish physically between the varieties of starch.

372. Into what compound is starch converted by heat?

373. What occurs when a mixture of starch and water is allowed to flow into hot diluted sulphuric acid?

374. If equal amounts of starch and water be heated, one containing a small quantity of ground malt, what effects ensue?

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375. Write a short article on the chemistry of "malting."

376. Explain *isomerism*, as illustrated by starch and dextrin.

377. Give examples of polymeric bodies.

378. State the formula of a body metameric with urea.

379. Mention the properties of the products of the action of nitric acid of various strengths on cellulose.

380. How are cane-sugar and grape-sugar analytically distinguished?

381. Write a few sentences on alcoholic fermentation.

382. What is the difference between fruit-sugar and honey?

383. Describe the effect of heat on cane-sugar.

384. Give the latest view of the constitution of mannite.

385. Define glucosides, and mention those of pharmaceutical interest.

386. Draw out an equation illustrative of the development of oil of bitter almonds.

387. By what process is the glucoside of the purple foxglove prepared?

388. State the circumstances under which elaterin, guaiacum, and jalap-resin yield glucose.

389. Mention a test for guaiacum-resin.

390. Enumerate the tests for salicin.

391. How is Santonin officinally prepared?

392. Explain the difference between Rectified Spirit, Proof Spirit, and Absolute Alcohol.

393. What quantity of water must be added to one gallon of spirit of wine, 56 degrees over proof, to convert it into proof spirit?

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394. Show how the formula of alcohol is obtained from its centesimal composition:—

Carbon	52·174
Hydrogen	13·043
Oxygen	34·783
	100·000

395. From the formula of aldehyd calculate its composition in 100 parts.

396. Give the supposed constitution of alcohol, and the formulæ of several compounds of ethyl.

397. What is the relation of aldehyd to alcohol? what to acetic acid?

398. Describe the officinal process for the preparation of Ether, giving equations.

399. Offer a physical explanation of the mode of producing local anæsthesia.

400. How is commercial ether purified?

401. Explain Redwood's process for the preparation of "sweet spirit of nitre."

402. By what method is the strength of "sweet spirit of nitre" estimated?

403. Give details of the production of chloroform from alcohol, tracing the various steps by equations.

404. Is chloroform an ethylic compound? What is its probable constitution?

405. Adduce evidence of the existence of ethyl.

406. Mention several radicals homologous with ethyl, and give their formulæ.

407. Define ethers, hydrides, alcohols, ethereal salts, aldehyds.

408. Name the source of methylic alcohol.

409. What is "methylated spirit?"

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410. In what relation does formic acid stand to methylic alcohol?

411. Describe the method by which methylated spirit is detected in a tincture.

412. Whence is amylic alcohol obtained?

413. Has valerianic acid any chemical relation to amylic alcohol?

414. Mention the systematic names of several artificial fruit essences.

415. Give the names and formulæ of compounds of radicals having the general formulæ C_nH_{2n-7}, $C_nH'_{2n-1}$, $C_nH'''_{2n-1}$, and C_nH_{2n}.

416. What are the uses, composition, and source of Carbolic Acid?

417. How is the so-called artificial oil of bitter almonds prepared?

418. Draw out an equation explanatory of the production of aniline.

419. Write the rational formula of glycol.

420. Sketch out the operations necessary for the detection of mercury, arsenicum, antimony, lead, or copper in an organic mixture, such as a vomit.

421. How are poisonous quantities of sulphuric, nitric, or hydrochloric acids detected in beer?

422. Describe the manipulations necessary in testing for hydrocyanic acid in the contents of a stomach.

423. By what method is oxalic acid discovered in infusion of coffee?

424. Give the process by which strychnine is isolated from partially digested food.

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425. Mention the experiments by which the presence of laudanum in porter is demonstrated.

