A handbook of chemical manipulation

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Section XXVII. Remarks on a Few of the Process and Reactions Employed in Some Researches

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REMARKS ON A FEW OF THE PROCESSES AND RE-ACTIONS EMPLOYED IN SOME RESEARCHES.

738. The matter contained in this section is intended to call the attention of the student to some of the broad principles upon which the examination of bodies is founded. In alluding to inorganic substances, I have seldom entered much into detail, because the chief part of the processes and reactions employed in this branch of the science are dwelt upon with more or less minuteness in most elementary works; but such matters have been mentioned as were considered likely to be instructive, and with which it is absolutely necessary every one should be familiar, if intending to make original experiments.

739. It will, of course, be presupposed that the student would not commence pursuing original experiments until acquainted with the methods of performing qualitative and quantitative analyses; and also that he has perused attentively some of the elementary treatises which exist in our language either as originals or translations.

740. It will also be unnecessary to point out the nature of the very simple calculations required, except in special instances, as they are to be found in all works on quantitative analysis.

741. Before entering further into the subject, it will be proper that we should endeavour to define the term "Chemical research." It must not be supposed that making analyses constitutes research; analysis is only one of the implements, if we may use the expression, employed in making researches. Strictly speaking, the term ought to be restricted to experiments having a distinct object in view; such, for example, as the production of a hitherto unknown body, the possible formation of which has been determined by mere reasoning. But the term has been so long used in a more extended sense, that it may also be made to include experiments undertaken to ascertain the nature and pro-

perties of unknown substances and compounds existing as natural
or artificial products. But, even then, we must not forget that
mere analysis does not constitute research; it is not sufficient
alone to determine the *composition*: it is essential also to fix the
constitution of new bodies, and their position among chemical
substances generally, to entitle the experiments to this appella-
tion.

742. It is more difficult to draw the distinctive line between
the directions belonging to this work, and those appertaining to
works on general analysis in inorganic than in organic chemistry,
because with the former the true constitution of a substance is
more quickly ascertained than with the latter; for, as soon as an
inorganic substance has been accurately analysed, it is generally
easy to determine its real nature; but with organic substances it
is seldom that the determination of the constituent elements
serves at once to establish beyond doubt its chemical relations.
The numerous instances of isomerism which are to be met
with among organic substances, at once show the insecurity of
founding any ideas of constitution upon the mere results of
analysis.

743. It becomes necessary, in consequence of what has been
said, to determine the nature of the products of decomposition
of organic substances, and also, if possible, the result of their
combinations with many other bodies, before pronouncing deci-
sively upon their true character.

744. We shall therefore divide the subject into two branches,
admitting each in its turn of subdivision, namely, *inorganic* and
organic. Inorganic research, as distinguished from mere ana-
lysis, is perhaps somewhat more limited than the organic depart-
ment of the science, in the variety of compounds of a novel kind
which are capable of being educed or formed.

745. The mere analysis of an inorganic substance gives at
once a clue to its position among chemical substances; and we
are consequently enabled to pronounce with some confidence as
to the particular class of compounds which it will form with
other bodies, and even in many instances their properties and

appearance. This is much less the case with organic substances, not merely for the reasons previously given, but also because their comparative instability causes a much greater tendency to decomposition and transformation.

746. Inorganic bodies may be divided into two classes, *non-metallic* and *metallic*. It is true that the line of demarcation is difficult to draw in its strictly scientific sense, but for the purposes of this work we shall understand by a metal, a body possessing the metallic lustre, and agreeing in general characters with the known metals.

747. *Non-metallic bodies.*—If the existence of a new non-metallic substance was announced, there are a few questions which would immediately be asked concerning it, namely, is it solid, liquid, or gaseous, at ordinary temperatures? and what class of bodies does it most resemble? Now whatever its physical condition may be, we can soon acquire a tolerable idea of its chemical relations.

748. One of the first and most important facts to ascertain with regard to all bodies, is its atomic weight. In order to accomplish this, we must carefully analyse some compound or compounds which it forms with substances the atomic weight of which is well known.

749. It has been said that the careful analysis of the substance or compound from which the new body was educed, will enable the student to form a tolerably good idea of the class of bodies with which the non-metallic element is to be associated; but it is not always easy to determine this point with accuracy, or, at all events, until the nature of a considerable number of its compounds has been established.

What, then, are the principal compounds which non-metallic substances yield, and how are they procured? Our space will not permit us to follow out all the compounds formed by non-metallic bodies; but, with a view to show the methods of pursuing this kind of subject, we shall glance at a few of the most prominent and instructive.

750. *All non-metallic bodies combine with oxygen.*—The follow-

ing are the principal methods by which these compounds are procured:—

I. By direct combustion in air or oxygen.

II. By passage of electric sparks in presence of oxygen.

III. By oxidation with nitric acid.

IV. By distillation with a peroxide.

V. By contact of elements and oxides, under certain circumstances.

751. Each of these methods of producing oxides requires certain precautions, and demands therefore a few remarks.

752. I. *By direct combustion.*—In this manner some of the non-metallic elements pass at once to their highest state of oxidation, others to one of the lower states; and, with some, the nature of the oxide depends upon the temperature at which the combustion occurs.

753. Sulphur and selenium burn in oxygen, and produce sulphurous and selenious acids; they therefore behave alike by this method of oxidation; we shall see presently that this similarity of deportment is not invariable. Sulphur and selenium do not by this method pass at once to their highest state of oxidation.

754. Hydrogen, as every one is aware, does not pass to its highest state of oxidation, but forms water only.

Nitrogen does not unite with oxygen by combustion in the ordinary manner.

Carbon passes at once to the highest known state of oxidation.

Phosphorus, at the temperature of actual ignition, passes into its highest state of oxidation, namely, phosphoric acid; but by slow combustion at ordinary temperatures, it forms phosphorous acid.

755. II. *By passage of electric sparks in presence of oxygen.*— Nitrogen by this process is converted into nitric acid; the reaction is facilitated by the presence of bases.

Hydrogen, carbon, and other bodies inflame and behave as at I.

756. III. *By oxidation with nitric acid.*—It is singular that, while selenium and sulphur by combustion in oxygen yield the

same acid, with nitric acid the reaction is different; and while selenium passes into the same acid as by the first mode of oxidation, sulphur, on the other hand, combines at once with the maximum amount of oxygen, forming sulphuric acid. This fact is instructive, and shows that, however closely two elements may resemble one another and run parallel for a considerable distance, they are liable suddenly to diverge from each other at a point least anticipated.

757. Phosphorus forms phosphoric, and iodine iodic acid when treated with nitric acid. Carbon, on the other hand, forms a most curious substance, or series of substances, of unknown composition, and called by their discoverer* artificial tannin.

758. If the student attentively considers the facts above detailed, he will find that the products of oxidation of non-metallic bodies with nitric acid vary with the nature of the element, and in no case is an oxide formed containing one atom of each constituent.

759. IV. *By distillation with a peroxide.*—This method, available under certain circumstances, results, with sulphur and peroxide of manganese, in the formation of sulphurous acid; it is not a method by which the atomic weight of an unknown non-metallic body could with ease and certainty be ascertained.

760. V. *By contact of elements and oxides, under certain circumstances.*—This is a method by which some of the oxides of such bodies as chlorine and iodine are to be obtained.

761. Non-metallic elements combine among each other to form a great variety of compounds, but few of them are of a class to enable the atomic weight of the resulting body to be determined with ease and certainty. To ascertain the combining proportions of a substance of this class, we should be guided by the nature of the element itself. If a gas, its density, —or if vaporizable at temperatures not too elevated, the density of its vapour,—should be carefully determined. It must not be forgotten, that with bodies not easily vaporized, the density of

* HATCHETT.—It is greatly to be desired that this subject should be re-investigated by modern methods.

the vapour should be taken at temperatures considerably above their boiling-point, if results are to be obtained from which the atomic weight is to be easily and precisely settled.

762. The vapour-density not only enables us, with non-metallic elements, to pronounce upon the atomic weight, but also, taken in conjunction with the analysis of a compound with silver, upon the class of bodies among which it is to be grouped.

763. For the purpose of determining the atomic weight of a substance, it is very desirable to obtain at least one compound that consists of one atom of each of its constituents. Now it is possible to obtain silver-salts of most of the non-metallic elements in which we are sure of the constitution being of the kind required. If, therefore, we analyse a salt of this description, we at once possess the data for determining its atomic weight. Let us suppose that a silver salt has yielded

<div align="center">

54·04 non-metallic element
45·96 silver

———

100·00

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we say

				At. wt. Ag.		At. wt. non-metallic element.
45·96	:	54·04	: :	108	:	126·98

764. Now, on determining the density of its vapour, the non-metallic element gave 8·716: how are we to know to what class of bodies it belongs? A very little reflection will show, that as hydrogen is received as unity for atomic weights, if we received it also as unity for gaseous and vapour densities, the atomic weights of bodies of the same vapour-volume would be expressed by their vapour-density. It is obvious, then, that if a substance possesses the same vapour-volume as hydrogen, its atomic weight will be obtained by dividing its vapour-density by the density of hydrogen. If, therefore, the number obtained by dividing the vapour-density of a non-metallic element by the density of hydrogen is identical with the number obtained by analysis of the silver-salt, it will be certain that the substance under examina-

tion possesses the same vapour-volume as hydrogen, nitrogen, chlorine, &c. Let us try this in the present instance. The vapour-density was, as we have said, 8·716, and if we divide this by 0·0692, we obtain 125·95 as the result, which, although differing somewhat from 126·98 obtained as the atomic weight by analysing the silver-salt, is still quite a sufficient approximation to indicate that the body we have examined has a vapour-volume the same as hydrogen. The body we have selected as an illustration is, as the student has probably perceived, iodine. If, on the other hand, it was necessary to divide the vapour-density by twice the density of hydrogen to obtain the atomic weight, we may infer with safety that the vapour-volume is that possessed by oxygen and elements of the same class.

The mode of obtaining the vapour-density of an organic body, by multiplying its atomic weight by half the density of hydrogen, has been pointed out in a former section (§ 127).

765. There are numerous points connected with the non-metallic elements which demand investigation.

Sulphur replaces the oxygen in carbonic acid, bisulphide of carbon resulting; but no sulphide analogous to oxalic acid has yet been formed.

766. It is said that sulphide of carbon heated under pressure in presence of water is decomposed, a gas being formed; if, now, the decomposition proceeds thus, $CS^2 + HO = CSO + HS$, we have an interesting substance, being carbonic acid, in which one of the equivalents of oxygen is replaced by sulphur. The experiment should be tried. Sulphur, selenium, and tellurium have many points in common; only the first, however, has had its compound with carbon investigated.

767. The action of ozone on various inorganic and organic bodies requires to be tried, and now that it can be prepared from the peroxide of barium, the chief barrier to its use is removed.

768. *On processes and reactions connected with metals.*—The examination of metals, or of minerals, or other substances containing them, is a matter of such every-day occurrence in almost all laboratories, that it is essential for the student to thoroughly

familiarise himself with their properties and peculiarities. The study of metallic substances has greatly advanced within the last few years; so much so, that metals which, until recently, have been considered rare, and obtained with difficulty, and were chiefly to be found on the shelves of museums, and, even then, in specimens of a few grains in weight, are now articles of commerce, and likely ere long to become valuable in the arts.

769. Moreover, our ideas of the rarer metals, as they were once called, are rapidly passing through a transition state, previous to undergoing a complete modification. The rarity of a metal depends upon two circumstances, either of which may cease to exist, and thus cause a metal rare to-day to be almost common to-morrow. These two circumstances are, difficulty of procuring the ore, or the expense of extraction. Now the ore of aluminium, or clay, is one of the most abundant of substances; and yet, until lately, aluminium was one of the rarest of chemical products. Again, vanadium has always been regarded as a metal of such extreme scarcity as to make it difficult to conceive its use in the economy of nature; but, quite recently, it has been found easy to obtain it in tolerably large quantities by an inexpensive process, from a waste product obtained in the preparation of uranium-yellow from the Joachimsthal ores*.

Now vanadium is a metal the reactions of which are so marked, that undoubtedly if obtainable in quantity at a reasonable price, it might be made available in the arts†.

770. No substance is to be regarded as useless because we are not aware of its value; the reproach applies not to the substance, but to our imperfect knowledge. There are instances on record of bodies which for years were not known to be of the slightest value or interest save to the scientific or theoretical chemist, and yet the same substances have at last been proved to possess

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* PATERA, Oesterreich.—Zeitschrift für Berg- und Hüttenwesen, 1856, No. 31; and Chemical Gazette, March 1857.

† The tannate of vanadium is said to be the most indestructible, and therefore the most valuable of inks.

powers that can only be properly appreciated by those whose sufferings have been relieved by their medicinal virtues.

771. The chemical history of the metals is full of interest. The very difficulty with which some of them are procurable in a state of purity, gives zest to the study of their properties. The extraordinary resemblance which some of them present to each other, and the fact that these assimilating metals are almost always found associated in nature, by countenancing the ideas which have of late been promulgated relative to their being compound, makes us feel that we are on the eve of discoveries which will possibly entirely modify our ideas of elementary bodies, and open new and most interesting tracks for the chemist to pursue.

772. In studying the chemical history of metals, nothing is to be regarded as unimportant which can throw any light upon their nature. It has often happened that the careful following out of a peculiarity in the reactions of a metal has led to brilliant discoveries. If, in examining a well-known metallic substance, any of its usual reactions should appear to be modified, it is most desirable to clearly ascertain the cause, as, by so doing, not only is some useful information certain to be gained, but it is possible that the result may be of greater value than could at first be anticipated. In 1817, while Stromeyer was examining the drugs of an apothecary at Hildesheim, he found that instead of the oxide of zinc ordered by the Pharmacopœia, the carbonate had been substituted. On inquiry, it transpired that the manufacturer had replaced the oxide by the carbonate, in consequence of his being unable to prepare the former in the usual white state, owing to some unknown impurity. A careful examination of this oxide resulted in the discovery of a new and most interesting metal, cadmium. On a subsequent occasion, the same chemist found that several apothecaries at Magdeburg had in their possession a preparation of zinc which had been confiscated on the supposition of its containing arsenic, because, when dissolved in an acid, the solution gave a yellow precipitate with sulphuretted hydrogen; his previous experiments on cadmium had shown him that that metal gave a yellow precipitate with

the same reagent; he was in consequence induced to examine
the suspected article, and found, as he had anticipated, that the
new metal had again led to difficulties between the apothecaries
and their inspectors.

773. It is also necessary that extreme care should be taken to
investigate with scrupulous minuteness the properties of any sub-
stance that may appear to differ from known metals. The history
of Chemistry shows numerous instances of substances being taken
for new metallic oxides which were in fact well-known bodies,
the reactions of which were disguised by the presence of some
impurity, or from the fact of their being in a state of combina-
tion, with the properties of which the operator was unfamiliar.
Among the most prominent instances of this kind, may be men-
tioned the substance in the form of a white powder, which Berg-
man obtained by treating cold short-iron with dilute sulphuric
acid, in his endeavour to determine the cause of the brittleness
of that variety of the metal. By fusing this powder with a flux
and charcoal, he obtained what at the time he believed to be a
new metal, but Klaproth showed that it was only a phosphuret
of iron formed by reduction of the phosphate of iron which con-
stituted the white powder. More recently, even Berzelius was
led to confer the name of Thorina upon the subphosphate of
yttria, under the impression that it was a new metallic oxide
(§ 174): fortunately for him the error was rectified by himself,
and, not long after, he discovered what really turned out to be a
new metallic oxide, and as its reactions had some analogies with
the substance formerly called thorina, he transferred the latter
name to it. Thorina has also, within the last few years, been
described as a new metal, under the name of donarium. An-
other recent instance of a well-known substance being mistaken
for a new metallic oxide, is in the case of the supposed new
earth Thalia, which was shown * to be nothing but magnesia
mixed with a little lime. The error arose from the fact, that strong
solutions of magnesia are, contrary to what is generally supposed,

* J. LAWRENCE SMITH.—'Chem. Gazette,' September 15, 1853, and 'Sil-
liman's Journal,' July 1853.

precipitated under certain circumstances by oxalate of ammonia. In short, it would be easy to mention many other mistakes of the same kind which chemists have committed through too hastily pronouncing upon the nature of substances the reactions of which were either not very decided, or closely resembled those of others.

774. *Physical properties of metals.*—In studying metals and their combinations, we must consider not only their chemical, but also some of their physical properties. It is essential to determine their density, and that under various circumstances; first, after fusion, then the button may be well hammered out or rolled by a flatting-mill, and the density again determined. We have already alluded to the fact, that metals in the state of fine powder have sometimes a higher density than when hammered. The hardness and malleability should be determined, and also the ductility. The immense difference in the properties of metals is strikingly illustrated in their degrees of hardness; for example, sodium can be easily cut with the nail, while chromium in its hardness actually rivals the diamond, and if it were less brittle, might even be used for dividing glass, as it not merely scratches but actually cuts it asunder. To determine the colour of a metal is generally easy by inspection, but it must not be forgotten, that as the apparent colour of a metal depends upon the nature of those simple rays which are most reflected by it, so the tint will not be exactly the same when the reflected rays are observed at varying angles of incidence; because, as the angle differs, so the proportion of the different rays reflected will vary.

