

## CHAP. I.

OF THE CHEMICAL ANALYSIS OF THE ARTICLES OF THE  
MATERIA MEDICA.

THE ultimate object of chemical investigations, is to discover the composition of bodies; and the result of these investigations is the reducing them into two classes, those which are Simple, and those which are Compound. The former are such as consist of parts perfectly alike; the most minute particles into which a simple body can be resolved, retaining all its essential properties, and being similar to each other. The latter can, on the contrary, be resolved into substances different in their qualities from each other, and from the compound which they form.

It is from the union of simple substances that compounds are produced. When two simple bodies are placed under those circumstances which favour the exertion of their mutual attraction, they unite and form a compound, having peculiar properties. These compounds are farther capable of combining with other simple bodies, or with each other, which gives rise to a series of bodies still more extensive; and these again are capable of new combinations, or of such intimate mixtures with each other, as to form many peculiar substances. There are thus produced, from a few simple substances, all the products of nature, and all those which are the results of the operations of art.

It is the province of Chemistry to trace these combinations; to determine whether bodies are simple or compound; and, if compound, to ascertain the number of their constituent principles, the proportions, and the modes in which they are combined.

The general process by which these objects are attained, is termed, in the language of Chemistry, Analysis. It is merely the separation of a compound body into its constituent parts, and is effected either by the agency of heat, or by the exertion of a superior attraction.

The analysis from the application of heat, differs according to the composition of the body analysed. If a compound, consisting of two simple substances, be exposed to heat, it in many cases happens, that the mutual attraction by which its principles were united ceases, and a decomposition or separation of these principles takes place. This is an example of pure analysis; no change being produced, but merely the separation of the component parts of the compound, so that each is obtained in its original state.

An analysis more complicated is that where several substances are combined together, in such a manner that their attractions are reciprocally balanced, and one compound is formed. When a compound of this kind is exposed to a high temperature, this balance is frequently subverted, and it suffers decomposition. But its constituent principles, instead of passing off pure, enter into new combinations with each other, and form other compounds, each of which may be collected, and in its turn analysed. It is in this manner that vegetable and animal substances are acted on by heat: the products afforded by their analysis are not such as pre-existed in them, but are compounds formed during the decomposition, by new combinations of their ultimate constituent principles. This is what has been named False or Complicated Analysis.

Chemical Analysis is also effected by the exertion of a superior attraction. If a compound be placed successively with different substances in situations favourable to the operation of chemical action, one or other of them may exert a superior attraction to either of its component parts; a decomposition will be produced, and from the products the constituent principles of the compound, as well as their proportions, may be determined.

As compound substances can combine together so as to form a new compound, it is obvious, that this compound may be resolved either into the immediate principles from the union of which it has been formed, or into those of which these consist. It is necessary, therefore, that these should be distinguished. The former are accordingly named the Proximate Principles of a compound; the latter the Ultimate Principles. The proximate principles are compounds; the ultimate principles are the elements of these compounds; and the results of analysis are extremely different, according as one or other of these is obtained.

When by analysis the constituent principles of a body have been obtained, they may often be combined again, so as to reproduce the substance analysed. This operation is named Chemical Synthesis, and, when it can be effected, is the surest proof of the accuracy of the analysis. It is seldom that it can be applied to those compounds which suffer a complicated analysis; and hence the composition of vegetable or animal substances can scarcely ever be confirmed by a synthetic experiment.

In analysing the various products of nature, we arrive ultimately at substances which we are unable to decompose, and which are therefore regarded as simple. The absolute simplicity of these is not indeed established; for our inability to decompose them may not arise from this, but from the imperfections of our modes of analysis; and it is even pro-

bable, that all the substances which are yet known to us may be compounds, and that a more refined chemistry may discover their composition. Until this be accomplished, however, they are regarded as simple, and they are so with regard at least to our knowledge of them. As the ultimate principles, therefore, of all analysis, they are first to be considered in proceeding to the general analysis of the articles of the *Materia Medica*.

Of these bodies, OXYGEN is the most important. There is no simple substance which exerts an attraction to so many others, or which gives rise to such important compounds. With a few exceptions, indeed, all the productions of nature are either capable of combining, or are already combined with this principle, and the developement of its agencies constitutes the most extensive and important part of chemical science.