426. Demonstrate the presence of albumen in urine.

427. Give the tests for sugar in urine.

428. What is the average quantity of urea in urine?

429. Write the rational formulæ of some compound ureas.

430. Sketch out a process for the chemical examination of urinary sediments.

431. A deposit is insoluble in the supernatant urine or in acetic acid; of what substances may it consist?

432. Mention the chemical characters of cystin.

433. Describe the microscopical appearance of the following urinary deposits:—

Uric Acid.	Tube casts.
Cystin.	Epithelial *débris*.
Triple phosphate.	Blood.
Earthy phosphates.	Pus.
Urates.	Mucus.
Calcic oxalate.	Fat.
Calcic carbonate.	Spermatozoa.
Hippuric Acid.	Sarcina.

434. Draw out a chart for the chemical examination of urinary calculi.

435. What is the composition of the "fusible calculus?"

436. State the characters of "mulberry" and "hempseed" calculi.

437. What are "chalk-stones" and "gall-stones?"

438. Enumerate the different classes of officinal galenical preparations.

439. Describe the general process for the preparation of green extracts.

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440. Give the general method for the isolation of volatile oils.

441. On what fundamental laws are the operations of quantitative analysis based?

442. How are variations in atmospheric pressure quantitatively determined?

443. Explain the construction and mode of action of a thermometer.

444. Give formulæ for the conversion of the degrees of one thermometric scale into those of another, (*a*) when the temperature is above the freezing-point of water, (*b*) below 32° F. but above 0° F., and (*c*) below 0° F.

445. State the best process for estimating the melting-point of fats.

446. What is understood by Gravitation, Weight, Specific Gravity, and Density?

447. Give a direct method for the determination of the specific gravity of liquids.

448. Define the gramme, litre, and metre of the metrical system of weights and measures.

449. Define the English grain, minim, and inch.

450. How many grammes are contained in 1000 kilogrammes?

451. How many grains are contained in one ton?

452. A certain bottle will hold 150 parts, by weight, of water, or 135·7 of spirit of wine; what is the specific gravity of the latter?

453. Equal volumes of benzol and glycerine weigh 34 and 49 parts respectively, and the sp. gr. of the benzol is 0·850; what is the specific gravity of the glycerin?

454. Explain the process employed in taking the specific gravity of solid substances in mass and in powder.

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455. Are stated specific gravities strictly correct?

456. State the method by which the specific gravity of a light body, such as cork, is obtained.

457. What modifications of the usual method are necessary in ascertaining the specific gravity of substances soluble in water?

458. In what does volumetric differ from gravimetric analysis?

459. Describe the various pieces of apparatus used in volumetric determinations.

460. One hundred cubic centimetres of solution of oxalic acid contain 6·3 grammes of the crystallized salt; what weights of acid carbonate of potassium and anhydrous carbonate of sodium will that volume saturate?

461. What weight of hydrate of potassium is contained in solution of potash 48·02 grammes of which are saturated by 50 c. c. of the standard solution of oxalic acid?

462. State the percentage of hydrate of calcium in lime-water 438 grammes of which are neutralized by 20 c. c. of the volumetric solution of oxalic acid.

463. Eight grammes of a sample of Rochelle salt, after appropriate treatment, require 54·3 c. c. of the oxalic-acid solution for complete saturation; what is the centesimal proportion of real salt present?

464. What percentage of real acid is present in diluted sulphuric acid 30 grammes of which are neutralized by 84 c. c. of the officinal volumetric solution of soda?

465. How much real nitric acid is contained in a solution 36 grammes of which are saturated by 94 c. c. of the standard solution of soda?

466. Explain the volumetric method of estimating the strength of aqueous solutions of hydrocyanic acid.

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467. Give equations illustrative of the reactions on which the use of a standard volumetric solution of iodine is based.

468. From what point of view may iodine be regarded as an oxidizing agent?

469. What reagent indicates the termination of the reaction between deoxidizing substances and moist iodine.

470. Write equations explanatory of the oxidizing-power of red chromate of potassium.

471. One hundred cubic centimetres of an aqueous solution of red chromate of potassium contain $\frac{1}{200}$ of the molecular weight of the salt in grammes; what weight of metallic iron, dissolved in hydrochloric acid, will this volume oxidize?

472. If 0·834 gramme of a specimen of crystallized ferrous sulphate require 93 c. c. of the standard solution of chromate for complete oxidation, what percentage of real salt is present?