775. The greater or less power of the metal for conducting electricity, as compared with other metals, should be ascertained, as also its conductibility for heat. Its fusibility and tendency to crystallize in passing slowly from the fluid to the solid state should be observed.

776. In determining the crystalline form of a metal, much will depend upon the nature of the metal itself. Sometimes it is easy to obtain crystals by fusing a considerable quantity in a

crucible and allowing the whole to cool very slowly, by surrounding the crucible with red-hot sand. As soon as the upper portion has solidified, an iron rod is to be forced through the crust, and the crucible being held by a pair of ring-tongs, the fluid is to be poured out. When cold, the solidified crust is generally found to indicate, more or less, traces of crystallization. When bismuth is treated in this manner, if the quantity be sufficiently large, very beautiful crystals are obtained, belonging to the cubic system. In consequence of excessively thin layers of oxide being formed, most brilliant shades of colour are generally observed on them. It is possible also to obtain crystals of lead, tin, and antimony by the same process, but they are very inferior in appearance. Crystals may also be obtained by electro-deposition, under certain circumstances.

777. At times it is possible to develope figures corresponding to the planes of cleavage of metals, by treating metallic surfaces by acids. Thus, if a plate of tinned iron be gently warmed, and a rag dipped in hydrochloric acid be passed over it, a beautiful crystalline appearance becomes manifest, commonly known as *moire métallique*. The Widmanstadt figures formed on meteoric iron by the action of acids, many beautiful specimens of which are to be seen in the British Museum, are instances of the same kind.

778. Daniell showed, in his ' Introduction to Chemical Philosophy,' that the crystalline texture of a metal might sometimes be developed by dissection with mercury, as in the case of tin.

An idea of the tendency to crystallize possessed by a metal may often be obtained, especially if it be a brittle one, by breaking a mass of it across. The larger the piece of metal the better is the nature of the crystallization observed, but even with a wire the lens often reveals a highly crystalline structure.

779. The tenacity of metals is also an important feature in their history. It would appear that this property is subject to great variation, according to the temperature at which it has been fused, or else that extremely small admixtures of foreign bodies affect the power of sustaining weights to a remarkable degree.

Thus the tenacity of the malleable metals, as measured by the weight that wires of the same diameter (2 millimetres) were capable of bearing without rupture, is given in the following Table* :—

Iron	250	kilogrammes.	Zinc	. .	50	kilogrammes.
Copper . .	137	,,	Nickel	.	48	,,
Platinum .	125	,,	Tin .	. .	16	,,
Silver . . .	85	,,	Lead	. .	12	,,
Gold . . .	68	,,				

780. But, quite recently, M. Wertheim, in the laboratory of M. H. Sainte-Claire Deville†, has determined the tenacity of nickel and cobalt prepared from the oxalate, and fused in the latter chemist's blast-furnace, to be described further on, and has found that wires of equal size of iron, nickel, and cobalt supported the following weights :—

Cobalt	115	kilogrammes.
Nickel	90	,,
Iron	60	,,

The diameter of the wires is not stated. The necessity of determining the tenacity and other physical properties of metals under varying circumstances as regards mode of preparation, &c., could not be more strikingly illustrated than by the above example, where, instead of nickel having only one-fifth the tenacity of iron, as indicated in the first Table, it appears to be able to support a strain one-half greater.

781. *Chemical properties of metals.*—In studying the processes and reactions used in researches connected with metals, we are immediately led to consider the tendency possessed by them to combine with oxygen. Their attraction for oxygen varies greatly with the different metals. While some cannot endure exposure to the air for an instant without becoming covered with a

* REGNAULT.—'Cours Élementaire de Chimie,' tome deuxième, p. 413.
† DEVILLE.—'Ann. de Chimie et de Phys.' [3] xlvi. 201.

film of oxide, others can only be made to yield oxides by circuitous methods.

782. It is not easy to determine the exact conditions under which some metals combine with oxygen, as it has been found that those which have only been prepared of late years in quantities sufficient for accurate experiment, combine with that element with greater or less avidity according to the method by which they have been prepared; that is to say, small variations in their physical states, and the presence of minute traces of certain impurities, greatly influence their tendency to oxidize. This fact introduces some difficulty into the method of classifying metals according to their oxidizability. As an instance of this it may be mentioned, that manganese, magnesium, and aluminium have until lately been considered to almost resemble the metals of the alkaline earths in their power of decomposing water, and even of absorbing oxygen from the air; but the researches of Deville and others have shown that magnesium is not much more liable to oxidize than zinc, and aluminium ranks in that respect next to silver, gold, and platinum. It is, in the present state of chemistry, exceedingly difficult to classify metals into natural families in a satisfactory manner, those which closely coincide in properties through a long series of reactions suddenly diverging off, and becoming in other respects so unlike as to render their being grouped under the same head impossible. This has been well shown with regard to aluminium *, and it would not be a difficult task to find other illustrations drawn from the history of many other metals.

783. It is most important for the student to study carefully the various compounds of metals with oxygen; they are so numerous that it is often many years before all the oxides of a metal become known. Some metals in combining with oxygen form powerful bases in the lower, and equally or still more powerful acids in the higher state of oxidation. It is an extremely fortunate circumstance for chemists that they are generally able,

* Tissier.—'Comptes Rendus,' Feb. 16, 1857, p. 350; and 'Chem. Gazette,' March 16, 1857.

without much difficulty, to effect at will the conversion of a metal into its oxides, and of the oxides back into the metallic state; for if it were not so, it would constantly happen that different oxides of the same metal would be taken for derivatives of several metals. This arises from the fact that various oxides of the same metal differ more in many instances than the same oxides of different metals. Thus the sesquioxide and teroxide of chromium are far more unlike each other in general properties than the sesquioxides of chromium and iron. The sesquioxide of chromium resembles the sesquioxide of iron in many respects, such as being soluble in acids, precipitable by ammonia, capability of replacing alumina in alums without altering the crystalline form of the salts, &c. But sesquioxide of chromium has no resemblance whatever to the teroxide; the former being a green powder insoluble in water, with the properties just mentioned, while the teroxide is a powerful acid of a ruby colour, capable of inflaming some organic bodies by mere contact, excessively soluble in water, forming splendid crystalline salts with the alkalies, &c., and precipitating metallic solutions with formation of varied and brilliant colours.

784. In some instances it has happened, with metals procurable only in small quantities and with great labour, that mixtures of two or more oxides of the same metal have been mistaken for the oxide of a new metal; thus a compound of sesquioxide and binoxide of niobium was thought to be derived from a new metal, to which was given the name of ilmenium, and the mixture was called ilmenic acid. A mixture of tantalic acid with niobate of niobous acid was also regarded as the acid oxide of a new metal, which was called pelopium.

785. The student will see how much care is requisite in examining metallic oxides with which he is unfamiliar. The description of the modes of separation of them from each other is the province of works on analysis, and will not therefore be dwelt on here.

786. Another point in the chemical history of metals which demands special attention, is their solubility in acids. It is gene-

rally found, in studying the properties of a metal, that there is one acid which dissolves it with peculiar facility compared with the others, and this acid is always one with which it forms a very soluble salt. It is also true, however, that a metal may be violently attacked by an acid and yet not be dissolved by it, but then the resulting product will generally be found to have an acid character, as with the peroxide of tin.

787. The solubility of metals in acids is so intimately connected with the nature of the oxides which they tend to form, that the two subjects cannot be studied separately. It sometimes happens that the same metal with the same acid yields two distinct salts, according to the temperature and state of concentration of the acid. Thus, as has already been mentioned (§ 145), iron in excess forms with cold dilute nitric acid a protonitrate, and with the ordinary acid and heat the pernitrate. The methods by which metals are obtained in solution in any required state of oxidation depend upon the peculiar characters of the substance itself. If, for instance, it is desired to obtain a protosalt of a metal which has great tendency to form persalts, we may proceed in two or three ways. In the first place, an acid is to be selected which has not a strong tendency to impart oxygen. The sulphuric and hydrochloric acids generally fulfil these conditions if the solutions are not made too concentrated, and the temperature is kept sufficiently low. The presence of an excess of metal is also advantageous. If it is feared that the atmospheric oxygen might take part in the reaction and cause the formation of a portion of persalt, a current of nitrogen, or, more conveniently, carbonic acid, may be made to pass through the fluid during the solution of the metal. The fluid for this purpose must be contained in a flask, the cork of which has two apertures, one to admit the tube conveying the carbonic acid, and the other to allow of its exit. The latter may be bent twice at right angles, and be made to dip a short distance into water or mercury.

788. If, on the other hand, it is desired to convert a per- into a protosalt, we may sometimes do so by a process more convenient than the last. For this purpose the metal is to be dissolved in

the acid most available under the circumstances (avoiding the nitric), and the peroxide formed is to be reduced to the state of protosalt by means of some reagent having a strong affinity for oxygen. Two of the most convenient of these are sulphuretted hydrogen and sulphurous acid. The first acts by means of the tendency of the hydrogen of the gas to form water, and the second in consequence of the readiness with which sulphurous acid takes up an equivalent of oxygen to become converted into sulphuric acid; thus, if we take in the most simple manner the way in which sulphuretted hydrogen and sulphurous acid reduce per-oxide of iron to the state of protoxide, we find that—

$$Fe^2 O^3, 3SO^3 + HS = 2(FeO, SO^3) + SO^3 HO + S$$
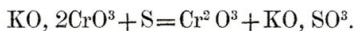$$Fe^2 O^3, 3SO^3 + SO^2 = 2(FeO, SO^3) + 2SO^3.$$
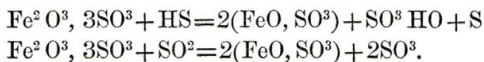
The first equation shows the reason why, when we pass sulphuretted hydrogen through a persalt of iron, a white or pale yellow precipitate is always obtained. If the iron exists as per-chloride instead of peroxide, the equation becomes

$$Fe^2 Cl^3 + HS = 2FeCl + HCl + S.$$
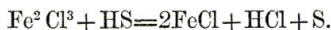
789. Reduction of oxides may also be effected in many other ways, all of which are advantageous under certain circum-stances. Chromic acid, for instance, may be converted into ses-quioxide of chromium by numerous processes; thus, if we heat bichromate of potash with chloride of ammonium and carbonate of potash, we find that

$$KO, 2CrO^3 + KO, CO^2 + 2(NH^4 Cl) = 2KCl + Cr^2 O^3 + 4HO + N$$
$$+ NH^4 O, CO^2.$$
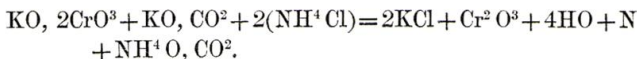
Again, by fusion of bichromate of potash with sulphur, we have—

$$KO, 2CrO^3 + S = Cr^2 O^3 + KO, SO^3.$$

By sulphurous acid we may reduce chromic acid to sesquioxide of chromium thus :—

$$KO, 2CrO^3 + 3SO^2 = Cr^2 O^3 + KO \, 2SO^3 + SO^3.$$
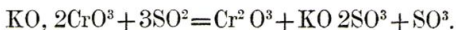
Charcoal will also reduce the acid, for

$$2(KO, 2CrO^3) + 3C = 2(KO, CO^2) + CO^2 + 2Cr^2O^3.$$
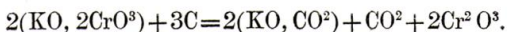
790. We have said that sulphur is capable of reducing chromic acid : it is also capable of reducing binoxide of manganese and other oxides to a lower state of oxidation. In the case of the peroxide of manganese, we have

$$MnO^2 + 2S = MnS + SO^2.$$
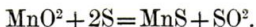
791. In selecting reducing agents, we are guided by the peculiar properties of the substance which is to be converted into a lower state of oxidation. If it be desired to remove oxygen from a compound gas, it is easy to pass it over a metal having a powerful tendency to absorb oxygen at high temperatures. Let us suppose it is desired to convert carbonic acid into carbonic oxide : it might be passed over potassium at a red heat, but we should defeat our intention through selecting too energetic a reducing agent ; in effect, we should have all the oxygen removed and obtain only charcoal and potash. But if we select a metal like zinc, with a moderate power of absorption of oxygen, our purpose will be effected without difficulty. The ordinary process for preparing carbonic oxide sufficiently illustrates this. Chalk is heated to redness with zinc- or iron-filings ; the gas, at the moment of its liberation, is decomposed thus :—

$$CaO,CO^2 + Zn = CaO + CO + ZnO.$$
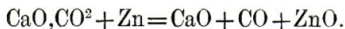
792. The reduction of a metallic oxide from a higher to a lower state of oxidation is seen therefore to be a process of constant occurrence in the laboratory. Another instance is afforded in the mode of estimating sugar, by ascertaining the quantity of oxide of copper which it is capable of reducing to the state of suboxide, after having been converted into grape-sugar by the action of an acid.

793. The reduction of oxides to the metallic state is also an operation necessary in numerous researches. The methods available are very many, the one to be selected depending not only on

the habitudes of the metal, but also on the fact of the operation being qualitative or quantitative. For the quantitative reduction of metals, no method is more convenient or exact than that by hydrogen gas; the details have already been described (§§ 297 and 477).

794. If the oxide is only reduced with great difficulty, it is generally necessary to convert it into some compound more easy of reduction, such as the chloride or fluoride. The former salt is frequently preferable. For the purpose of reduction, recourse is had to some substance the affinity of which for chlorine at high temperatures is very great. Potassium and sodium fulfil these conditions, but the latter is much cheaper and more convenient to use. The details of the operation depend upon the properties of the metal it is wished to isolate. If it is only moderately fusible and not very volatile, we may use M. Deville's method of preparing aluminium from the chloride, a description of which will be found in the scientific journals, and most of the recently published elementary works.

795. We may also produce the readily oxidizable metals by electrolysis of their chlorides in a state of fusion, as in the processes described by MM. Bunsen and Matthiessen *.

796. We have said that the solubility of metals in acids is an important feature in their general history, and it not unfrequently happens with metals which until recently have been prepared only in small quantities, that very erroneous views are prevalent on what appears so simple a matter, and it is quite evident that no conclusion can safely be drawn as to their habitudes with solvents, unless the experiments are made upon pure substances. Moreover, the state of concentration of the acid modifies the nature of the result in a remarkable manner.

It is extremely difficult to decide beforehand upon the manner in which a metal will behave towards a solvent. It would be supposed that silver would not dissolve in hydriodic acid, because we should imagine that, as iodide of silver is an insoluble salt like the chloride, the hydrochloric and the hydriodic acids would

* MATTHIESSEN.—Liebig's ' Annalen,' xciii. p. 277.

behave in the same manner. But, in fact, an aqueous solution of hydriodic acid acts violently on silver with formation of a peculiar compound, which appears to be a hydriodate of iodide of silver. It is merely necessary, to effect the solution, that the acid should be of the proper degree of concentration.

797. From what have always, until recently, been our ideas of the nature of aluminium, we should suppose that it would be readily oxidized by an acid so prone to yield oxygen as the nitric, but, in reality, that acid scarcely acts upon aluminium even at a boiling-heat.

798. It is necessary therefore, in determining the solubility of a metal in acids, to study with care the variations produced by dilution, and also the effect which different temperatures may have on the result. Some metals are dissolved by alkaline solutions with evolution of hydrogen, but this generally happens when the oxide which the metal most strongly tends to form, either has acid properties, or at least is easily soluble in alkalies.

799. The same metal may behave in a totally different manner towards the same acid, according to the conditions under which they are presented to each other; thus iron may be kept for almost any length of time in concentrated nitric acid without any action ensuing, while a dilute acid will act upon it with violence.

800. The various oxides of the same metal behave quite differently in the presence of acids, and the manner in which the two react often affords a clue to the nature of the oxide. The protoxide of lead is readily soluble in acids, while the binoxide is not only quite insoluble in them, but appears to possess the characters of a feeble acid. The intermediate oxide, minium, or red lead, is acted on by acids, but the result indicates that it is a compound of the two other oxides, as protoxide of lead dissolves, while binoxide remains behind. Many metals yield oxides the properties of which differ still more than those of lead; for instance, manganese yields a basic protoxide, while its higher oxides are powerful acids. In fact, the latter metal has a certain amount of analogy with chlorine, inasmuch as permanganate of potash,

KO, $Mn^2 O^7$, is isomorphous with the perchlorate of the same base, KO, ClO^7, a fact which has not escaped the notice of Laurent[*].

801. Some oxides are rather anomalous in their reactions, inasmuch as with acids they combine to form salts, while with bases they behave as if possessing acid characters; alumina is an example of this kind. We have said that minium is acted on by acids with formation of a salt of the protoxide, while the binoxide is left behind as an insoluble residue. Minium is therefore a compound of two oxides of lead, and is an instance of a peculiar class of bodies formed from the union of a basic with a more or less acid oxide of the same metal; in the same manner, the protoxide of iron takes the part of a base towards the sesquioxide, which reacts like an acid in combining with the former to produce an intermediate oxide having the constitution of a salt. Many other instances of the same kind are afforded by other metals, particularly antimony, chromium and manganese. This kind of combination is still more common among the sulphides, which are particularly prone to unite with each other, the resulting compounds being called sulphur-salts.