Oxygen, when uncombined, always exists in the gaseous state: and its descriptive characters are therefore taken from it as it exists in the aërial form. Like other gases, it is invisible and elastic; its specific gravity is rather greater than that of atmospheric air; it is absorbed by water, but in a very small proportion.

The distinguishing properties of oxygen gas are those of supporting respiration and combustion. An animal lives longer in this air than it does in any other; and combustion in it is more vivid, and continues longer. It is the only air, indeed, which, strictly speaking, can support either of these processes; other aëriform fluids doing so only from the oxygen they contain.

Its capacity of supporting combustion is more particularly to be assumed as its characteristic chemical property; combustion being nothing but the combination of oxygen with combustible bodies, accompanied with the emission of heat and light. It also frequently, however, enters into combina-

tion without the phenomena of combustion being apparent, more especially when the absorption of it takes place slowly, or when it is transferred from a compound in which it exists to another substance. The combination of a body with oxygen is termed Oxygenation, or Oxidation. The products of this combination have either certain common properties, belonging to a class of chemical agents long distinguished by the appellation of Acids; or they are destitute of these properties, and they are then denominated Oxides.

Oxygen forms one-fourth part of atmospheric air; and it is principally on its agency that the many chemical changes produced in bodies by that air depends. Combined with another elastic fluid, hydrogen, in the proportion of 85 parts to 15, it forms Water, the substance which has the most extensive operation in promoting chemical action by the fluidity it communicates, and which more directly produces many important chemical changes, by affording oxygen to bodies. Oxygen exists too as a constituent principle of acids, and communicates to them their energy of action. It is also an ingredient in the composition of the alkalis and earths, and it is therefore the principle of alkalinity as well as of acidity. With all the metals it combines, communicating to them a greater susceptibility of chemical action, and greater activity in their relation to the living system; and it exists as a constituent part of nearly all the vegetable and animal products. Hence no principle is more extensively diffused, and none has a more marked influence in the combinations into which it enters.

The elastic fluid which, with oxygen gas, composes atmospheric air, is named AZOTE or NITROGEN. Its chemical agency is less powerful, nor does it possess any very remarkable property by which it can be characterized; hence it is distinguished rather by negative qualities. It is lighter than

oxygen gas, is incapable of supporting combustion or respiration, is scarcely sensibly absorbed by water, and is not combustibile in the strict sense of the term; for although it combines with oxygen, the combination is not rapid; it does not, after it has commenced, proceed of itself, and it is not attended with any sensible emission of heat or light.

Nitrogen gas forms nearly four-fifths of atmospheric air, the remaining fifth being oxygen gas. In more intimate combination with oxygen, and in that proportion in which they are mutually saturated, it forms a very powerful acid, the nitric acid; and in lower degrees of oxygenation it forms compound gases which have no acid powers. With hydrogen it forms ammonia, one of the alkalis; it exists in some vegetable substances, and is a constituent principle of nearly all the varieties of animal matter. This substance must still be regarded as simple, for although, from some researches connected with the action of potassium on ammonia, conjectures had been formed with regard to the composition of nitrogen, these were always doubtful, and it now appears were founded on inaccurate results.

ATMOSPHERIC AIR, of which oxygen and nitrogen are the essential constituent parts, has merely the aggregate properties of these two gases, their combination being so slight that no new powers are acquired from it; and, as the oxygen is the more energetic ingredient, the chemical agencies of this air depend chiefly on the operation of this principle. It yields oxygen to a number of substances, with more or less rapidity, and thus changes their chemical constitution. It sometimes acts too by communicating humidity; and in a few cases, by affording an elastic fluid, carbonic acid gas, which is diffused through it in small proportion. Its nitrogen exerts no active power, but apparently serves merely to dilute, and thus to moderate the action of the oxygen gas.

HYDROGEN is another elastic fluid, which in the system of modern chemistry has been regarded as elementary. In its ærial form, in which form only it can be obtained uncombined, it is the lightest of all the elastic fluids, and the lightest substance therefore whose gravity we can ascertain. It is distinguished farther by its high inflammability; it burns when an ignited body is approached to it in contact with atmospheric air, and explodes if previously mixed with the air. The product of its combustion is water, which is therefore considered as a compound of it with oxygen. Combined with nitrogen, it forms ammonia: with the primary inflammables, sulphur, carbon, and phosphorus, it forms compound gases: it dissolves even some of the metals, and it is an abundant ingredient in vegetable and animal substances.