473. For what purposes is the officinal volumetric solution of hyposulphite of sodium used?

474. On what reaction is based the quantitative employment of hyposulphite of sodium?

475. Describe the operations included in the estimation of the strength of bleaching-powder.

476. By what reagent is the complete absorption of free iodine by hyposulphite of sodium indicated?

477. Give details of the manipulations observed in gravimetrically estimating salts of potassium or ammonium.

478. What quantity of chloride of sodium is contained in a sample of rock-salt 0·351 gramme of which yields 0·44 of sulphate of sodium?

479. To what amount of the officinal alum is 0·894 of a gramme of the double chloride of platinum and ammonium equivalent?

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480. Find the weight of sulphate of barium obtainable from 0·522 of nitrate.

481. Describe the usual method by which salts of calcium are estimated.

482. By what quantitative processes may the officinal salts of magnesium be analyzed?

483. Calculate the proportion of pure sulphate of zinc in a sample of crystals 0·574 of which yield 0·161 of oxide.

484. Ascertain the weight of alumina (Al_2O_3) which should be obtained from 1·814 gramme of ammonium alum.

485. Explain the gravimetric process by which the strength of the officinal solutions of ferric chloride, nitrate, and sulphate are determined.

486. Mention the various amounts of ferrous and ferric salts equivalent to 100 parts of metal.

487. State the precautions necessary to be observed in estimating arsenicum or antimony in the form of sulphide.

488. In what form are the officinal compounds of bismuth weighed for quantitative purposes?

489. Give an outline of the process by which mercury may be isolated from its officinal preparations and weighed in the metallic condition.

490. Describe three methods for the quantitative analysis of salts of lead, and the weights of the respective precipitates, supposing 0·56 of crystallized acetate to have been operated on in each case.

491. Describe the processes by which silver is estimated in the forms metal, chloride, and cyanide.

492. What proportions of nitrate of silver are indicated, respectively, by 15 of metal, 9·8 of chloride, and 8·1 of cyanide?

493. Define cupellation.

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494. What quantity of pure rock-salt is equivalent to 4·2 parts of chloride of silver?

495. State the percentage of real iodide of potassium contained in a sample of which 8 parts yield 10·9 of iodide of silver.

496. What is the strength of a solution of hydrocyanic acid 10 parts of which, by weight, yield ·9 of cyanide of silver?

497. How are nitrates quantitatively estimated?

498. By what processes may the strength of sulphides be determined?

499. How much real sulphate of sodium is contained in a specimen 10 parts of which yield 14·2 of sulphate of barium?

500. Give details of the operations performed in the quantitative analysis of carbonates.

501. What amount of carbonic acid gas should be obtained from 10 parts of acid carbonate of potassium?

502. To what operation and what quantities of materials does the following equation refer?

$$Na_2C_2O_4 + MnO_2 + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + 2CO_2.$$

503. Explain the lead process for the estimation of phosphoric acid in the officinal solution.

504. State the amount of superphosphate of calcium equivalent to 7·6 parts of pyrophosphate of magnesium.

505. Carbonate of potassium is said to lose 16 per cent. of water on exposure to a red heat; give the details of manipulation observed in verifying this statement.

506. Write a few paragraphs descriptive of the processes of ultimate organic analysis.

507. In what forms are carbon, hydrogen, and nitrogen weighed in quantitative analysis?

508. In the combustion of ·41 of a gramme of sugar, what weights of products will be obtained?

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509. Describe De Vry's process for the assay of commercial quinine.

510. Give the officinal method for the estimation of morphine in opium.

511. Mention the operations necessary for the estimation of the proportion of sugar in saccharated carbonate of iron, or in a specimen of diabetic urine.

512. In a mixture of honey and starch, how may the proportion of the latter be directly determined?

513. Give two processes for the estimation of the percentage of alcohol in tinctures, wines, or beer.

514. Define dialysis.

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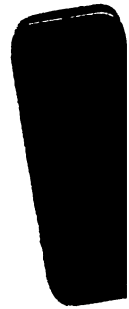
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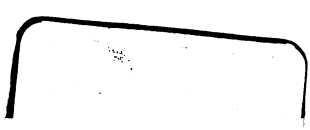
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