The tendency of metals to unite with oxygen is sometimes singularly variable according to the temperature; thus mercury, which preserves its metallic state perfectly at ordinary temperatures, combines slowly with oxygen at 700° or 800°, and the oxide is again decomposed into metal and the gas at a rather more elevated temperature, such as that of dull redness. A somewhat similar peculiarity is observed in some oxides which combine with oxygen at one temperature, and again yield it at a higher. Baryta exposed in a current of air or oxygen to a temperature about the same as that at which mercury combines with oxygen, has, like the latter metal, a tendency to absorb the gas, but the reaction occurs far more readily, and as the peroxide formed again yields its oxygen at bright redness, may even be used to extract that element from the air by a continuous process. It is interesting to observe that other oxides than that of barium absorb oxygen at about 750°, and again yield it up when heated to a still higher temperature.

[*] LAURENT.—' Chemical Method,' &c., p. 10.

The protoxide of lead in this manner becomes converted into red
lead, which in its turn is converted into the protoxide at a greater
heat. It has recently been found* that the presence of a base,
such as lime, has the effect of inducing the conversion of oxide
of lead into red lead at the ordinary temperature in moist air.
This curious fact might in all probability be made the point of
departure of some interesting experiments.

802. *Action of the non-metallic elements on metallic oxides.*—
Having thus briefly glanced at some of the more prominent fea-
tures connected with the combinations of the metals with oxygen,
we turn our attention to some of the phenomena which present
themselves by acting on the oxides with non-metallic elements
and their compounds.

803. In the first place, we will consider the action which sul-
phur has on metallic oxides. With the oxides of the metals of the
alkalies and alkaline earths, sulphur acts in a manner which is
partly due to the presence of oxygen; we have therefore both sul-
phides and sulphates formed. It is easy to prevent the formation
of sulphates by the addition of a substance having a tendency to
combine with oxygen at high temperatures; if, therefore, we re-
act upon the oxides mentioned with a mixture of sulphur and char-
coal, the sulphide formed is not accompanied by sulphate.

804. Some other metallic oxides yield sulphides by the action
of sulphur at high temperatures, but it is generally preferable to
mix charcoal with the oxide and pass the gaseous sulphur over
the oxide contained in a tube which should be heated intensely;
few metallic oxides resist this method of treatment.

805. The action of hydrogen and of carbon on metallic oxides
at high temperatures, is dependent on their powerful tendency
to combine with oxygen. Most oxides are therefore reduced to
the metallic state by them if the temperature is sufficiently high,
and the circumstances under which they react are properly
managed. Thus carbon at a full white heat decomposes even the
fixed alkalies, potash and soda. Hydrogen is also used in nume-
rous cases for the purpose of procuring many of the metals in a

* LEVOL.—' Ann. de Chim. et de Phys.' [3] xlii. p. 196.

state of purity from their oxides. There are, nevertheless, many instances in which hydrogen fails to decompose oxides at all; in others it merely reduces them from a higher to a lower state of oxidation.

806. Chlorine acts on metallic oxides in various ways, dependent on the precise circumstances under which they are presented to each other. The action is not only modified by temperature, but also by the fact of more than one substance being present. There are numerous examples which might be cited; it will be sufficient to allude to one or two. If chlorine be passed into a solution of the oxides of cobalt and nickel in hydrochloric acid, the cobalt is converted into peroxide, but not the nickel; and the former may be precipitated by carbonate of baryta, the nickel remaining in solution. An instance of the effect of the presence of a second substance in modifying the action of chlorine on a metallic oxide, is afforded by alumina. If chlorine be passed over alumina at a white heat, no action is perceptible; but if charcoal be present to combine with the oxygen of the alumina, the chlorine unites with the aluminium to form the volatile sesquichloride. The method found to answer best of obtaining the alumina mixed with carbon in a state fit for conversion into sesquichloride, is by calcining alumina with coal-tar.

807. The action of chlorine upon solutions of the oxides of the metals of the alkalies varies with the temperature, the strength of the solution, and the presence of other substances. If it be desired to obtain oxidation as much as possible, that is to say, to procure the maximum amount of chlorate of potash, the precautions first suggested by Mr. Crace Calvert should be adhered to[*].

808. If, on the other hand, it is desired to avoid the formation of chlorate, and it is wished to procure hypochlorite of potash, the solution is to be made weak, and also to be kept cold. The formation of the hypochlorite is accompanied by that of chloride of potassium, thus:—

$$2Cl + 2KO = \underbrace{KO, ClO,}_{} + KCl.$$

Hypochlorite of potash.

* CALVERT.—'Quart. Journ. of the Chem. Soc. of London,' vol. iii. p. 106.

809. A very interesting class of reactions taking place between metallic oxides and chlorides and non-metallic substances, are those which result in the formation of alkaloids by the substitution of metals for the hydrogen in ammonia or ammonium. The subject is one of considerable intricacy, arising from the great variety of compounds and the numerous methods by which they are obtained. With platinum alone, an immense number of bases are formed, which have been examined by Gros, Reiset, Peyrone, Gerhardt, Magnus and others. It is singular that the metals found associated with platinum have a special tendency to form bodies of this class. Thus palladium, rhodium and iridium are known to form alkaloids. An interesting class of bases also exists containing cobalt. It would be exceedingly desirable to know what metals do, and what do not, possess the power of performing this function, as such a knowledge would perhaps lead to a rational classification.

810. We have thus gone through a very few of the more prominent features which present themselves to our notice on reacting with non-metallic upon metallic bodies. They have been selected with the view of calling the student's attention to some important reactions, which, when studied more in detail, will lead to the accumulation of a mass of information having important bearings upon almost every train of experiments occurring in the laboratory.

811. *On the determination of the atomic weights of metals.*—In determining the equivalent or atomic weight of a substance, it is necessary to form a compound of it with some other body, the general character of which compound has been well established, that is to say, we must be aware of the number of atoms existing in it. It is also desirable that the compound should be of a character which will permit the estimation of its constituents with as few operations as possible. It is not merely necessary that the general formula of the compound be known, but it is also imperative that the atomic weight of the combining body be perfectly well established. There are a few processes especially well adapted for ascertaining the atomic weights of metals; for example,—

I. The conversion of a metal into an oxide the formula of which is known.

II. The formation of a chloride.

III. The analysis of a carbonate decomposable by heat.

IV. The reduction of an oxide to the metallic state by hydrogen.

We will illustrate each of these by an example.

812. I. There is every reason to believe that the compound formed by treating tin with nitric acid is a binoxide; if, therefore, the amount yielded by a given weight of tin were accurately known, it would be easy to ascertain the atomic weight of that metal. Now it has been found that 100 parts of tin yield 127·2 of peroxide, and as we take the atomic weight of oxygen as the point of departure of our calculation, we say that if 27·2 parts of oxygen unite to 100 parts of tin, what will two equivalents of oxygen unite with; we have, therefore,—

$$27\cdot2 \quad : \quad 100 \quad : : \quad \underbrace{16}_{2 \text{ eq.}} \quad : \quad \underbrace{58\cdot82}_{\text{At. wt. of tin.}}$$

813. II. The second case is equally simple. Chemists are agreed that chloride of silver is a compound of one equivalent of silver and one of chlorine; they are also agreed that the atomic weight of chlorine is 35·5. Now as 100 parts of silver yield 132·856 of chloride, we obtain the atomic weight of silver, as follows:—

$$32\cdot856 \quad : \quad 100 \quad : : \quad \underbrace{35\cdot5}_{1 \text{ eq. chlorine.}} \quad : \quad \underbrace{108\cdot04}_{\text{At. wt. of silver.}}$$

814. It will be evident that we may assume 108 as the atomic weight of silver, and it appears to be one of those metals the equivalents of which are multiples by a whole number of that of hydrogen.

815. III. It is well established that the atomic weight of carbon is 6 and of oxygen 8; if, therefore, the carbonate of a metallic oxide be ignited so as to obtain the pure oxide, we possess all the necessary data for determining the equivalent of that oxide, and to obtain that of the metal, it is merely necessary to deduct the atomic weight of oxygen. It has been found that 100 parts

of pure crystallized carbonate of lime yield, on powerful ignition, 56 parts of lime; the composition of carbonate of lime is,—

$$\begin{array}{ll}
\text{Lime} & 56{\cdot}00 \\
\text{Carbonic acid} & 44{\cdot}00 \\
\hline
& 100{\cdot}00
\end{array}$$

Therefore

$$44 \quad : \quad 56 \quad : : \quad 22 \quad : \quad 28,$$

At. wt. of   At. wt. of
carb. acid.   lime.

and $28-8=20$, the atomic weight of calcium.

816. IV. It is universally admitted that the peroxide of iron belongs to the class of sesquioxides, its formula being $Fe^2 O^3$. To obtain the atomic weight of iron, it is merely necessary to submit this oxide to accurate analysis. By passing hydrogen gas at a red heat over pure sesquioxide of iron, it has been found that $35{\cdot}783$ yield $25{\cdot}059$ of metal. It is plain from this, that $35{\cdot}783$ of the oxide consists of—

$$\begin{array}{ll}
\text{Iron} & 25{\cdot}059 \\
\text{Oxygen} & 10{\cdot}724 \\
\hline
& 35{\cdot}783
\end{array}$$

Admitting the formula of the oxide to be as above stated, we obtain the atomic weight of iron, thus:

$$10{\cdot}724 \quad : \quad 25{\cdot}059 \quad : : \quad 24 \quad : \quad 56{\cdot}08,$$

3 eq. of O.   2 eq. Fe.

and $\dfrac{56{\cdot}08}{2}=28{\cdot}04$. The latter number represents the atomic weight of iron, for which we may substitute $28{\cdot}00$, as the difference doubtless is due to error of experiment. Allowing the latter to correctly represent the atomic weight of iron, it follows that, like so many others, it is a multiple by a whole number of that of hydrogen.

817. The equivalents of many metals are determined by much more complex processes than those given as examples; but whenever such is the case less confidence is felt in the result;

the nearer, therefore, a process for determining an atomic weight approaches simplicity, the nearer it approaches perfection.

818. *General considerations on the elements.*—It is extremely interesting to study the properties of elementary bodies considered as series. It often happens that chemical elements fall naturally into groups of threes, the properties considered most characteristic of them advancing in a distinct and evident manner. M. Dumas has shown that if, in these triads, we take half the sums of the equivalents of the extremes of the series, we shall obtain as a mean, a number closely approximating the equivalent of the middle body, thus:—

	Atomic weight.
Chlorine	35·5
Bromine	80·0
Iodine	127·0

Let us add together the atomic weight of iodine and chlorine, and we obtain 162·5 and $\dfrac{162·5}{2}=81·2$. Again, sulphur, selenium and tellurium fall into a natural triad, the properties of which advance in an evident manner, as do also their atomic weights.

	Atomic weight.
Sulphur	16
Selenium	39·5
Tellurium	64·5

On repeating the process before given, we find that

$$64·5 + 16 = 80·5 \text{ and } \frac{80·5}{2} = 40·2,$$

being a number closely approximating to the equivalent of the middle body, selenium; and if the atomic weights of the last two members of this group were better known, perhaps the coincidence might be still closer.

As it would be improper to make assertions of this kind unless corroborated by a greater amount of evidence than that afforded by two examples, let us take others, for instance,—

		Atomic weight.
Lithium .	. . . .	6·43
Sodium .	. . . .	23·00
Potassium	. . .	39·00

And $6·43+39·00=45·43$ and $\dfrac{45·43}{2}=22·71$, a number closely approaching that of sodium. We will take one more example from the metals of the alkaline earths :—

		Atomic weight.
Calcium .	. . . .	20·00
Strontium	. . .	44·00
Barium .	. . . .	68·64

819. Applying the rule before given, we have

$$20·00+68·64=88·64 \text{ and } \frac{88·64}{2}=44·32,$$

or almost exactly the equivalent of strontium. It is also to be observed, that with the three triads given, the chemical and physical properties frequently advance in a manner quite in accordance with the arithmetical ratio of the equivalents ; thus, with the first group given, the chemical energy of the elements is inversely as the atomic weight ; moreover, while chlorine is a permanent gas, bromine is a volatile fluid and iodine a volatile solid.

820. Again, this gradation of properties is well defined in the second, and also in the third triad, where we have compared the properties of the three metals. But in the fourth it is still better marked. The sulphate of lime is more soluble than the sulphate of strontia, and the latter than the sulphate of baryta, and other properties present the same progressive tendency. We will not discuss at any length the conclusion which M. Dumas drew from these facts, which was, that the elements were compounds, and that bromine resulted from the union of half an atom of chlorine with half an atom of iodine, and so on of the rest, because such an argument can only be decided by experiments, and these must be of a nature quite different from those at present known to chemists, and involving methods of research to which

at present we have no clue ; but the consideration of the arithmetical relations of the equivalents of bodies may lead us to equally interesting, and perhaps more profitable trains of research. We do not find any triad into which fluorine will enter with the same chemical and arithmetical relations as are observed with chlorine, bromine, and iodine ; and on looking through the lists of atomic weights, we do not observe the metals generally falling into natural triads. However, from the very complete manner in which the examples given fulfil the desired conditions, it may be safely inferred that numerous other instances of the same kind would be found if we were better acquainted with the substances existing in nature. Great steps are every day being made in this direction, and the results lead us to group together, by very strong analogies, bodies which until lately were not considered to possess any resemblance. Thus it is now ascertained that boron, when properly crystallized, is exceedingly like the diamond, to which also it is only second in hardness. The refractive power is also equal to the last-named substance, so that if procurable in crystals of sufficient size and purity, it would be equally beautiful. Moreover, it appears to be more unalterable than the diamond, for it is not affected by nitre at a red heat.

821. Another singular circumstance is, that bodies having great similarity in a chemical point of view are generally found associated in nature. Thus chlorine, bromine and iodine are all found in sea-water. The arithmetical relations of these three haloids have already been noticed. Silver and lead are so often found together that it is difficult to procure lead free from silver, unless it has been carefully purified. Common sheet-lead submitted to cupellation will almost invariably yield a minute button of silver. Now silver and lead have both high atomic weights, and they do not very greatly differ. Thus lead is 103·7 and silver 108·0. Again, iron, manganese, cobalt and nickel are almost always found associated in minerals. In many respects, also, they have chemical resemblances, such as their power of forming sesquioxides, &c. Their atomic weights are also very close, iron being 28, manganese 27·6, cobalt 29·5, and nickel 29·6. Chromium,

which also forms a sesquioxide, has an atomic weight of 26·7. Again, aluminium is always found in nature associated with iron; they both form sesquioxides, which, like that of chromium, are capable of forming alums; but the equivalent of aluminium is low, and appears to remove it from the group with which we have associated it. If, however, we multiply the equivalent of aluminium by 2, we have 27·34, a number intermediate between chromium and iron. Again, we find certain minerals occurring in nature containing metals of such great similiarity, that sometimes the mineral is known for many years before it is suspected to contain more than one oxide. Thus cerite contains cerium, lanthanium, didymium, and perhaps others. There is no doubt that chemists have more than once allowed the discovery of a new metal to escape them from its reactions not having been examined with sufficient minuteness.

822. The ores of platinum also contain several metals, the properties of which show many points of resemblance; and moreover the atomic weights of nearly all the metals associated with platinum have equivalents the same, nearly approximating, or else more or less approaching a multiple of the equivalent of rhodium, thus:—

	Atomic weight.
Rhodium	52·1
Ruthenium	52·1
Palladium	53·3
Platinum	99
Iridium	99
Osmium	99
Lead	104
Silver	108
Gold	197

823. It is difficult to see so marked a tendency in substances to associate together, their atomic weights having an equal tendency to oscillate between certain numbers or multiples of numbers, without thinking that there must be something more than chance in it; in fact, chance it cannot be, and it remains for us to learn the cause.

824. A somewhat similar peculiarity is observable in the metals tungsten and molybdenum. These metals have numerous points of resemblance, and their atomic weights bear a very simple relation to each other, thus:—

	Atomic weight.	Specific gravity.
Molybdenum . . .	46	8·6
Tungsten	92	17·6

It is singular, that while the atomic weight of tungsten is exactly double that of molybdenum, its specific gravity is also about double.

PROCESSES AND REACTIONS USED IN ORGANIC RESEARCHES.

825. The separation of organic bodies from complex mixtures with the view of examination or analysis, is in many laboratories a problem of everyday occurrence, but it would be difficult to direct the student to a source of information as to the method to be pursued. It is true, that, by the study of such works as the ' Traité de Chimie Organique' of M. Gerhardt, any student may ascertain the modes which chemists have adopted in individual cases, but few works treat especially of the steps by which the chemist is to proceed to separate and examine organic substances generally. The design of this book is too limited to permit of entering into the subject at any length, but it is intended to give a sketch of the processes for isolating and determining the nature of a few of the most important.

826. In order to simplify the study of this subject, we shall divide organic bodies into three classes, which in their turn admit of several subdivisions; these are—

Acids.

Bases.

Neutral bodies.

827. In going through organic bodies arranged in series, we are startled to find, in spite of the immense amount of labour that has been expended on them of late years, that at almost every step there is ample material for investigation; where such cases occur directly in our path, they will be noticed.