WATER, of which hydrogen is the base, is a substance extremely peculiar in its chemical relations. Its power of combination is extensive, there being few substances on which it does not act, or with which it does not combine; yet in the greater number of these combinations no energetic action is displayed; it in general scarcely produces any alteration of properties; and hence its most important operation is the communicating that state of fluidity to bodies which is necessary to their mutual chemical actions. It is more peculiarly the solvent of all saline substances, and of the greater number of the earths; and it dissolves many of the vegetable and animal products. When it communicates oxygen, it produces more important changes. Several of the metals are slowly oxidated by it; and when they are dissolved by acids, it often acts by affording to them that oxygen which is necessary to the solution. Vegetable and animal substances often suffer chemical changes from the oxygen which water imparts, as well as from the fluidity it communicates favouring the re-action of their constituent parts; and in their decom-

position at elevated temperatures, the elements of the water they contain enter into the composition of the products which these decompositions afford.

There are three substances supposed to be simple, distinguished by the property of inflammability, and hence named Simple Inflammables, which exist as constituent principles of a number of natural products. These are carbon, sulphur, and phosphorus. Some researches appear to favour the conclusion, that they contain portions of hydrogen, and perhaps of oxygen, whence it is doubtful if their pure inflammable base have been obtained. They are destitute of the metallic splendour, opacity, and specific gravity, and are connected chiefly by the common property of inflammability. When united with oxygen, they form acids.

**CARBON.** The ultimate base to which the name of carbon ought to be appropriated is perhaps still unknown to us; but there are several substances of which it constitutes the greater part, and in which it appears to exist in a state nearly pure. Wood charcoal in burning is almost entirely consumed, forming with the oxygen with which it combines a peculiar elastic fluid, carbonic acid, and leaving only a small residuum of earthy, saline, and metallic substances. As a discriminating appellation of the pure inflammable matter which thus combines with oxygen, the term Carbon was introduced, and it denoted therefore simply this matter free from the other substances mixed with it in charcoal, and apparently not essential to its constitution. It was afterwards discovered, that the Diamond, which was known to be a combustible body, affords in burning precisely the same product as charcoal, and hence therefore consists of the same inflammable matter. Different opinions were advanced with regard to the difference between charcoal and diamond; as they combine in burning with the same proportion of oxygen,



and afford precisely the same product, the difference appears to be merely in aggregation; charcoal in its common state, however, always contains a portion of hydrogen, and it is doubtful if it can be entirely freed from it. In the substance named Plumbago, the carbonaceous base is united with a small quantity of iron. It is to the inflammable matter common to all these substances, composing nearly the whole of their weight, and forming with oxygen a peculiar acid, that the term carbon is appropriated.

Carbon, besides existing as an element in the composition of many mineral substances, is an abundant ingredient in the products of the vegetable and animal systems. Not being volatile, it forms the principal part of the residual mass when these are decomposed by heat; and it is by this decomposition of vegetable matter, especially of the wood of plants, that it is obtained in the form of charcoal. With oxygen, combined in different proportions, it forms two elastic fluids, carbonic oxide, and carbonic acid. With hydrogen and oxygen, in different proportions, it forms various inflammable gases. Alkohol, or pure ardent spirit, which is the product of the fermentation of saccharine matter, is a similar compound; and ether, which is formed from alkohol by the action of acids upon it, is of the same composition with a larger proportion of hydrogen. Lastly, the ternary combination of carbon, hydrogen, and oxygen, in various proportions and modes of combination, appears to constitute the principal varieties of vegetable matter.

SULPEUR is found in nature principally as a constituent part of mineral bodies. It exists combined with many of the metals; and united with oxygen, forming sulphuric acid, it enters into the composition of a number of saline and earthy compounds. It is highly inflammable; in burning it combines with oxygen, principally in that proportion which forms

an elastic fluid, pungent and suffocating, sulphurous acid. With a larger proportion of oxygen, it forms a dense inodorous liquid acid, sulphuric acid. With hydrogen, it forms an inflammable gas, sulphuretted hydrogen, which exists in nature impregnating water in the sulphurous mineral waters; and this compound, either alone, or with an additional proportion of hydrogen, forming what is named super-sulphuretted hydrogen, enters into combination with alkalis, earths, and metallic oxides, forming several important pharmaceutic preparations. Lastly, sulphur exists as a constituent part of animal substances: hence sulphuretted hydrogen is generally evolved in the decomposition of these by heat or putrefaction: it has also been detected in the composition of a few vegetables. In its common state, sulphur appears to contain a portion of hydrogen.

PHOSPHORUS exists chiefly as an ingredient of animal matter. Combined with oxygen, in the state of an acid, it also enters into the composition of several of the products of the mineral kingdom. It is of a soft consistence like wax, semi-transparent, and of a white or yellowish colour; it is so highly inflammable that it burns spontaneously when exposed to the air. It combines with two proportions of oxygen, forming two acids, the phosphorous and the phosphoric. With hydrogen it forms a gas highly inflammable; and it unites with sulphur and with the metals. It had been supposed to contain minute quantities of hydrogen and oxygen, but there is no conclusive proof that this is the case.

The class of METALS is an extensive one, the substances to which this name is appropriated being numerous, and the number being still farther augmented, if the bases of the alkalis and earths are to be admitted into the class. The physical properties, characteristic of the metals, are opacity, great lustre, density, ductility, and malleability. These are

possessed in different degrees by the different metals, and if the bases of the alkalis and earths are to be admitted as metals, the property of density cannot be considered as distinctive, as some of these are even lighter than water. With regard to chemical properties, the metals are fusible, in general not volatile except at very intense heats; they are capable of combining with oxygen, with hydrogen, sulphur, carbon, and phosphorus, with each other, and when oxidated they unite with acids, alkalis, and earths.

Of these combinations, that with oxygen is the most important; and in relation to the object of this outline, the only one requiring any farther observations. This combination is effected in various modes. When heated in contact with the air, they attract its oxygen: if the temperature be very highly elevated, as in that produced in the galvanic circuit, they display during this oxidation the phenomena of combustion; even if the temperature is less elevated, several of them burn more or less rapidly; but the greater number are oxidated more slowly, and without any sensible extrication of light. Several metals are slowly oxidated by water, or by the joint action of air and water at natural temperatures. And all of them can be oxidated by acids, the acid either directly imparting oxygen to the metal, or enabling it to attract this principle from the water which is present.

The compounds of metals with oxygen belong in general to the order of oxides. They are destitute of the physical properties of the metals, and have an earthy-like appearance. Two or three metals acquire, in their highest state of oxygenation, acid powers.

In combining with oxygen, different metals unite with very different quantities of it. Each of them combines too with different proportions of oxygen, giving rise to the production from the same metal of oxides having different properties;

and these different oxides form the bases of compounds which are often also extremely dissimilar,—a circumstance of much importance, as is to be afterwards pointed out, with regard to the pharmaceutical processes on the metals.

When the metals are combined with oxygen, they become capable of combining with the acids, and they then acquire greater activity and power of chemical action. This previous oxidation of a metal is always necessary to its combination with an acid, and hence, when acids act on metals, they first impart to them oxygen, or enable them to attract oxygen from the water, or sometimes from the air, and then combine with the oxide that is formed. As the same metal is capable of existing in different states of oxidation, so by combining in these states with the same acid, it forms very different compounds; and these compounds are farther diversified by the different proportions of acid combined in them.

Metals are rendered active on the living system, principally by being thus combined with oxygen, or farther combined with acids. In their metallic state, they seldom produce any sensible effect; and any effect they do produce appears to arise from their being chemically acted on by the gastric fluids. When oxidated, they become more active; and still more so when the oxide is combined with an acid. And even the degree of oxygenation considerably influences their powers; so that from the same metal preparations of very different degrees of medicinal activity may be obtained, though all agreeing in the kind of action they exert.

It would be foreign to the object of this sketch to give the description of the individual metals: it is sufficient to have stated with regard to them these general facts. Few of them exist as common ingredients in the composition of natural substances, with the exception of iron.

The class of EARTHS comprizes a few substances, possess-

ing certain common properties, which are the ultimate principles of the various compounds, not metallic or inflammable, which occur in the mineral kingdom. An analogy had often been observed to exist between these substances and metallic oxides, which led even to the conjecture that they are of similar constitution, or consist of metallic bases combined with oxygen. Their decomposition has accordingly been effected by the application of galvanism; they are compounds of certain bases with oxygen, and these bases possess general properties, so nearly allied to those of metals, as to be sufficient perhaps to justify the placing them in that class, yet still so far different as to afford some reason for regarding them at least as a peculiar order.