828. The mode of treating the subjects will be as follows:—
Sources from whence obtained.
Method of separating from other bodies.
Mode of determining nature and composition.
General remarks.

829. The number of substances of organic origin already known to chemists is so immense, that it is quite impossible in a book of limited extent like the present, to attempt to describe more than a few of the methods of obtaining and estimating the substances discussed, and even then only those of most general application. When we remind the student that in the single department of organic acids 800 are already known, it will be evident that a very restricted plan must be adopted.

We shall consider them under the following heads : acids derived from—

    I. The vegetable kingdom.

    II. Animal products.

    III. Treatment of organic bodies by oxidizing agents.

    IV. Fermentation.

    V. Treatment of organic bodies by acids to form conjugated acids.

    VI. Action of heat on acid salts of ammonia yielding acid amides.

    VII. Destructive distillation of organic matters, &c.

Great numbers of derived acids are also known in which the hydrogen of an acid is replaced by one or more atoms of chlorine, bromine, iodine, hyponitric acid, &c.

830. We shall study the modes of obtaining and determining the constitution and properties of a few acids from one or two of these sources.

I. *Acids derived from the Vegetable Kingdom.*—It will be proper to consider these acids under two heads, namely, volatile and fixed.

831. *Volatile acids.*—It is to be observed that these acids are equally produced from animal and vegetable sources ; but as the most important of them, namely, the acetic, has been longest

known as a vegetable acid, we shall study them under this head.

832. The manipulation connected with the investigation of the volatile acids of the series $C^n H^n O^4$, is generally of a very simple character. It has been found that they seldom occur singly. If, therefore, any process or experiment has indicated the presence of a volatile acid, great care must be taken to ascertain whether more than one be present. This may be done in several ways. We will suppose that on adding a mineral acid, preferably the sulphuric, to some organic product, the peculiar odour of a volatile acid is perceived, the whole is to be acidified with dilute sulphuric acid, and the fluid submitted to distillation. As the distillate is often exceedingly weak, it is to be neutralized with carbonate of soda and evaporated over the naked fire until the solution has been concentrated to a considerable extent, when it may be finished over a sand-bath. It is to be observed that the soda-salts of the principal volatile acids are perfectly stable, and no fear of decomposition need be entertained even if the mass should become dry; and, in fact, it is often advantageous to fuse it, of course at as low a temperature as possible, in order to drive off empyreumatic impurities. The resulting salt, or a portion of it, is to be dissolved in distilled water, and, if necessary, filtered. To the clear solution nitrate of silver is to be added in small quantities, and the precipitate filtered off. Although in experiments of this kind the greatest care must be taken to avoid impurities in the reagents, yet as traces of chlorine might exist in the carbonate of soda, it is proper to reject the first precipitate, which should not, therefore, be large in amount. A small quantity of nitrate of silver is then to be added to the filtrate from the first precipitate, the resulting salt filtered off, and the operation again repeated on the filtrate from the last. In this manner three or four precipitates are to be obtained one after the other, and by determining the silver in each, it will be ascertained whether more than one volatile acid exists in the fluid under examination. The precipitates are to be well washed before being dried. To dry the silver-salts in the water-bath would scarcely be advisable,

until it had been ascertained whether they would endure a temperature of 212° without decomposition.

It must not be forgotten that silver-salts must, if dried *in vacuo* over sulphuric acid, be kept in the dark, or they are liable to blacken and decompose. If a variation in the amount of silver is found in the precipitates, the course next to be adopted will depend upon the amount of material in the operator's possession. It is probable that the silver in one or more of the precipitates will coincide with the theoretical quantity for some of the volatile acids, in which case a combustion may be made, and the result, if successful, combined with the silver determination, will be sufficient proof of the existence of the acid.

833. If the volatile acid has been obtained by acting with nitric acid on organic matters, some difficulty may at first be found in determining the silver, owing to the explosive nature of the salts formed by the nitro-acids; in such a difficulty the salt may be mixed with a little carbonate of soda and ignited, and the soda be afterwards washed out, or it may be moistened with hydrochloric acid, and the silver be estimated as chloride. If a sufficient quantity of acid is to be procured, it is very desirable that its boiling-point should be ascertained, to corroborate the result of the analysis of the silver-salt. If of the $C^n H^n O^4$ series, and it be required to determine the vapour density, it must not be forgotten that the determination must be made far above the boiling-point, in order to obtain a correct result[*].

834. If a sufficient quantity is to be procured, and it is desired to obtain them separate, Liebig's method by partial saturation (§ 357) may be adopted.

835. *Fixed vegetable acids.*—The methods of separating and determining the fixed vegetable acids depend to a great extent upon the nature of those present. Tables of the modes of testing for the most common ones are to be found in the manuals of qualitative analysis. If in the course of experiments on vegetables, acids are encountered, the nature of which it is desired to ascertain, the first step is for the student to refer to some

* See also § 136 on this subject.

extensive work on organic chemistry, in order to ascertain whether the vegetable or plant has been previously examined.

836. Some acids, such as the citric and tartaric, are obtained by taking advantage of the insolubility of their lime-salts, which are obtained by neutralizing the vegetable juice with chalk, filtering off the precipitate, and decomposing it with dilute sulphuric acid; the solution contains the acid, while the comparatively insoluble sulphate of lime is removed by the filter. The liquid, on careful evaporation, yields crystals of the acid.

837. In separating organic acids for the purpose of determining their nature and constitution, no opportunity must be neglected of ascertaining any peculiarities in their properties or specialties in their salts, for it often happens that by this means we are enabled to remove other bodies with which they may be associated in plants, and which may so much resemble them in their habitudes as to mask their reactions and lead to confusion. If, for instance, it was intended to separate malic acid from the juice of any of the numerous plants which contain it, by adding acetate of lead, we should incur the danger of precipitating tartrate of lead along with the malate; but, by availing ourselves of the peculiar properties of the malate of lime, we are enabled to obtain a pure salt, from which we may procure the acid with ease in a state fit for examination. If we nearly saturate with chalk, or hydrate of lime in fine powder, the juice containing the malic acid, and, after filtration, boil the liquid, malate of lime is precipitated in a state of considerable purity. By decomposing the last-named salt with acetate of lead, we obtain a pulverulent or curdy precipitate, which has the peculiar property of spontaneously changing, if left in the liquid, into fine silky crystals.

838. Lead salts of organic acids, such for instance as that last described, are often decomposed by sulphuric acid or sulphuretted hydrogen, for the purpose of obtaining the acid in a free state. The gas has the advantage of yielding sulphide of lead, which acts as a powerful decolorizer, and frequently prevents the necessity of using animal charcoal.

839. In separating acids from the juices of plants by salts of

lead, we must be on our guard against the possibility of precipitating sulphates and phosphates at the same time.

840. In some instances it is convenient to remove inorganic acids like those named, by first saturating the juice by carbonate of soda, and then cautiously adding acetate of baryta until they are removed. If, then, the acid to be isolated is precipitable by acetate of lead, that reagent may be added, and the rest of the process performed as described above.

841. In examining the nature of organic acids, great care must be taken to ascertain their degree of basicity. If they have any tendency to form acid salts, the question is at once determined as to their not being monobasic, for acids of this class never form acid salts.

II. *Acids derived from the Animal Kingdom.*—Acids derived from the animal kingdom are, as a rule, less easily obtained in a finely crystallized condition than those from plants. While numerous acids of great beauty and theoretical interest have for many years been known to chemists as products of the vegetable world, it is of comparatively recent date that distinct and certain knowledge has been obtained of the constitution of those derived from animals. In fact, the very high atomic weights of many of the animal acids render it exceedingly difficult in many cases to construct formulæ that leave no doubt upon the mind as to their correctness, because, in most instances, the analytical results will bear more than one interpretation, and it is this fact which, perhaps more than any other, renders it desirable that, where it is possible, the products of their decomposition should be examined with the view of corroborating the formula derived from the analysis.

842. Animal acids are obtainable by a variety of processes from the crude substances which contain them; we shall therefore glance briefly at one or two of the most important, with the view of obtaining an idea of the mode of proceeding.

843. *Solid fatty acids.*—These acids exist both in animal and vegetable products, and sometimes the same acid is derivable from both sources. The difficulties experienced in determining the true constitution of some of the solid fatty acids of high atomic weights

are so great, that even with stearic acid, one of the most fully investigated of them, it can scarcely be said that the formula is established in a perfectly satisfactory manner.

844. Acids of this class are generally obtained by saponifying the fatty matters containing them, by boiling with potash and decomposing the soaps by means of hydrochloric acid. The acids thus set free are crystallized repeatedly until their melting-point is no longer raised by the process.

845. Sometimes the alcoholic solutions of the fatty acids or their soaps are precipitated with the acetates of lead, baryta or magnesia, and the resulting precipitates are decomposed by boiling with dilute hydrochloric acid. The methods of forming the salts of organic acids will be given in the general remarks on organic acids.

846. Some organic acids may be isolated from fluids in which they are contained, by adding, after evaporation, a metallic salt, the base of which forms an insoluble or comparatively insoluble salt with the acid present: hippuric acid, for example, may be separated from the urine of the horse by this means; the metallic salt is afterwards to be decomposed by a mineral acid, in order to set the acid free.

847. Acids of sparing solubility are sometimes separated from complex organic mixtures by treating the latter with cautic potash, filtering the alkaline and somewhat dilute solution to remove the insoluble impurities, and precipitating the substance sought by the addition of a mineral acid. If it be desired to separate uric acid from guano*, the alkaline solution is to have carbonic acid gas passed into it, in order to separate the sparingly soluble acid urate of potash. The latter may be washed with water until quite white, and after being dissolved in boiling-water, precipitated by hydrochloric acid.

848. Lactic acid will be treated of in describing the preparation of acids by means of the fermentation of neutral organic bodies.

* The preparation of uric acid from guano promises to become of great importance in the arts, in consequence of the valuable dyeing properties which have been recently discovered in murexide.

849. A very useful process for extracting not only acids but many other bodies from complex organic substances, is by exhausting the mass with alcohol and adding ether; this frequently causes the separation of the substances which it is desired to isolate, owing to their being less soluble in a mixture of alcohol and ether than in alcohol alone. This method may be adopted in separating cholic acid from dry bile.

850. III. *Acids produced by treating organic bodies with oxidizing agents.*—The number of acids produced by this method is very great, so that only a few can be noticed, and those of most general interest. It is to be observed that organic bodies are oxidized in the laboratory by a variety of methods, among which may be mentioned the following:—

> Fusion with alkalies.
>
> Treatment with nitric acid.
>
> Treatment with peroxides.

851. *Formation of acids by fusion of organic substances with alkalies.*—By this process a feebly oxidizing action is obtained; the products are of course liable to variation, according to the temperature employed and the nature of the materials. Sometimes an acid appears to be formed at one step of the process, but is decomposed on continuing the heat with evolution of other substances, products of its metamorphosis. Thus in distilling indigo with potash for the purpose of obtaining aniline, anthranilic acid appears to be formed at one stage of the process and subsequently destroyed, as in the following equation:—

$$C^{14} H^7 NO^4 = 2CO^2 + C^{12} H^7 N$$

Anthranilic acid.　　　　Aniline.
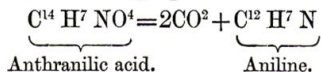
The oxidizing action of hydrate of potash at elevated temperature is manifested in the conversion of camphor into campholate of potash, thus:—

$$C^{20} H^{16} O^2 + KO, HO = C^{20} H^{17} KO^4$$

Camphor.　　　Campholate of potash.
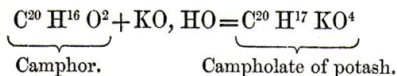
Other acids are often formed in this method of operation, as oxalates and acetates, but they generally undergo a secondary

decomposition, resulting in the formation of other products, such as carbonic acid, hydrogen, hydruret of methyl, &c.

852. *Formation of acids by treatment of organic substances with nitric acid.*—The action which nitric acid exerts on organic substances varies greatly, according to the nature of the body, and the greater or less state of concentration of the acid itself. Thus, blue indigo, which contains $C^{16} H^5 NO^2$, when submitted to the action of weak nitric acid for a moderate time, yields isatine, $C^{16} H^5 NO^4$, the effect of the acid being only to fix the element of oxygen on to the indigo; but if the action be maintained longer, a further change is developed, the carbon is attacked, and a more considerable oxidation is effected, resulting in the production of indigotic acid, $C^{14} H^5 NO^{10}$. And if this indigotic, nitrosalicylic, or anilic acid as it is also called, is treated with strong nitric acid, we obtain picric acid, $C^{12} H^3 N^3 O^{14}$, still more of the carbon and some of the hydrogen being removed, while the proportion of oxygen and nitrogen is increased. The last-named acid is a very common product of the metamorphosis of organic substances under the influence of nitric acid.

853. In treating organic matters with this acid, care must be taken to avoid too violent a reaction, which would result in the expulsion of the substance from the vessel, and perhaps still more unpleasant consequences. Sometimes it is proper to cool the organic substance and the acid separately, and drop the former, if a fluid, into the latter, still retained in a freezing mixture. The fluid is then to be diluted with water and neutralized by an alkaline carbonate, with the intention of procuring a salt. This process is required in obtaining trinitrocresylic acid from the hydrate of cresyl existing in coal-tar*.

* I have ascertained that alcohols of acid properties higher up than the cresylic exist in coal-tar; in fact, by selecting coal-oils of very high boiling-point, volatile acids, apparently homologues of phenol, may be obtained up to and beyond the range of the mercurial thermometer, and yet readily soluble in potash. When the less volatile tarry acids remaining in the retort are dissolved in solution of potash, a fluid is obtained of singular properties. If a piece of calico be plunged into it, and removed in the hand so as not to meet the air, it is almost colourless; but on opening the hand, and allowing

854. It has been said that nitric acid sometimes acts merely by the fixation of oxygen without removing the carbon, as with isatine from indigo; that this is not an isolated case, is evident from the fact that by oxidation camphor becomes converted into camphoric acid without alteration of its carbon.

$$\underbrace{C^{20}\ H^{16}\ O^2}_{\text{Camphor.}} + O^6 = \underbrace{C^{20}\ H^{16}\ O^8}_{\text{Camphoric acid.}}$$
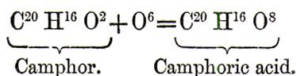
Sometimes, on the other hand, not only both carbon and hydrogen are greatly diminished and the oxygen is increased, but there is also a considerable formation of oxalic acid at the same time, as in the formation of Warren De la Rue's nitrococcussic acid from carminic acid. In acting on organic matters, animal or vegetable, with nitric acid, we must always be prepared to find oxalic acid as one of the products. The salt of nitro-acids are generally explosive, and with some, as for instance the last alluded to, the detonation is so violent as to be dangerous. In acids of this class we recognize a fixation of hyponitric acid which replaces hydrogen; thus picric acid is hydrate of phenyl, carbolic acid, phenic acid, or whatever we choose to designate phenol, in which three atoms of hydrogen are removed and replaced by hyponitric acid.

855. It is curious that in these reactions the resulting acid has sometimes no perceptible relation to the original matter, and even at times appears to be derived from an unisolated body; thus nitrococcussic acid is isomeric, but not identical, with trinitroanisic acid; it is therefore derived from an acid isomeric with anisic acid.

When such problems as these arise, they are very difficult to solve, and, at the time, perhaps impossible, but doubtless in the above case the isomer of anisic acid, of the formula $C^{16}\ H^8\ O^6$, will one day be discovered, and then the true relation of nitrococcussic acid will be better understood. It is the more to be desired in

the cloth to become exposed, it rapidly becomes blood-red. Probably it is here we should search for Runge's rosolic and brunolic acids.

the above case, because the products of the decomposition of anisic acid in presence of the alkaline earths are of great interest, and it would be exceedingly interesting to compare the products of the destructive distillation of the unknown acid with them.

856. *Treatment with peroxides.*—When we boil those organic bodies which contain much oxygen with peroxide of lead, formic and carbonic acid are produced. In general, when peroxides are used, there is a very complete decomposition, but the resulting products are those which have no decided relation to the original matters, because the action goes too far. This is particularly the case if acids are used simultaneously with the peroxide.
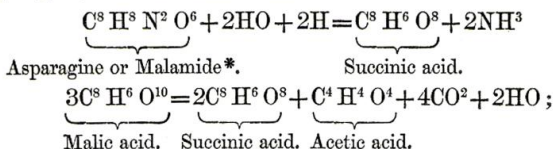
857. Some substances treated with peroxide of lead yield products of great interest, but not being acids they will not be described here.

858. IV. *Production of acids by fermentation.*—Fermentation which acts by reduction, nevertheless often results in the formation of acids, by removal of oxygen from other acids. Even an amide, or a substance resembling an amide, may, by fermentation, be made to produce acids, as will be seen below. Sugar fermented with decomposing cheese, yields lactic acid, which, if allowed to ferment still further, generally produces butyric acid, but sometimes propionic acid instead.