The Primary or Simple Earths, as they are named, to distinguish them from the various earthy aggregates which exist in nature, have been described as substances insipid, insoluble in water, fixed, and nearly infusible by heat, uninflam- mable, and capable of combining with acids, so as to neutralize the acid properties. All these characters are not equally appropriate; for there are several of the earths which have a pungent taste, and are soluble in water to a considerable extent, and all of them may be fused by very intense heats.

The principal earths are Silex, Argil, Magnesia, Lime, Barytes, and Strontites. Zircon, Glucine, and Ittria, have more doubtful claims to be ranked in this class, or exist in such minute quantities as to be comparatively unimportant.

SILEX is an abundant ingredient, not only in mineral substances, but is frequently contained in vegetable products, and forms part of the earthy residuum of their decomposition. It is tasteless, nearly infusible and insoluble in water, and is peculiarly distinguished by its inertness, and comparatively limited range of combination; among the acids it combines only with the fluoric, and even scarcely neutralizes its pro-

erties. It is dissolved by the fixed alkalis, and it unites by fusion with them, and with the other earths, and the metallic oxides.

ARGIL is insipid, soft to the touch, infusible, insoluble in water, and particularly distinguished by forming with that fluid a ductile plastic mass, which hardens and contracts considerably when heated. With the acids it forms compounds, which have generally a sweetish styptic taste, and which possess the property of astringency.

MAGNESIA exists in the form of a very light white powder, smooth and impalpable; infusible, insoluble in water, and not forming with it a coherent paste; it has a slightly bitter taste, changes the more delicate vegetable blue colours to a green, and combines with acids, forming compounds, in general very soluble, and having a bitter taste. In its pure form it is medicinally employed as an antacid, and its saline compounds have in general a cathartic power.

LIME, or Calcareous Earth, displays still greater energy of action. It is so far soluble in water, as to communicate to the solution a very harsh styptic taste, and the power of changing the vegetable colours to a green. Being usually obtained by the decomposition of limestone, chalk, or marble, by heat, it is in the form of a hard mass; but when it imbibes water, either directly, or from exposure to the atmosphere, it splits, and falls down into a white powder perfectly dry. It is infusible. Combined with the acids, it neutralizes their properties. Its action is considerable on the animal system. Directly applied to animal matter, it acts chemically, producing decomposition, and thus operating as an escharotic. Given in solution, it exerts an astringent and tonic power, which power is also displayed in several of its saline combinations; and by its chemical agency it acts as an antacid, and, as has been supposed, likewise as a lithontrip-

tic. Its base, Calcium, as it has been named, has been obtained, though not perhaps perfectly insulated; it has the metallic lustre, and is highly inflammable.

BARYTES surpasses lime in energy of chemical action. Like it, when in a solid mass, it absorbs water rapidly, and falls into a dry white powder; its taste is harsh and caustic: when water is combined with it, it fuses by a heat comparatively moderate; but when this is dissipated, the heat requires to be raised to a much higher point. It is more soluble in water than any of the earths, cold water dissolving a twenty-fifth of its weight, and boiling water even more than half its weight; this latter solution depositing, as it cools, transparent prismatic crystals. Its solution changes the vegetable colours to a green. This earth combines with the acids, and either from the superior strength of its attractions, or the influence of cohesion on its combinations, it decomposes the greater number of the salts of the other earths and the alkalis. It exerts affinities to the other earths, and to sulphur and phosphorus. Of all the substances of this class, it is the one which acts most powerfully on the living system. Even in small quantities, it occasions unpleasant symptoms, and its preparations prove poisonous to animals. From this quality, and from another, the great specific gravity of several of its saline combinations, particularly the native sulphate and carbonate, barytes was often more peculiarly supposed to be of a metallic nature. Its decomposition has been effected by the application of galvanism, and a base obtained from it, of a metallic appearance, having the colour of silver, considerably heavier than water, fusible at a heat below redness, not volatile, inflammable, and reproducing barytes when combined with oxygen.

STRONTITES, the last of these earths, bears a close resemblance to barytes in many of its properties. Like it, it has

a pungent acrid taste, is soluble in water, crystallizable from its saturated solution by cooling, changes the vegetable colours to a green, combines with the acids, and decomposes a number of the compounds which they form with the other alkalis and earths. Its native compounds, too, have a considerable specific gravity. It is, however, much less soluble in water than barytes; it requires nearly 200 parts of cold water to dissolve it; boiling water dissolves it in much larger quantity. Barytes decomposes its salts. It is not poisonous, nor does it appear to exert any marked action on the living system. A characteristic property of it is that of its salts causing inflammable bodies to burn with a blood-red flame.

Following the series of substances according to their chemical relations from the metallic oxides through the earths, it is terminated by the ALKALIS. These possess the chemical property most characteristic of the whole class, that of combining with acids, neutralizing the acid properties; and they form compounds, analogous in general properties to those formed by the earths and metallic oxides with the acids. But they display still more energy in their chemical actions than the earths do, and are more remote in their qualities from the oxides of the common metals. Their taste is extremely acrid; they are highly caustic; abundantly soluble in water; they change the vegetable blue and purple colours to a green, the yellow to a brown, and they combine with oils, rendering them diffusible or soluble in water. Two of the alkalis, Potassa and Soda, exist naturally in a concrete state, but they are easily fused, and at a heat not exceeding ignition are volatilized. The third, Ammonia, exists when uncombined as a permanent gas, but it is instantly condensed by water, and absorbed by it in large quantity.

The alkalis present a singular anomaly in chemical constitution. At an early period of the researches of pneumatic



chemistry, the decomposition of Ammonia was effected, and it was found to be a compound of hydrogen and nitrogen. This suggested the conjecture, that the two fixed alkalis might be of similar composition, containing at least one or other of these elements as a common principle. This conclusion from analogy has not, however, been established. Sir H. Davy, by the application of galvanic action in high intensity, succeeded in decomposing potash and soda; the bases obtained from them are substances of a metallic appearance and lustre; and these bases are combined with oxygen. The analogy of the fixed alkalis to the common metallic oxides was thus so far established, and the earths being afterwards found to be of similar constitution, this analogy was extended to them, and all those substances, distinguished by the common property of neutralizing acids, appeared to be of similar constitution. Ammonia alone remains insulated, and it presents the singularity, that while it possesses the same general property, and strictly resembles the other alkalis in its chemical qualities, no traces of oxygen can be discovered in its composition. The analogy therefore either fails with regard to it, or if it be an oxidated substance, nitrogen or hydrogen must be compound, and contain oxygen as a constituent principle.

The bases of the fixed alkalis are substances of very peculiar properties. They have the lustre, opacity, and tenacity of metals; but they want the most characteristic metallic property, that of density; they are lighter even than water. They are very fusible and volatile, and pass through these changes of form, as well as different states of cohesion, within a very limited range of temperature. They are highly inflammable, they combine with oxygen with the phenomena of combustion, and are susceptible of different degrees of oxidation. These substances have been regarded as the simple bases of the alkalis; but some facts favour the opi-

nion that they contain hydrogen, and are metallic hydrurets, instead of being simple metals.

POTASH, or, as it ought to be named, (in conformity to the rule of giving a similar termination to the names of substances belonging to the same order), POTASSA, is obtained from the incineration of vegetables, especially from the woody part; the saline matter remaining after the wood has been burnt, consists principally of this alkali, in combination with carbonic acid. It is freed from the impurities by lixiviation; the acid is abstracted by the action of lime, the alkali is obtained in solution, and, by evaporation, can be obtained in a solid state. It is of a white colour, crystallizable, fusible, and volatile at a red heat; abundantly soluble in water, soluble also in alcohol, powerfully caustic, and possessed of all the alkaline properties in a high degree. There is some uncertainty, whether it exist in the vegetable matter from which it is procured in the state in which it is obtained, or whether its base is a constituent principle of that matter, and is oxygenated during the combustion: one reason for admitting the latter opinion, at least in part, is, that the alkali cannot be extracted in so large a quantity by any other process as by burning.