859. The transformation of lactic acid into butyric acid may be represented thus :—

$$\underbrace{C^{12} H^{12} O^{12}}_{\text{Lactic acid.}} = \underbrace{C^8 H^8 O^4}_{\text{Butyric acid.}} + 4CO^2 + 4H.$$
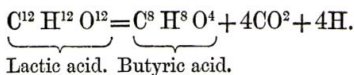
860. Succinic acid may be produced by fermentation from asparagine, and also from malic acid, thus :—

$$\underbrace{C^8 H^8 N^2 O^6}_{\text{Asparagine or Malamide*.}} + 2HO + 2H = \underbrace{C^8 H^6 O^8}_{\text{Succinic acid.}} + 2NH^3$$

$$\underbrace{3C^8 H^6 O^{10}}_{\text{Malic acid.}} = \underbrace{2C^8 H^6 O^8}_{\text{Succinic acid.}} + \underbrace{C^4 H^4 O^4}_{\text{Acetic acid.}} + 4CO^2 + 2HO ;$$

* According to the recent researches of Demondésir, malamide is only isomeric with dry asparagine, from which he states it to differ in form,

or more simply, and disregarding secondary products,

$$C^8 H^6 O^{10} - 2O = C^8 H^6 O^8.$$

Malic acid.   Succinic acid.
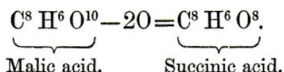
861. We have said that lactic acid by fermentation yields butyric acid, and that malic acid yields succinic acid by the same process; now malic acid also yields butyric acid under certain circumstances; the decomposition may be rendered thus:—

$$2C^8 H^6 O^{10} = C^8 H^8 O^4 + 8CO^2 + H^4.$$

Malic acid.   Butyric acid.

862. V. *Treatment of organic bodies with acids to form conjugated acids.*—In conformity with the rule generally adopted among chemists, we have considered some acids derived by substitution of hyponitric acid for hydrogen apart and among acids formed by oxidizing agents; but this is, perhaps, not the most proper way of looking upon these bodies in a chemical point of view.

863. Picric acid should undoubtedly be regarded as a conjugated acid, as much as sulphobenzoic acid. Even their mode of formation is similar, namely, by bringing the two substances together in the free state; for instance, sulphacetic acid, $C^4 H^4 O^4, 2 SO^3$, is prepared by cautiously mixing monohydrated acetic acid with anhydrous sulphuric acid, carefully cooling after each addition. After keeping the mixture at a temperature not exceeding 140° F. for some hours, the whole is to be poured into a large quantity of cold water, and is then to be saturated by carbonate of lead or baryta; the excess of carbonate being removed by filtration, the sulphacetate is left to crystallize out. Sulphuretted hydrogen may be used to remove the lead from the sulphacetate of that base, and the acid is obtained in deliquescent needles by evaporation *in vacuo* over sulphuric acid.

864. Most of the sulpho-acids are made by more or less analogous processes, such as sulphovinic acid, &c. They are decom-
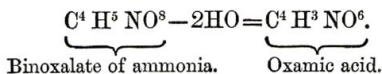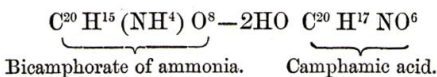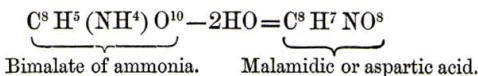
and chemical properties. Moreover, its rotating power is said to be different.

posed when heated, with production of sulphurous acid. The salts formed by neutralizing conjugated sulphuric acids, such as the sulphovinic acid, with lime, potash, &c. are valuable as the raw material for the production of many substances.

865. Sulphuric acid forms conjugated acids with a great number of substances; for example,—

|		
With alcohols	as	Sulphovinic acid.
With acids	as	Sulphobenzoic acid.
With hydrocarbons	as	Sulphonaphthalic acid, &c.

VI. *On acid amides.*—While *neutral* salts of ammonia by loss of water form amides, so *acid* salts of ammonia form acids by the same process, thus:—

$$C^8 H^5 (NH^4) O^{10} - 2HO = C^8 H^7 NO^8$$

Bimalate of ammonia.   Malamidic or aspartic acid.

$$C^{20} H^{15} (NH^4) O^8 - 2HO \quad C^{20} H^{17} NO^6$$

Bicamphorate of ammonia.   Camphamic acid.

$$C^4 H^5 NO^8 - 2HO = C^4 H^3 NO^6.$$
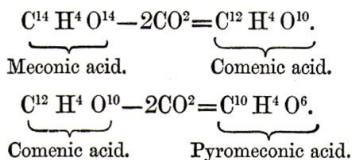
Binoxalate of ammonia.   Oxamic acid.

Although, as represented in the last equation, the formation of an amidic acid appears exceedingly simple, yet, in fact, if it be attempted to prepare oxamic acid by heating binoxalate of ammonia, it is found that many other products are formed, including ammonia, oxamide, hydrocyanic acid, carbonic acid, and carbonate of ammonia. The amidic acids are, in fact, sometimes prepared by somewhat circuitous methods.

866. VII. *Production of acids by destructive distillation.*—The study of organic acids produced by destructive distillation naturally divides itself into two branches: in one we are able to trace the relation of the products formed, to the original substance; in the other we are not. Many organic acids, when exposed to heat with proper care, yield a new acid differing from the original by

two equivalents of carbonic acid, as, for example, gallic acid, which under the influence of heat is converted into pyrogallic acid, thus:—

$$C^{14} H^6 O^{10} - 2CO^2 = C^{12} H^6 O^6.$$

Gallic acid.　　　Pyrogallic acid.
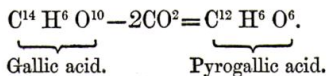
867. Sometimes, by carefully regulating the temperature, two acids are formed, one after the other, two equivalents of carbonic acid being removed to form one acid, and two more subsequently to convert the first pyro-acid into the second. This is well illustrated in the case of meconic acid, which, by heating, yields comenic acid in the first place, and by continuing the heat, pyromeconic acid, according to the following equations:—

$$C^{14} H^4 O^{14} - 2CO^2 = C^{12} H^4 O^{10}.$$

Meconic acid.　　　Comenic acid.

$$C^{12} H^4 O^{10} - 2CO^2 = C^{10} H^4 O^6.$$

Comenic acid.　　　Pyromeconic acid.

868. Some acids of considerable interest are formed under circumstances which do not permit of our tracing the relation between the parent matter and the resulting substances, and yet these same products may be obtained by definite processes also. As an instance of this, the substance known under the synonyms of carbolic acid, phenic acid, phenol, hydrate of phenyl, and phenic alcohol, is produced abundantly during the distillation of coal, it being obtained in considerable quantity from gas-tar, in which it occurs associated with numerous other acid, alkaline and neutral substances. It is also to be obtained in a perfectly intelligible manner by heating salicylic acid with lime or baryta, thus:

$$C^{14} H^6 O^6 - 2CO^2 = C^{12} H^6 O^2.$$

Salicylic acid.　　　Carbolic acid.
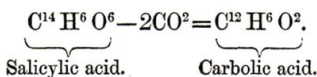
869. Acids of this kind being volatile and not readily obtained in the form of well-defined salts, are best studied by the careful analysis of the acids themselves, and the determination of their
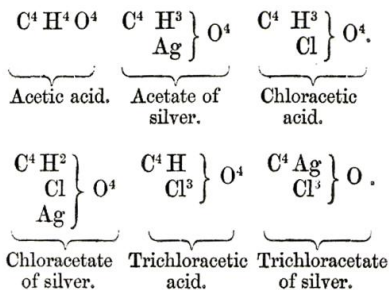
vapour density. The products of their decomposition should also be carefully ascertained, as the derived acids are often more easily investigated than the original one.

870. Many acids, on distillation with an alkaline earth, yield hydrocarbons the composition of which stands in such simple relation to the original acid, that their study is capable of yielding important corroborative evidence of the constitution of the acid as deduced from its analysis and that of its salts. These hydrocarbons will be described presently.
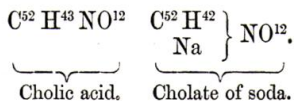
871. *General remarks on organic acids.*—It is to be observed with acids, as also with other organic bodies, that the number of equivalents of carbon, hydrogen and oxygen must be divisible by two. In salts, however, the metal replaces hydrogen, and therefore the number of equivalents of hydrogen and metal added together must make an even number. If nitrogen be present, the hydrogen and nitrogen added together must make an even number; and in the salts, the hydrogen, nitrogen and metal must be divisible by two.

872. If the acid be one in which hydrogen is replaced by hyponitric acid, chlorine, iodine or bromine, &c., the number of atoms of the replacing element must be equal to the number of atoms of hydrogen removed; and in the salts, the atoms of hydrogen, replacing element, and metal must together be divisible by two.

As instances of what has been said, let us trace the formulæ of acetic acid under the circumstances detailed:—

$$C^4 H^4 O^4 \qquad \left. \begin{array}{c} C^4\ H^3 \\ Ag \end{array} \right\} O^4 \qquad \left. \begin{array}{c} C^4\ H^3 \\ Cl \end{array} \right\} O^4.$$

Acetic acid.   Acetate of silver.   Chloracetic acid.

$$\left. \begin{array}{c} C^4 H^2 \\ Cl \\ Ag \end{array} \right\} O^4 \qquad \left. \begin{array}{c} C^4 H \\ Cl^3 \end{array} \right\} O^4 \qquad \left. \begin{array}{c} C^4 Ag \\ Cl^3 \end{array} \right\} O.$$

Chloracetate of silver.   Trichloracetic acid.   Trichloracetate of silver.

Take also the formula of an acid containing nitrogen, and see how the law holds:—

$$C^{52} H^{43} NO^{12} \qquad \left. \begin{array}{l} C^{52} H^{42} \\ Na \end{array} \right\} NO^{12}.$$

Cholic acid.   Cholate of soda.

Even in more complex instances we still find the same regularity of arrangement, thus:—

$$C^{12} H^6 O^2 \qquad \left. \begin{array}{l} C^{12} H^5 \\ (NO^4) \end{array} \right\} O^2 \qquad \left. \begin{array}{l} C^{12} H^3 \\ (NO^4)^3 \end{array} \right\} O^2.$$

Phenic acid.   Nitrophenic acid.   Trinitrophenic or picric acid.

$$\left. \begin{array}{l} C^{12} H^2 \\ Ag \\ (NO^4)^3 \end{array} \right\} O^2 \qquad \left. \begin{array}{l} C^{12} H^2 \\ (NH^4) \\ (NO^4)^3 \end{array} \right\} O^2.$$

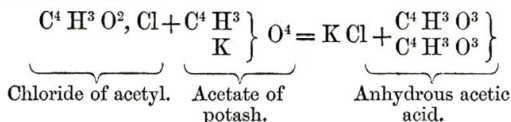Trinitrophenate of silver.   Trinitrophenate of ammonia.
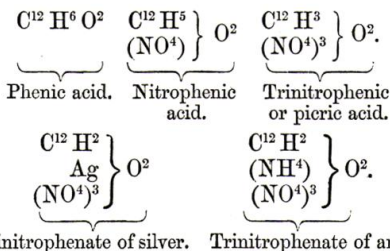
873. In the last illustration the metal ammonium is seen to stand exactly in the same position, and therefore fulfil the same function as the silver in the trinitrophenate of silver. This law of even atoms is of the highest value in research as a means of controlling formulæ. We shall, under other heads, notice the nature of the formulæ of other bodies of different constitution.

874. A new and most interesting series of bodies have recently been described by the late deeply lamented and illustrious chemist M. Gerhardt; they are regarded as being what were, until lately, conceived to be merely hypothetical bodies, namely, anhydrous monobasic acids. It is singular that, in one respect, they resemble the curious hydrocarbons discovered by MM. Frankland and Kolbe, and by them regarded as the alcohol radicals*, viz. that their formula for four volumes of vapour is double that

* In submitting the substances produced by destructive distillation of the Torbane-hill mineral to careful examination, I have succeeded in isolating four distinct hydrocarbons, remarkable for having absolutely the same composition, boiling-point and density, both in the state of fluid and also of vapour, as the organic radicals.

which they possess in their compounds ; in this respect, the ethers, the radicals and the anhydrous acids resemble each other. The method of preparation of these anhydrous acids is sufficiently simple ; it is thus :—

$$C^4 H^3 O^2, Cl + \left.\begin{array}{c} C^4 H^3 \\ K \end{array}\right\} O^4 = K\,Cl + \left.\begin{array}{c} C^4 H^3 O^3 \\ C^4 H^3 O^3 \end{array}\right\}$$

Chloride of acetyl.   Acetate of   Anhydrous acetic
               potash.   acid.

875. These anhydrides easily pass into the ordinary acid in presence of water.

When anhydrous acetic acid is treated with metals, acetates are formed, and, at the same time, a volatile, somewhat oily fluid is produced of agreeable odour, but of which the nature is at present unknown*.

876. We have already alluded to the necessity for ascertaining the degree of basicity of acids (§ 841). It is also to be noticed, that if the acid is bibasic, two amides may be formed from it, one having the properties of an acid, and the other being a true amide ; the former being derived from the acid, and the latter from the neutral ammonia salt. Instances of these are to be found in malamidic acid and malamide, or, as it is generally called, asparagine. The former is obtained from acid malate of ammonia by the loss of two equivalents of water, and the latter from *neutral* malate of ammonia by the same process.

877. The most useful salts for determining the atomic weight of acids are those of silver, lime and baryta. But acids, as they differ in properties, differ also in the way in which they form salts. Sometimes one metallic oxide may be used with greater advantage than any other with one, and yet be entirely useless with another acid.

878. The remarkable researches of Pasteur have opened a wide field of investigation as to the action of heat on the salts of organic acids ; it is necessary, therefore, to be familiar with the crystallographic and optical characters of organic salts, and particularly their relations towards polarized light.

* I have undertaken the examination of this subject.

879. The salts of organic acids, on distillation, frequently yield what are termed ketones, or bodies analogous to acetone. Unless, however, the atomic weight of the acid is very low, the ketone is almost always accompanied by other bodies.

880. *On organic alkaloids.*—These substances are now becoming more numerous every day ; and, in fact, before long, it is not impossible they may even rival in number organic acids. They are found to exist in the animal and vegetable kingdoms, and are also produced by a great variety of reactions ; we shall glance at some of the principal ones under the following heads : alkaloids derived from :—

I. The vegetable kingdom.
II. The animal kingdom.
III. The action of potash on the cyanic and cyanuric ethers.
IV. The action of ammonia on the hydriodic ethers, &c.
V. The action of reducing agents on the nitro-compounds of certain hydrocarbons.
VI. The action of reducing agents on nitro-compounds of oxidized bodies.
VII. Destructive distillation.

881. *Alkaloids obtained from the vegetable kingdom.*—Plants remarkable for their powerful action on the system, are generally found to contain organic alkaloids, most of them being highly valuable as medicaments. Few alkaloids can be taken internally, except in very small quantities, without occasioning violent symptoms, many being deadly poisons. It would be occupying far too much space were we to do more than select a few of the most instructive cases for study ; we shall endeavour therefore to select one or two of the most well-marked bases, to examine their properties, and the modes by which they are obtained.

882. In the very first rank stand those obtained from the cinchona barks, and from opium. Solid bases capable of forming crystalline salts like those from the former source, are extracted by rather dilute acids. The solution is precipitated by milk of lime, and the deposit, after powerful pressure, is treated

with alcohol, to dissolve the alkaloids which are separated by fractional crystallization, taking advantage of their different degrees of solubility. Sometimes the colouring matter of the bark is removed by caustic alkalies before extracting the bases with acid, thus rendering the subsequent bleaching of the alkaloids by animal charcoal unnecessary. The extraction of the alkaloids of the cinchona barks has become so important a process in consequence of their extreme value as remedial agents, that great skill has been expended by various manufacturers in perfecting the various operations, so as to avoid the production of uncrystallizable and dark-coloured bases.

883. With the opium alkaloids, a different mode of proceeding is adopted, in consequence of the substances sought existing in a state which permits their extraction by means of water instead of acids. Morphia, the most valuable constituent of opium, appears to exist partially as sulphate and partially as meconate; if, therefore, to the aqueous solution of opium a solution of chloride of calcium be added, a precipitate of sulphate and meconate of lime is obtained; and, on carefully evaporating the mother-liquid, the morphia crystallizes out, and is powerfully expressed to remove the adherent fluid. The base is then recrystallized from water, and bleached by animal charcoal until sufficiently white. The first black mother-liquid contains a great variety of alkaloids, many of them of great interest; they are capable of being separated by tolerably easy but somewhat circuitous processes, and yield numerous products of decomposition; the details, however, cannot be entered into here.

884. In examining alkaloids extracted by processes of the kind alluded to above, it is absolutely necessary to make combustions of them after different numbers of crystallizations, in order to ascertain if repetitions of the process alter the composition of the alkaloid by removing other substances. It often happens that two or more bases may be extracted by acids from various parts or products of plants, and on being crystallized they are obtained together, and unless the operation is repeated a great many times, an impure product would be analysed. It is therefore of great

importance to try the action of various solvents upon them, in order to ascertain whether the substance supposed to be homogeneous, may not in reality be a mixture capable of separation into two or more distinct alkaloids. This is one of the circumstances which make it fortunate that organic bases form so many compounds, because each new combination becomes a process of purification.

885. The well-marked salts which such bases form are very numerous, and comprise sulphates, hydrochlorates, nitrates*, chlorates, perchlorates, hydriodates, periodates, hyposulphates, hyposulphites, arsenites, formiates, oxalates, ferrocyanates, sulphocyanides, acetates, tartrates, citrates, valerianates, picrates, and many others. They also form double salts with many metals; this is especially the case with their hydrochlorates, which combine with many metallic chlorides, including, probably, all those which form double salts with the hydrochlorates of the volatile organic bases, to be described presently.

886. These solid crystalline oxidized vegetable alkaloids almost invariably yield volatile bases by distillation with potash; quinine, cinchonine and strychnine, for instance, yield chinoline†.

887. It is extremely curious that the greater part of these bases act with the alcohol radicals as if they were nitriles, that is to say, as if one molecule of them contained three compound radicals. And it is no less strange, that all the volatile bases produced by their metamorphosis under the action of heat are nitriles also.

888. Piperine, the formula and constitution of which are by no means well established, yields by its destructive distillation two volatile bases, only one of which, namely piperidine, has as yet been examined. This, the more volatile, the formula of which

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* Where the base is one that would be decomposed by the contact of free nitric acid, it is generally easy to procure a nitrate by double decomposition of the sulphate with nitrate of baryta.

† I have found that cinchonine, instead of only affording chinoline, as had been supposed, yields pyrrol, pyridine, picoline, lutidine, collidine, chinoline, and lepidine; and it is most probable that quinine and strychnine undergo an equally complex decomposition.

was first determined by Dr. Anderson, has been fully studied by
M. Cahours*; it is an exception to the usual rule of bases pro-
duced in this manner, inasmuch as it is capable of taking up
two equivalents of a radical to form an ammonium base; piperidine
has therefore the constitution of an imide, or perhaps it con-
tains a bibasic radical. It would be of interest to ascertain
whether piperine itself is similarly constituted to piperidine, as
regards the number of radicals it is capable of assimilating.

889. The vegetable kingdom also yields volatile bases, which
sometimes exist ready formed in the plant, and at others appear
to be produced by the action of alkalies on either acid or basic
substances. An instance of the production of an alkali from an
acid by the action of heat and alkalies has already been given in
§ 851, in describing the production of aniline from anthranilic
acid. Apophyllic acid also, by destructive distillation, yields an
alkaloid of which the nature is at present unknown, and in con-
sequence of the great difficulty of preparing the material by the
action of nitric acid on cotarnine, is likely to remain so, or at least
until a new mode of obtaining apophyllic acid is discovered, which
is greatly to be desired, as it possesses high theoretical interest.
Its preparation by the decomposition of platino-chloride of cotar-
nine is not likely to be a very economical mode of procuring it.

890. *Bases from the animal kingdom.*—It is not always easy
to assign alkaloids a place among either animal or vegetable pro-
ducts, as they may sometimes be derived from both sources.
When such bases as methylamine, or, in fact, any volatile ones,
are obtained from animal matters, it is generally, if not always,
to be inferred that they are produced by the metamorphosis of
bodies of more complex constitution, either under the influence
of putrefaction, heat, or some other disruptive agency.

891. The juice of flesh yields creatine†, which, as it has never
been found in vegetables or plants, may with propriety be called
an animal alkaloid. But creatine on distillation with soda-lime
yields methylamine, an alkaloid also obtainable from vegetable

* CAHOURS.—'Ann. de Ch. et de Phys.' [3] xxxviii. p. 76.
† LIEBIG.—'Ann. de Chim. et de Phys.' [3] xxiii. 129.

sources. Sarcosine, a derivative of creatine, also yields methyl-amine on distillation. The volatile bases of the alcoholic series are equally produced by the decomposition of either animal or vegetable matters.

892. The only base derived exclusively from the animal king-dom, which we shall study as to the mode of isolation, is crea-tine; and this has been selected because its preparation is exceedingly instructive as a guide in such trains of research as are likely to be undertaken by the student on basic substances of animal origin.

893. Creatine exists ready formed in the juice of the flesh of almost all animals; at least it has been found in that of the Horse, Ox, Sheep, Pig, Deer, Hare, Fox, Marten, Fowl, Pigeon, Turkey, Skate, Haddock, Salmon, Herring, Turbot, Cod, Dog-fish, Pike, Whale, and Alligator. If, to the chopped flesh of the animal, water to the extent of the weight of the flesh be added, and the whole be well pressed, a fluid is obtained which contains the creatine, but little is obtained on evaporation, because it is de-composed by the free acid. But if, after heating the juice to coagulate the albumen, it be filtered, and neutralized by baryta-water, and then evaporated at about 130° Fahr., a thin jelly is obtained, from which the creatine crystallizes out in hard brilliant prismatic crystals*, having the formula $C^8 H^9 N^3 O^4 + 2HO$. By weak acid or alkaline liquids it is not altered, but strong acids convert it into creatinine, another alkaloid, thus:—

$$C^8 H^9 N^3 O^4 = C^8 H^7 N^3 O^2 + 2HO.$$
$$\underbrace{\qquad\qquad}_{\text{Creatine.}} \underbrace{\qquad\qquad}_{\text{Creatinine.}}$$
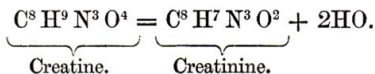
894. We see, therefore, that one alkaloid may, by mere loss of water, be converted into another. A parallel case is found in Wertheim's conhydrine, an alkaloid recently extracted from *Conium maculatum*. The reaction is precisely analogous, except that the resulting base contains no oxygen:—

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* Fluids of a gelatinous consistency are peculiarly adapted for yielding well-defined crystals.

$$\underbrace{C^{16} H^{17} NO^2}_{\text{Conhydrine.}} = \underbrace{C^{16} H^{15} N}_{\text{Coniine.}} + 2HO.$$
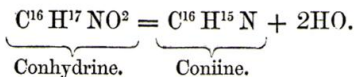
Creatine forms well-defined salts, including hydrochlorate, sulphate, and nitrate. Creatinine yields salts, and also combines with chloride of zinc. The hydrochlorate gives a double salt with bichloride of platinum.
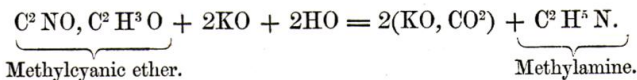
895. *Production of bases by the action of alkalies on the cyanic and cyanuric ethers* [*].—This method of obtaining volatile organic bases, discovered by M. Wurtz, has had the most important consequences, in entirely modifying our ideas of basic combinations, and, by leading M. Hofmann to an examination of the action of ammonia on the hydriodic ethers, caused the discovery of a general method by which we are enabled to determine the constitution of all the other natural and artificial alkaloids.

896. Previous to describing the reactions by which the bases are produced, it is necessary to remind the student that the alcohol radicals, regarded as two volume-formulæ, are precisely analogous to hydrogen ; they fulfil the same functions, and are capable of replacing it without destroying the original type of the compound. If, therefore, we could replace one of the three equivalents of hydrogen in ammonia by methyl, or, in fact, by any alcohol radical, we might anticipate that the resulting compound would, to a certain extent, resemble the original base. Now, let us see the reaction which takes place between the caustic alkalies and the above-mentioned ethers. In the first place, cyanic acid is decomposed by potash in the following manner :—

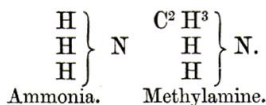$$\underbrace{C^2 NO, HO}_{\text{Cyanic acid.}} + 2KO + 2HO = 2(KO, CO^2) + NH^3.$$
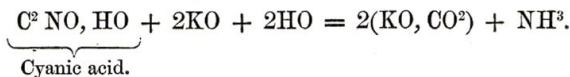
In methylcyanic ether, an equivalent of hydrogen in the cyanic acid is replaced by methyl; if, then, the ether is acted on in the same manner as the acid, we have,—

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* WURTZ, 1849. And, *in extenso*, Mémoire sur les ammoniaques composées. Extrait du tome xi. des mémoires présentés par divers savants à l'Académie des Sciences.

$$\underbrace{C^2 NO, C^2 H^3 O}_{\text{Methylcyanic ether.}} + 2KO + 2HO = 2(KO, CO^2) + \underbrace{C^2 H^5 N.}_{\text{Methylamine.}}$$

897. If, now, we merely multiply the last equation by three, we obtain the reaction of the alkali on the cyanuric ethers, because the latter are polymeric with the cyanic ethers. The bases are also formed by the action of potash on the compound ureas; but we shall only notice the first method at length.

898. If the formulæ given for ammonia and methylamine in the last equation be examined, it is plain that they might be written thus :—

$$\left.\begin{array}{c} H \\ H \\ H \end{array}\right\} N \qquad \left.\begin{array}{c} C^2 H^3 \\ H \\ H \end{array}\right\} N.$$
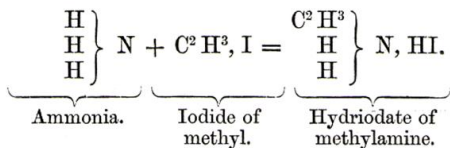
Ammonia. Methylamine.

Where we see at once that one of the equivalents of hydrogen in ammonia is replaced by methyl, the type remaining intact.

899. If we now consider what the most obvious properties of ammonia are, and also what are the characteristics of methylamine, we shall see at once the extraordinary resemblances between them. They are both gases, soluble in water, affording solutions of extreme pungency, which fume on approach of a rod dipped in hydrochloric acid; the solution precipitates metallic oxides like ammonia, and affords well-crystallized salts. In fact, methylamine so greatly resembles ammonia in its properties, that it has repeatedly been mistaken for that alkali. One of the best means of distinguishing, and even of separating them when mixed, is by treating the dry hydrochlorate with strong alcohol, which readily dissolves hydrochlorate of methylamine, but scarcely dissolves sal-ammoniac.
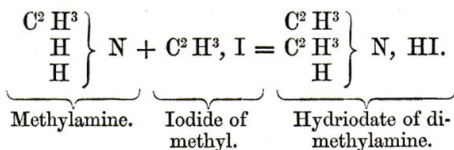
900. The idea immediately strikes us, on viewing the formula of methylamine, whether it would not be possible to replace more than one equivalent of hydrogen in ammonia by alcohol radicals; and in the next paragraph we shall study the very simple method by which M. Hofmann has determined this question.

901. *Production of bases by the action of ammonia on the hydriodic ethers**.—If we consider for a moment what it is that we desire to effect, we shall find that the reagent required, is an alcohol radical in combination with an element having a powerful affinity for hydrogen. The reason for this is very simple; it is because we wish to remove an equivalent of hydrogen from ammonia, and substitute the radical in its place. We shall still use methyl as our illustration. If, then, we place an alcoholic solution of ammonia in contact with excess of iodide of methyl, and after sealing up the mixture in a pressure-tube (§ 303), expose the apparatus for some time to a temperature of 212° Fahr., we shall find that the ammonia disappears, and the solution contains the hydriodate of a new base. We shall disregard secondary reactions, and suppose that the reaction is simply confined to the production of one substance, because the others that are, under certain circumstances, formed simultaneously will be more conveniently studied afterwards. If, now, the excess of iodide of methyl be distilled off, we find, on evaporation of the fluid, that a crystalline salt is deposited having the formula $C^2 H^5 N$, HI, or the hydriodate of methylamine. The salt is formed in accordance with the following equation:—

$$\left.\begin{array}{c} H \\ H \\ H \end{array}\right\} N + C^2 H^3, I = \left.\begin{array}{c} C^2 H^3 \\ H \\ H \end{array}\right\} N, HI.$$

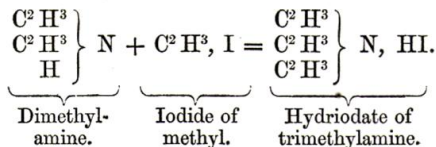| Ammonia.	Iodide of methyl.	Hydriodate of methylamine.

It is plain that there is no reason why the above reaction should not take place equally well with the new base instead of ammonia, and accordingly we find that on distilling the hydriodate of methylamine with an alkali, so as to obtain the free base, and then submitting the latter to the action of iodide of methyl, we obtain the result expressed in the annexed equation:—
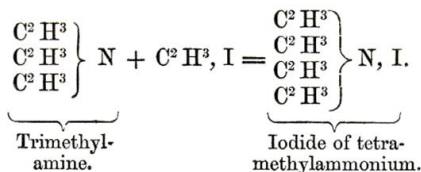
* HOFMANN.—Phil. Trans. 1850.

$$\left.\begin{array}{c} C^2\,H^3 \\ H \\ H \end{array}\right\} N \;+\; C^2\,H^3,\, I \;=\; \left.\begin{array}{c} C^2\,H^3 \\ C^2\,H^3 \\ H \end{array}\right\} N,\, HI.$$

Methylamine.   Iodide of   Hydriodate of di-
                 methyl.   methylamine.

And, again, by proceeding exactly as before :—

$$\left.\begin{array}{c} C^2\,H^3 \\ C^2\,H^3 \\ H \end{array}\right\} N \;+\; C^2\,H^3,\, I \;=\; \left.\begin{array}{c} C^2\,H^3 \\ C^2\,H^3 \\ C^2\,H^3 \end{array}\right\} N,\, HI.$$

Dimethyl-   Iodide of   Hydriodate of
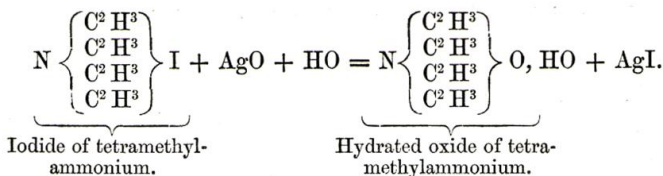amine.   methyl.   trimethylamine.

902. All the bases thus formed are powerful alkalies, and it is to be observed that they become less volatile and more oily as the greater number of equivalents of hydrogen in ammonia become replaced.

The question next presents itself, whether, regarding ammonium as the type of basic organic bodies, the fourth equivalent of hydrogen may not be replaced by methyl to form a compound ammonium ; and if we repeat the treatment of the base as before, we have—

$$\left.\begin{array}{c} C^2\,H^3 \\ C^2\,H^3 \\ C^2\,H^3 \end{array}\right\} N \;+\; C^2\,H^3,\, I \;=\; \left.\begin{array}{c} C^2\,H^3 \\ C^2\,H^3 \\ C^2\,H^3 \\ C^2\,H^3 \end{array}\right\} N,\, I.$$

Trimethyl-   Iodide of tetra-
amine.   methylammonium.

903. The last base is therefore constituted exactly in the same manner as the iodide of ammonium. To obtain the free base, it is necessary to adopt a different method to that which was employed with the first, second, and third bases, because the last is no longer volatile. But if, to the aqueous solution of the iodide of tetramethylammonium, obtained by the last process, we add oxide of silver, a new base is obtained, not volatile without decomposition. The following equation explains the reaction :—

$$N \begin{Bmatrix} C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \end{Bmatrix} I + AgO + HO = N \begin{Bmatrix} C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \end{Bmatrix} O, HO + AgI.$$

Iodide of tetramethyl-   Hydrated oxide of tetra-
ammonium.   methylammonium.

The hydrated oxides thus obtained by the reactions given, and with the iodides of methyl, ethyl, &c., are most powerful alkalies, the solutions of which resemble solutions of caustic potash so perfectly that they might be easily mistaken for that substance by mere qualitative testing.

We have entered thus minutely into the reactions which produce these bodies, because it is essential for the student to comprehend them, in order to follow out the methods of examining alkaloids—to be presently described.

904. *Action of reducing agents on the nitro-compounds of certain hydrocarbons.*—Many hydrocarbons when treated with fuming nitric acid in the manner to be described further on, yield substances retaining the type of the original body, but having one of the equivalents of hydrogen replaced by hyponitric acid. These nitro-compounds, by treatment with reducing agents, yield alkaloids which always belong to the first class, that is to say, they are ammonias in which one equivalent of hydrogen is replaced by a radical. The following represents the nature of the decomposition which takes place when an alcoholic solution of nitrobenzole is treated with sulphuretted hydrogen :—

$$C^{12} H^5 NO^4 + 6HS = C^{12} H^7 N + 4HO + 6 S.$$
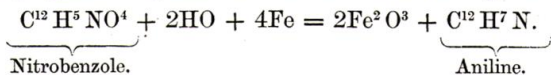
Nitrobenzole.   Aniline.
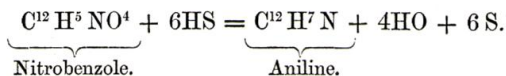
905. This process does not yield the base nearly so easily, or in so pure a state, as the following, given by M. Béchamp*. It is founded on the strong tendency of the proto-salts of iron to become oxidized at the expense of the oxygen of any substances with which it may be in contact. An acetate of iron is pre-

* BÉCHAMP.—'Chem. Gaz.' March 1855; and 'Ann. de Chim. et de Phys.' [3] xlii. p. 186.

pared, containing three parts of iron to one of the nitro-compound, and the two being mixed, are heated on the water-bath, in a capacious flask, provided with a tube leading to a well-cooled recipient. If 100 grammes of nitro-compound are used, the heating on the water-bath requires about an hour. When cooled, the mass in the flask has water added to it, and the whole is filtered; the mass on the filter is to be washed with hot water, and the united fluids are distilled until nine-tenths have passed over. The acetate of aniline and acetic acid both distil over. It is necessary to ensure efficient condensation, as, in presence of steam, acetate of aniline is so volatile that much would be lost if this precaution were not taken. The distillate is to have 40 grammes of concentrated oil of vitriol added for every 100 grammes of nitrobenzole used. On distillation the sulphuric acid displaces the acetic acid, which accordingly distils over, and when the greater part has been obtained, the sulphate of aniline is to be distilled with excess of a strong solution of caustic potash. The aniline is thus obtained in a very pure condition.