POTASSIUM, as the base of potash has been named, is at the temperature of  $32^{\circ}$  a solid substance, hard and brittle, of a white colour, opaque, and with the lustre of polished silver; at  $50^{\circ}$  it becomes soft and malleable; at  $60^{\circ}$  it is in the form of small globules, somewhat consistent; at  $70^{\circ}$  it becomes more mobile and liquid; and at  $100^{\circ}$ , or according to Gay Lussac and Thenard at  $136^{\circ}$ , it is completely so. It requires a temperature near to a red heat to volatilize it. It is lighter than water, or even than alcohol or ether. It is highly inflammable, when heated to its vaporific point, burning with intense heat and vivid light; at lower temperatures

it combines more slowly with oxygen ; and such is the strength of its affinity to this principle, that it takes it rapidly from water, and from all the acids. It is susceptible of various degrees of oxidation, which Gay Lussac and Thenard have ascertained. In its rapid combustion it combines with the *maximum* proportion of oxygen : the oxide thus formed is not potash, but a substance of a yellow colour containing nearly three times more oxygen than the alkali does, which is fusible, and acts with energy on inflammable and metallic substances, by imparting its excess of oxygen. The degree of oxidation which forms potash, is established almost exclusively by the agency of water ; it is thus produced by decomposing water by potassium, or by adding water to the oxide at the maximum, the excess of oxygen in the latter being disengaged : the proportions in the real alkali are, according to Gay Lussac and Thenard, 83.37 of potassium, and 16.63 of oxygen. Besides these, there exists an oxide at the *minimum*, formed by the slow absorption of oxygen by potassium from atmospheric air ; it is brittle and inflammable, and decomposes water, attracting a sufficient quantity of oxygen to convert it into potash.

SODA, or Mineral Alkali, as it has been denominated in contradistinction to the other alkali, which has been distinguished by the epithet of vegetable, exists as a constituent principle of several saline mineral substances ; but it is usually extracted from the combustion of marine plants. It is afforded by the combustion, combined with carbonic acid, and associated with various other saline substances, and is obtained pure by the same general process as that applied to potash. Whether it pre-exist in sea-plants, or whether these, in common with land-vegetables, afford potash in burning, which decomposes the muriate of soda with which they are impregnated from their situation, so as to afford soda, has

not been well determined. In its physical properties, this alkali bears a considerable resemblance to the other. It is solid and white, crystallizable, though with difficulty, from its watery solution; extremely acrid and caustic, fusible and volatile from heat, having a strong attraction to water, changing the vegetable colours to a green, and possessing all the alkaline properties. From potash it is principally distinguished by the different compounds it forms.

SODIUM, the base of soda, is white and opaque, and has the lustre and appearance of silver; is soft and malleable; is somewhat lighter than water; it is less fusible than potassium, not losing its cohesion at a lower temperature than  $120^{\circ}$ , and requiring for its perfect fusion a heat of  $180^{\circ}$ ; it is also less volatile. When heated to ignition, it burns vividly; at lower temperatures it absorbs oxygen without undergoing combustion; it abstracts oxygen from water, and from the acids, frequently with inflammation. It appears, like potassium, to be susceptible of various degrees of oxidation; that which forms the alkali is established almost exclusively by the agency of water; the proportions are 74.63 of sodium, and 25.37 of oxygen. Besides this, Gay Lussac and Thenard have shewn, that in its rapid combustion sodium combines with a quantity of oxygen one and a half greater than that which exists in soda, forming an oxide at the *maximum* of oxidation. And there is also an oxide at the *minimum*, formed by the spontaneous absorption of oxygen by sodium at a low temperature.

AMMONIA. This alkali has usually been denominated volatile, from its volatility compared with the others, even when it is combined with water, being considerable. In its insulated state it exists as a permanently elastic fluid; its odour is extremely pungent; water absorbs it in very large quantity, and this solution forms what is named Liquid Am-

monia. Its tendency to assume the elastic form, and its comparative dilution, lessen the energy of its action; and hence, though possessed of the general alkaline properties, it appears weaker than the others in the affinities it exerts. Its composition was established at an early period of the researches of pneumatic chemistry, nitrogen and hydrogen appearing, both from analytic and synthetic experiments, to be its constituent principles. When the composition of the fixed alkalis was discovered, and they were proved to be oxides, analogy evidently suggested the conjecture, that oxygen might exist in ammonia, and Davy, from some experiments, concluded that this is the case. It has since been shewn that these are incorrect, and that ammonia, by decomposition, is resolved into hydrogen and nitrogen alone. The analogy in the chemical constitution of ammonia to that of the fixed alkalis, appeared to be established in another respect, that of its having a metallic base; Berzelius and Pontin, Swedish chemists, having found, that when the alkali is placed at the negative wire in the galvanic circuit in contact with quicksilver, the quicksilver increases in bulk, becomes thick, and at length a soft solid,—changes similar to what are produced in it by the addition of metallic matter, and which can scarcely be conceived to arise from any other cause. They concluded, therefore, that in this experiment the ammonia had suffered decomposition, and its metallic base had combined with the quicksilver. And they affirmed, that when the amalgam is exposed to atmospheric air or dropt into water, it absorbs oxygen, hydrogen is disengaged, denoting a decomposition of the water and a transfer of its oxygen to the metallic matter, while in both cases ammonia and quicksilver are reproduced,—results which Davy confirmed. Gay Lussac and Thenard, however, have shewn, that so far as relates to the absorption of oxygen, they are incorrect;