906. A still more convenient process is to mix in a spacious retort 1 part of nitrobenzole with 1·2 of bright iron-filings and 1 part of commercial acetic acid. In a few minutes a violent reaction takes place, and unless the receiver be well cooled, all might be lost. When the action has ceased, and the retort cooled, the fluids which have distilled over are to be returned to the retort, and the whole is distilled to dryness. The distillate merely requires to have excess of potash added to it to separate the base, which may be removed from the alkaline fluid, and be digested with sticks of caustic potash to remove moisture. The following equation explains the reaction which takes place:—

$$C^{12} H^5 NO^4 + 2HO + 4Fe = 2Fe^2 O^3 + C^{12} H^7 N.$$

$\underbrace{\qquad\qquad}_{\text{Nitrobenzole.}}$ $\underbrace{\qquad\qquad}_{\text{Aniline.}}$

Almost all ordinary nitro-compounds may be decomposed in the same manner as nitrobenzole, with formation of oily or crystalline alkaloids. For example, nitronaphthaline yields naphthalamine, nitrocymol cymidine, &c. To form the last-named

nitro-compound, it is necessary to cool the hydrocarbon and the nitric acid by means of a freezing mixture, before allowing them to react on each other.

907. *Action of reducing agents on the nitro-compounds of oxidized bodies.*—Some oxidized bodies by reduction yield alkaloids. The only example which we shall adduce is coumaramine*. In the case of this substance, neither sulphuretted hydrogen nor nascent hydrogen yield any satisfactory results; but if a mixture of iron filings and dilute acetic acid be used, and the mixture, with the nitrocoumarine, be heated on the water-bath, action soon commences, sesquioxide of iron separates, and on cooling, yellow needles of coumaramine are deposited. This substance is a true alkaloid, forming a crystalline hydrochlorate and a double compound with bichloride of platinum. There are many oxidized natural and artificial alkaloids and proximate principles the nitro-compounds of which have not been studied, and which, under the influence of acetate of iron, would doubtless yield facts of interest. This is more especially the case now that we know the precautions necessary in forming nitro-compounds with substances which decompose with nitric acid if the temperature be allowed to rise. We have previously alluded to this in describing the method of forming trinitrocresylic acid from the hydrate of cresyl, § 853.

908. *Formation of alkaloids by destructive distillation.*—The number of bases formed in this manner is very considerable, and it is probable that no nitrogenized animal or vegetable matters can be submitted to distillation without their appearing in the distillate. The subject has been very fully investigated during the last few years. The first person who took up the subject was, it is believed, Unverdorben, who ascertained the presence in Dippel's oil, or as it is commonly called, bone-oil, of a very peculiar class of substances of decidedly alkaline properties. He merely described their reactions. Runge afterwards followed in the same track, and found that coal-naphtha also contained organic

* FRAPOLLI and CHIOZZA.—'Chem. Gaz.,' Oct. 15, 1855; and Liebig's 'Annalen,' xcv. p. 252.

bases and acids, but he also depended entirely on reactions. Hofmann made an examination of the bases in coal-naphtha, and separated aniline and leukol or chinoline. Anderson subsequently found picoline in coal-naphtha; and still later, he discovered in bone-oil the whole series of which picoline is a member, as well as many of the bases of the alcohol series. I have also been occupied for some years with the subject, and have ascertained several facts, and added a few new bases to the list of those previously known.

909. Several fixed alkaloids found in nature yield oily bases by distillation with alkalies; thus cinchonine yields chinoline, &c. Narcotine yields trimethylamine, and probably other bases*.

910. Nitrogenized non-alkaline bodies also yield bases; indigo for instance affords aniline in a state of purity by careful distillation with hydrate of potash; and it is worthy of remark, that, contrary to what happens generally under similar circumstances, no other base appears to be formed. Recent researches appear to indicate that pure amylamine may be obtained by destructive distillation from horn and also from leucine; my own experiments upon feathers, made some years ago, lead me to believe, however, that the reaction is not so simple.

911. The general mode of extraction of bases from the oils produced by destructive distillation of nitrogenized organic matter, is to agitate the oil with dilute sulphuric acid, and, after allowing the fluids to rest some time, in order to promote the separation of the oil and acid, to siphon off the latter, which contains the bases in solution. The acid solution of the bases is to be boiled in a large open copper vessel for a long time, until no reaction of pyrrol is obtained by exposing to the escaping steam a slip of deal wood moistened with concentrated hydrochloric acid, §§373, 445. This procedure also resinifies many tarry matters, which would otherwise cause much trouble in the after processes. The cake of resin which usually appears on the surface

* The products of the distillation of narcotine with potash require examination.

of the acid is then to be removed, and the whole fluid filtered through coarsely powdered charcoal. The liquid should now have an excess of slaked lime added, and the whole is to be distilled.

912. The distillation requires care, in order that the more volatile products may not be lost. For this purpose, the end of the condenser should fit into an adapter which is connected with a large tubulated receiver. The tubulature of the receiver should have a tube passing from it into some moderately strong hydrochloric acid, in order to condense any exceedingly volatile bases, such as methylamine, &c.

913. The fluid collected in the receiver should be again submitted to distillation on the water-bath, to separate any very volatile bases; the latter may then be saturated with hydrochloric acid, and the solution is to be evaporated to dryness on the water-bath. The dry mass is to be extracted with very strong alcohol, which will dissolve the volatile bases as hydrochlorates, leaving the sal-ammoniac behind. The alcoholic solution is to be again evaporated to dryness, and the treatment with alcohol is to be repeated. The purified hydrochlorates, freed from any trace of alcohol by exposure for some time to 212° F., are then to be dissolved in water, and treated with bichloride of platinum; the precipitate, if any, being analysed, and the mother-liquid being evaporated over sulphuric acid, the succeeding crops are to be examined to see whether more than one base is present.

914. The fluid containing the less volatile bases is now to have potash in excess added, to separate them. When they have risen to the surface, the alkaline fluid may be removed by a siphon. The bases, as thus procured, retain about a third of their bulk of water, which is to be removed by repeated digestion with sticks of fresh potash.

915. The various bases existing in a mixture obtained in the manner indicated from products of destructive distillation, are to be separated from each other by fractional distillation, § 353.

916. *General remarks on organic alkaloids.*—In order to de-

termine the constitution of organic bases, there are several processes which are more especially necessary. These are,—

> Analysis of salts.
> Action of alcohol iodides.
> Formation of bodies analogous to urea.
> Vapour density.

917. The metamorphoses which organic alkaloids may be made to undergo are excessively numerous, and cannot be described here ; they may be studied in the various papers scattered through the chemical journals.

918. *Some processes and reactions connected with neutral bodies.*—The number of existing organic bodies possessing neither acid nor alkaline properties is so immense, and the processes by which they are separated from others so various, that we shall only touch upon a few of the most important, and even then in a very cursory manner. Those which we shall consider are,—
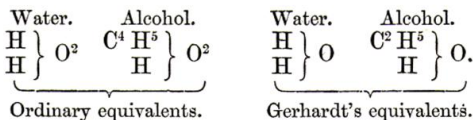
> Alcohols.
> Ethers.
> Aldehydes.
> Hydrocarbons.

919. By the term alcohol is understood a substance derived from the type water by the substitution of one atom of an electro-positive radical for an equivalent of hydrogen. But we must remember, if we use the equivalents ordinarily employed in this country, that the alcoholic group is formed on the type of two equivalents of water ; on the other hand, by considering with Gerhardt the atomic weight of oxygen to be 16 and that of carbon 12, we have the alcohols derived from one equivalent of water. The following represents the formulæ according to these views :—

$$\text{Water.} \qquad \text{Alcohol.} \qquad\qquad \text{Water.} \qquad \text{Alcohol.}$$

$$\left.\begin{array}{c}\text{H}\\\text{H}\end{array}\right\}\text{O}^2 \quad \left.\begin{array}{c}\text{C}^4\,\text{H}^5\\\text{H}\end{array}\right\}\text{O}^2 \qquad\qquad \left.\begin{array}{c}\text{H}\\\text{H}\end{array}\right\}\text{O} \quad \left.\begin{array}{c}\text{C}^2\,\text{H}^5\\\text{H}\end{array}\right\}\text{O.}$$

$$\underbrace{\hspace{5cm}}_{\text{Ordinary equivalents.}} \qquad \underbrace{\hspace{5cm}}_{\text{Gerhardt's equivalents.}}$$

920. Vinic alcohol (common alcohol) is the second member of that great series of bodies of which such an immense number of

derivatives are known, commencing with wood-spirit and ascending to the wax alcohols.

921. Several of these bodies may be obtained by fractional distillation of fusel oil, especially that obtained from the grape-marc.

922. The constitution of an alcohol cannot be satisfactorily demonstrated with the same readiness as that of an acid or a base. Its formula must be substantiated by the study of several of its derivatives. In the first place, the substance when obtained pure must be analysed, and its vapour density be determined. The vapour densities of alcohols do not generally require to be taken at temperatures much above the boiling-point. At 36° above the boiling-point of common alcohol the density comes out 1·65, theory requiring 1·59 ; at somewhat higher temperatures the experimental value is almost exactly the same as that required by theory. An alcohol should have its conjugate sulphuric acid compound examined; also the acid bearing the same relation to it that the acetic does to common alcohol. It is easy to obtain the volatile acid corresponding to an alcohol, by various processes of oxidation ; the following equation represents the nature of the reaction :—

$$C^4 H^6 O^2 + 4O = C^4 H^4 O^4 + 2HO.$$

$$\underbrace{}_{\text{Alcohol.}} \qquad \underbrace{}_{\text{Acetic acid.}}$$
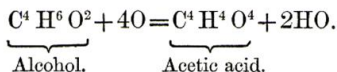
If of the vinic class, it should also have the iodide or bromide of its radical obtained ; also the alkaloid derived from ammonia by the substitution of its radical for an atom of hydrogen in ammonia. The simple ether should also be obtained. It will be essential also to determine (if belonging to known series) whether it obeys Kopp's law of boiling-points. Alcohols possess one property which assimilates them to monobasic acids, that is to say, when treated with potassium or sodium they are decomposed with formation of a compound possessing an equivalent of the metal in the place of an equivalent of hydrogen.

923. The aldehyde corresponding to the alcohol should also be studied ; it may be procured by a process of oxidation less energetic than that required to form the acid of the series. The annexed equation illustrates the conversion of common alcohol into aldehyde :—

$$C^4 H^6 O^2 + 2O = C^4 H^4 O^2 + 2HO.$$

Alcohol.   Aldehyde.
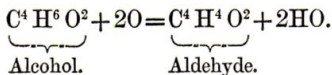
924. Alcohols vary greatly in their physical conditions, even when belonging to the same homologous series; for while methylic alcohol, $C^2 H^4 O^2$, is a colourless mobile fluid, boiling at $66°\cdot5$ Cent., the melissic alcohol, $C^{60} H^{62} O^2$, is a crystalline solid, having a fusing-point as high as $85°$ Cent.
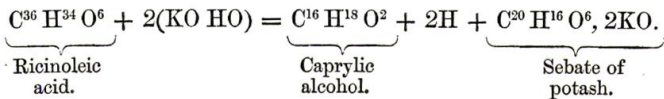
When heated with caustic potash, the alcohols of the vinic class are decomposed, with formation of an acid corresponding to it, hydrogen being disengaged, thus:—

$$C^2 H^4 O^2 + KO, HO = C^2 HO^3 KO + 4H.$$

Wood-spirit.   Formiate of potash.
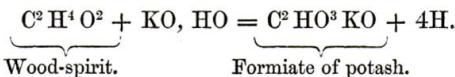
Even when so high up in the series as the melissic alcohol, the reaction is precisely similar, for

$$C^{60} H^{62} O^2 + KO, HO = C^{60} H^{59} O^3, KO + 4H.$$

Melissic alcohol.   Melissate of potash.
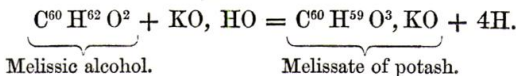
925. Alcohols are obtainable from several sources, and are produced by more than one interesting reaction. The greater number are products of fermentation, such as the ethylic, propylic, amylic, &c. The methylic alcohol, the first of this series, is obtained by the distillation of wood, while the caprylic is a product of metamorphosis of ricinoleic acid at a high temperature, under the influence of hydrate of potash.

$$C^{36} H^{34} O^6 + 2(KO\ HO) = C^{16} H^{18} O^2 + 2H + C^{20} H^{16} O^6, 2KO.$$

Ricinoleic acid.   Caprylic alcohol.   Sebate of potash.

926. One of the most interesting reactions connected with alcoholic groups, is that by which we are enabled to pass from certain kinds of aldehydes to alcohols of the same class. This happens when bitter-almond oil, otherwise known as benzoic aldehyde, is treated with alcoholic potash.

$$2\,C^{14}H^6O^2 + KO, HO = C^{14}H^8O^2 + C^{14}H^5O^3, KO.$$

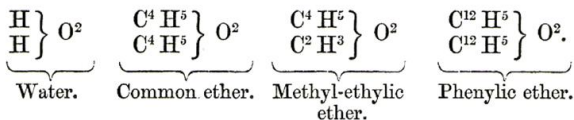| Bitter-almond oil. | Benzoic alcohol. | Benzoate of potash. |
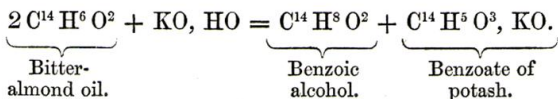
927. It has already been mentioned that the phenylic and cresylic alcohols are products of the destructive distillation of wood and coal (§§ 373, 853, 868). It must not be forgotten that the benzoic is isomeric, not identical, with the cresylic alcohol, the latter being homologous with carbolic acid.
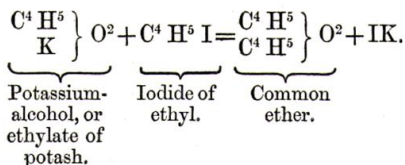
928. The above sketch of the more prominent features in the reactions connected with alcoholic groups, is sufficient to show the extreme interest belonging to the subject; it cannot, however, be pursued further here, as we must now turn our attention to one of the most important derivatives of the alcohols.

929. *Ethers.*—These bodies are either simple or compound. The simple ethers come first in the order of study.
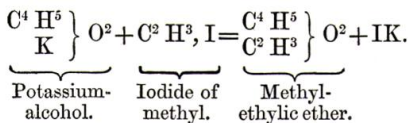
We have seen (§ 919) that an alcohol may be defined as two equivalents of water in which *one* equivalent of hydrogen is replaced by an electro-positive radical. In simple ethers, on the other hand, we have two equivalents of water in which both equivalents of hydrogen are replaced by an electro-positive radical. But numerous ethers exist which contain two different radicals, *i. e.* derived from two equivalents of water, in which both atoms of hydrogen are replaced, but by two different radicals. Nevertheless, if both the replacing radicals belong to alcoholic groups, the ether is still said to be simple. The following are examples of simple ethers placed by the side of their type for the sake of comparison:—

$$\left.\begin{array}{c}H\\H\end{array}\right\}O^2 \qquad \left.\begin{array}{c}C^4H^5\\C^4H^5\end{array}\right\}O^2 \qquad \left.\begin{array}{c}C^4H^5\\C^2H^3\end{array}\right\}O^2 \qquad \left.\begin{array}{c}C^{12}H^5\\C^{12}H^5\end{array}\right\}O^2.$$

| Water. | Common ether. | Methyl-ethylic ether. | Phenylic ether. |

930. The simple ethers may generally be obtained by distillation of the corresponding alcohols with sulphuric acid, or by the action of the alcoholic iodides on the sodium or potassium alcohols. The annexed equation represents the latter reaction:—
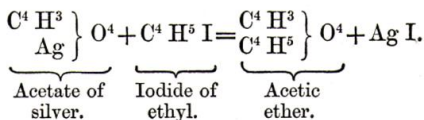
$$\left.\begin{array}{c} C^4\,H^5 \\ K \end{array}\right\}O^2 + C^4\,H^5\,I = \left.\begin{array}{c} C^4\,H^5 \\ C^4\,H^5 \end{array}\right\}O^2 + IK.$$

Potassium-   Iodide of   Common
alcohol, or   ethyl.   ether.
ethylate of
potash.

If it be desired to produce an ether containing two different
alcoholic radicals, we proceed in the manner indicated by the an-
nexed equation:—

$$\left.\begin{array}{c} C^4\,H^5 \\ K \end{array}\right\}O^2 + C^2\,H^3, I = \left.\begin{array}{c} C^4\,H^5 \\ C^2\,H^3 \end{array}\right\}O^2 + IK.$$

Potassium-   Iodide of   Methyl-
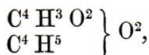alcohol.   methyl.   ethylic ether.

It is plain that by varying the nature of the alcohol containing
the potassium, or the alcoholic iodide, we may obtain a great
variety of these mixed ethers.

931. *Compound ethers.*—These differ from the mixed ethers
mentioned above, inasmuch as the two atoms of hydrogen in the
water are replaced, the one by the radical of an acid, and the
other by the radical of an alcohol. They are formed by a very
considerable number of reactions, among which may be mentioned,
the distillation with strong sulphuric acid of a salt of the acid
which it is desired shall enter into the ether with the alcohol,
the radical of which shall also enter into the ether. Another
method very often employed is to pass a current of hydrochloric
acid gas into a mixture of the organic acid and alcohol. The
reaction of the alcohol iodides on silver salts may be made use
of to prepare compound ethers, thus:—

$$\left.\begin{array}{c} C^4\,H^3 \\ Ag \end{array}\right\}O^4 + C^4\,H^5\,I = \left.\begin{array}{c} C^4\,H^3 \\ C^4\,H^5 \end{array}\right\}O^4 + Ag\,I.$$

Acetate of   Iodide of   Acetic
silver.   ethyl.   ether.

The formula of acetic ether is perhaps more correctly written—

$$\left.\begin{array}{c} C^4\,H^3\,O^2 \\ C^4\,H^5 \end{array}\right\}O^2,$$

because it is generally considered that the oxidized radical $C^4 H^3 O^2$, known as acetyl or othyl, exists in it.

932. The subject of the compound ethers is one of considerable interest in a theoretical point of view, but it cannot be entered upon here, and for further information the student is referred to works specially devoted to organic chemistry.

933. *Aldehydes.*—The aldehydes are rapidly becoming better known, and are scarcely to be surpassed in the interesting nature of their reactions.
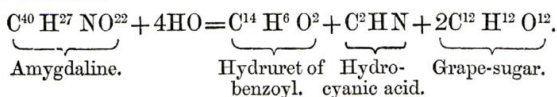
934. The aldehydes, in the present state of our knowledge, may be regarded from several points of view, each of which has certain advantages; the most convenient is perhaps to consider them as derived from the hydrogen type. In this way we look upon ordinary aldehyde as

$$H$$
$$H,$$

in which one of the atoms of hydrogen is replaced by the radical of acetic acid. The duplex character of the free radicals will be made more apparent in treating of the hydrocarbons. The formula of aldehyde is therefore $C^4 H^3 O^2$, H, or hydruret of acetyle.

935. Aldehydes are derived from numerous sources. We have already considered their production by the action of oxidizing agents on the alcohols in § 923.

936. One of the most interesting reactions resulting in the formation of an aldehyde, is that by which the benzoic aldehyde, hydruret of benzoyl or oil of bitter almonds, is produced from amygdaline. The substance which causes the metamorphosis of the last-named body does not, strange to say, enter into the resulting compound. It merely acts as a ferment; it is known as emulsine or synaptase, and exists in the bitter almond together with the amygdaline. The following equation explains the nature of the reaction:—

$$C^{40} H^{27} NO^{22} + 4HO = C^{14} H^6 O^2 + C^2 HN + 2C^{12} H^{12} O^{12}.$$

| Amygdaline. | Hydruret of benzoyl. | Hydro-cyanic acid. | Grape-sugar. |

937. The above equation is sometimes written so as to include

the production of formic acid, but its formation is generally considered to be due to a secondary decomposition of the hydrocyanic acid.

938. The aldehydes are also obtained by destructive distillation; œnanthylic aldehyde is by this means obtained from castor oil. They are also found in nature in plants, such as cinnamic aldehyde in oil of cassia, cuminic aldehyde in oil of cumin, &c. The oil of rue, according to Gerhardt, consists of capric aldehyde mixed with a small quantity of an unknown hydrocarbon*. The formation of an aldehyde by fermentation has been mentioned above.
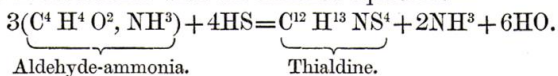
939. The aldehydes are often capable of assuming isomeric conditions. The lime-salts of several acids, moreover, yield isomers of the aldehydes by destructive distillation. One of the most important peculiarities of the aldehydes is their remarkable tendency to combine with the alkaline bisulphites, especially those of soda and ammonia. These compounds are not limited to the aldehydes of the alcohols of the vinic type, for cinnamic aldehyde and its congeners equally possess the property of combining with the alkaline bisulphites.

940. The ammoniacal compounds of this class yield bases by distillation with lime. In this manner triphenylamine is said to be produced from the bisulphite of the ammoniacal cinnamic aldehyde†.

941. The aldehydes combine with ammonia to form crystalline salts; ordinary aldehyde for instance yields the following compound,—

$$C^4 H^4 O^2, NH^3.$$
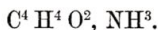
The above, when acted on by sulphuretted hydrogen, gives thialdine in accordance with the annexed equation:—

$$3(\underbrace{C^4 H^4 O^2, NH^3}_{\text{Aldehyde-ammonia.}}) + 4HS = \underbrace{C^{12} H^{13} NS^4}_{\text{Thialdine.}} + 2NH^3 + 6HO.$$

Thialdine is said to yield chinoline when distilled with hydrate of lime; this is, however, most improbable in a theoretic point of view, and some experiments made by myself, although on too

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* Some researches of my own now in progress indicate the composition of oil of rue to be more complex than has been hitherto supposed.

† Gössmann.—Liebig's ‘Annalen,’ c. p. 57.

small a scale to work out the true nature of the decomposition, decidedly indicate the entire absence of chinoline from the products of the reaction.

942. In separating aldehydes from complex mixtures, we must endeavour to obtain a compound with an alkaline bisulphite, and after pressing the latter between folds of bibulous paper until nothing more is extracted, or recrystallizing it from alcohol, distil with water, when the aldehyde will be obtained in a state that merely requires washing and drying previous to analysis.

943. The tendency of the aldehydes to acidify by contact of the air must not be lost sight of in determining their vapour density (§ 479).

944. *Hydrocarbons.*—The number of bodies known to chemists consisting solely of carbon and hydrogen is so great, that a volume would be required to give anything like a complete account of the processes and reactions employed in investigating their constitution.

The methods by which hydrocarbons are obtained are very numerous, but prominent among them stands destructive distillation. Out of the numerous families of them we shall select three, the properties of which are so varied, that a short description of their principal habitudes will illustrate, as fully as falls within the province of this work, the methods adopted for the examination of hydrocarbons; they are the benzole series, the radicals of the alcohols, and the homologues of olefiant gas. We shall also glance slightly at some of the derivatives of naphthaline.

945. *The benzole series.*—This very important group has been as thoroughly investigated as perhaps any other bodies known to chemists, but such is their tendency to form compounds, which in their turn are liable to numerous metamorphoses, that much yet remains to complete their history.

946. The most important member of them is of course the first term benzole, and as the other homologues yield almost exactly analogous derivatives, we shall confine ourselves to it in our formulæ, it being understood by the student that the same reactions in almost all cases apply to the other homologues.

2 A 2

It is to be observed that benzole is regarded with the other hydrocarbons as formed on the hydrogen type, being HH, in which one of the equivalents of H is replaced by phenyl; or, in other words, it is the hydruret of that radical.

947. The hydrocarbons of this class are obtainable in the largest quantity, and with the greatest ease and economy, from coal-naphtha, of which they form the chief bulk. They are separated by fractional distillation (§ 353), the first member also being capable of further purification by crystallization (§ 419). The volatility of benzole enables us to obtain it in a tolerably pure state (without the necessity for a great number of fractionations), by means of the double-headed stills represented in § 380. After two distillations performed in that apparatus, the purification of the benzole may be completed by freezing and draining away the uncrystallizable hydrocarbons. Although benzole and its homologues combine with sulphuric acid, they do so less readily than the $C^n H^n$ class which coexist with them in coal-naphtha; much advantage is therefore found by treating toluol and its less volatile congeners with sulphuric acid two or three times before proceeding to form new compounds.

948. It has been said that coal-naphtha is the most economical source of benzole; it can, however, be obtained in several ways, and it appears to be almost universally formed during the destructive distillation of highly complex organic matters. Benzole is produced from benzoic acid by the removal of two, and from phthalic acid by the removal of four equivalents of carbonic acid. To obtain it from these sources, the acid to be decomposed is mixed with an excess of lime or baryta and distilled.
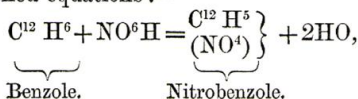
949. The derivatives of benzole are highly interesting, but their history is as yet by no means complete. Poured into excess of chlorine, a crystalline compound is obtained, in which six equivalents of the gas have combined with the hydrocarbon without removal of hydrogen. This new substance, by treatment with alcoholic potash, loses three equivalents of hydrochloric acid with the production of trichlorobenzole. The reaction may be expressed thus :—

$$C^{12}H^6Cl^6+3KO = \left.\begin{array}{c}C^{12}H^3\\Cl^3\end{array}\right\} +3KCl+3HO.$$
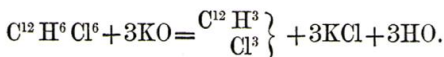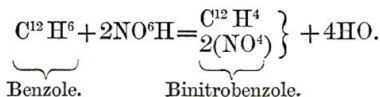
950. The last product is in the form of an oil, and distils without alteration. It would be very interesting to treat it with sodium, with a view to the production of new hydrocarbons.

951. Benzole and its homologues combine directly with sulphuric acid when treated with the latter in a fuming state, forming well defined conjugate acids which yield crystalline salts with bases.

952. The derivatives of benzole with nitric acid are also most interesting. Treated with precaution with fuming nitric acid, it dissolves, and on pouring the solution into water an oil precipitates; this is nitrobenzole, or benzole in which an equivalent of hydrogen is replaced by hyponitric acid. By mixing the nitric with sulphuric acid previous to the addition of the benzole and employing heat, the reaction proceeds further, two equivalents of hydrogen being removed and replaced by hyponitric acid, in accordance with the annexed equations :—

$$\underbrace{C^{12}H^6}_{\text{Benzole.}} + NO^6H = \underbrace{\left.\begin{array}{c}C^{12}H^5\\(NO^4)\end{array}\right\}}_{\text{Nitrobenzole.}} +2HO,$$

and

$$\underbrace{C^{12}H^6}_{\text{Benzole.}} + 2NO^6H = \underbrace{\left.\begin{array}{c}C^{12}H^4\\2(NO^4)\end{array}\right\}}_{\text{Binitrobenzole.}} +4HO.$$

953. The two compounds last described yield new derivatives when treated with reducing agents. The equation expressing the conversion of nitrobenzole into the highly interesting alkaloid aniline, has been given in §§ 469, 906. Binitrobenzole in its turn yields nitraniline, when treated with reducing agents.

Nitrobenzole yields another interesting body, azobenzide ($C^{24}H^{10}N^2$), when distilled with alcoholic potash; azobenzide, by the action of reducing agents, gives the singular alkaloid benzidine ($C^{24}H^{12}N^2$).

954. We are unable to devote more space to the derivatives of benzole; it is true they can hardly be surpassed for interest, whether we regard their beauty or the peculiar reactions by which

they are formed ; but we must proceed to the study of hydrocarbons belonging to a different series of organic groups.

955. *The alcohol radicals.*—This very important group has hitherto been obtained by three methods, namely,—

Decomposition of the hydriodic ethers by certain metals.

Electrolysis of the fatty acids.

Destructive distillation of certain kinds of bituminous coal.

956. They are all formed on the hydrogen type, and are regarded by most chemists as H H, in which both equivalents of hydrogen are replaced by alcoholic (electro-positive) radicals.

957. The radicals are all very light, mobile, highly refractive, fragrant hydrocarbons, acted on with some difficulty by acids.

958. To determine the nature of an organic radical, it is necessary to make a most accurate analysis of it, to determine its boiling-point, density in the states of liquid and vapour, and also to try the action of concentrated nitric and sulphuric acids on it.

959. It is more than probable that the organic radicals have, in addition to the marsh-gas series, numerous isomers; but in the present state of our knowledge, it would be difficult to prove by strictly chemical evidence, that a body possessing the same composition, boiling-point, density in the fluid and gaseous states, and acted on with difficulty by acids, was not a radical. We want a general method, like that used by chemists to determine the nature of organic bases, by which we can determine the true constitution of a hydrocarbon. It is certain that this is merely a question of time.

960. *Hydrocarbons homologous with olefiant gas.*—These bodies, of course formed on the hydrogen type (HH), are regarded as the hydrurets of the aldehyde radicals. They are pre-eminently distinguished by their tendency to combine with iodine, bromine, and chlorine. The iodine and bromine compounds of hydrocarbons of this class have become of considerable interest lately, in consequence of the highly important products which have been obtained from them.

961. When hydrocarbons of the formula $C^n H^n$ are treated with chlorine or bromine, it is usual for two equivalents of the latter

to unite to the former, propylene becoming therefore $C^6 H^6 Cl^2$. By treatment with alcoholic potash, HCl is removed, giving rise to the new derivative, $C^6 H^5 Cl$. To remove the last equivalent of the halogen, it is necessary to employ potassium or sodium. The formula represented above corresponds to 4 volumes of vapour; and if the chlorine be removed, we have the same phenomenon as with the hydriodic ethers, namely, the carbon and hydrogen becomes doubled for the same vapour-volume. For example, iodide of allyle, when treated with sodium, acts as represented in the annexed equation:—

$$\underbrace{2C^6 H^5 I}_{\text{Iodide of allyl.}} + 2Na = \underbrace{C^{12} H^{10}}_{\text{Allyl.}} + 2NaI.$$
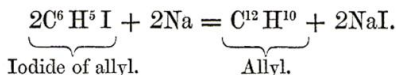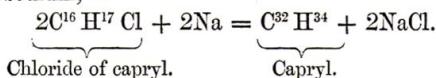
962. The boiling-point of derived hydrocarbons obtained by a reaction of this kind is always greatly above that of the original hydrocarbon from which the halogen compound was procured. Where, however, the number of equivalents of carbon is high, there is a tendency to split up into simpler combinations*, and this tendency is the greater the higher the temperature at which

* As an illustration of this, I may mention that I have found when the naphtha from the Torbane-hill mineral, boiling between 180° and 190° F., is treated with bromine in presence of water, the latter is decolorized in the same manner as happens with turpentine (§ 436). If, to ensure a definite product, a slight excess of bromine be added, which excess is afterwards removed by agitation with mercury, a very dense colourless aromatic oil is obtained. This oil, on keeping for some time, separates into two layers. The upper layer is decomposed by alcoholic potash with great development of heat, bromide of potassium being deposited in large quantity. The whole, on being distilled to dryness, gave a distillate from which, on treatment with water, a heavy oil separated; which, when cohobated repeatedly over sodium, yielded a hydrocarbon, evidently a $C^n H^n$, for it contained,—
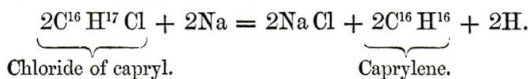
	Experiment.		Calcul., $C^n H^n$.
Carbon	85·4	85·7	85·7
Hydrogen	14·3	14·2	14·3
	99·7	99·9	100·0

Its vapour-density was 3·01, which points to the formula $C^{12} H^{12}$, requiring 2·91. The boiling-point was 165° F. During the cohobation the metal acquired a brilliant blue colour.

the sodium acts on the compound. As an illustration of this, let us see what happens when chloride of capryl is treated in the cold with sodium,—

$$2C^{16}H^{17}Cl + 2Na = C^{32}H^{34} + 2NaCl.$$

$\underbrace{\phantom{2C^{16}H^{17}Cl}}$ Chloride of capryl. $\qquad$ $\underbrace{\phantom{C^{32}H^{34}}}$ Capryl.

But if heat is employed, we have

$$2C^{16}H^{17}Cl + 2Na = 2NaCl + 2C^{16}H^{16} + 2H.$$

$\underbrace{\phantom{2C^{16}H^{17}Cl}}$ Chloride of capryl. $\qquad$ $\underbrace{\phantom{2C^{16}H^{16}}}$ Caprylene.

963. *Naphthaline.*—Few substances have been so much studied as this. Laurent, whose researches upon naphthaline alone fill a large volume, has discovered an immense number of bodies, chiefly derived from it, by substitution of chlorine, bromine, or hyponitric acid for hydrogen. By the action of chlorine, a number of most curious bodies are procured, several of which are susceptible of isomeric modifications.

964. The so-called bichloride of naphthaline, $C^{20}H^{16}Cl^4$, is a most beautiful substance; crystallized from benzole, it forms rhombs indistinguishable by the eye from Iceland spar. I find, moreover, that it distinctly possesses the property of double refraction (§ 419).

965. Naphthaline yields numerous acid and basic derivatives; the acids produced from naphthaline are especially interesting, from the fact that oxynaphthalic acid is, perhaps, identical with alizarine, one of the colouring matters of madder.

966. In spite of the immense mass of work which has been done on naphthaline, there are many interesting points in its history which remain to be examined; not the least of these is the as yet untouched field of the action of sodium upon its numerous solid and fluid chlorinated derivatives.