the ammoniacal amalgam, they find, is resolved by decomposition merely into quicksilver, ammonia, and hydrogen, and they regard it therefore as a compound of these, the ammonia and hydrogen being retained by the quicksilver by a very weak affinity, and in a state of slight condensation. It still appears, therefore, that ammonia is a compound of hydrogen and nitrogen, the proportions being from 72 to 74 of hydrogen, with from 28 to 26 of nitrogen.

The last important class of chemical agents is that of **ACIDS**. Their characteristic properties are a sour taste, the power of changing the blue, purple, and green colours of vegetables to a red, and that of combining with the alkalis, earths, and metallic oxides, forming compounds, in which, when the combination is established in the due proportion, the properties of the acid, and of the base with which it is united, are equally neutralized. The more powerful acids have a considerable degree of causticity; they have a strong attraction to water, and they act with energy on inflammable and metallic substances.

All the acids are compounds of oxygen, and this element is therefore regarded as the principle of acidity. This truth was established by Lavoisier, with regard to a number of the acids, and extended by analogy to a few which had not been decomposed. The bases of the acids are either inflammable or metallic. The production of acidity is usually the result of their full oxygenation, and in some cases the base combines with two proportions of oxygen, forming two acids, different in their properties from each other.

On these facts, with regard to the chemical constitution of the acids, their nomenclature is founded. The base being specific with regard to each acid, while the oxygen is common to them all, it is from the name of the former that the name of the acid is derived; and, by a variation in the

termination of this name, the different acids which may be formed from the base, by a difference in the degree of oxygenation, are distinguished; the name terminating in the syllable *ic*, when the acid is that which contains the larger proportion of oxygen, and in the syllable *ous* when it contains the smaller proportion. Thus sulphur forms two acids, by combining with two proportions of oxygen; the term sulphur is the radical whence the names of these are derived, and according to the above principle, the one is denominated the sulphuric, the other the sulphurous acid. Where a large quantity of oxygen can be farther combined with an acid without increasing, but rather diminishing its acid powers, the name is expressed by prefixing the epithet *oxy*, as oxy-muriatic acid.

Acids have an extensive power of combination. From the numerous affinities they exert, and from the facility with which they afford oxygen, they are the most active of any of the compound chemical agents, and are hence employed in many pharmaceutic operations. Those of most importance under this view are the sulphuric, nitric, and muriatic.

The **SULPHURIC ACID**, formed from the full oxygenation of sulphur, exists combined with a small quantity of water in the form of a liquid of great density, and from this state of concentration acts powerfully, exerting strong attractions to other bodies; and though, from the strength of affinity between its principles, it does not directly afford oxygen with facility to many substances, it enables them to attract oxygen from water, and thus subjects them to chemical change. The **SULPHUROUS ACID**, which is formed from the same base in a lower degree of oxygenation, existing naturally in the elastic form, which is an obstacle to its entering into combination, and not being very largely absorbed by water, so as to form a concentrated solution, is much weaker in its action.

**NITRIC ACID** is the result of the full oxygenation of nitrogen; and the oxygen, not being retained in the combination by a strong attraction, the acid yields it readily, and hence acts with more facility and energy on inflammable and metallic substance than any other acid,—oxidating the former, and first oxidating, then combining with the latter; hence in pharmacy it is used as the most general solvent of the metals. What is named **NITROUS ACID**, is the nitric, with an impregnation of nitric oxide gas; it is of a yellow colour, and emits similar coloured dense fumes, while the other is colourless: the chemical agencies of both are nearly the same.

**MURIATIC ACID** exists when uncombined in the aërial form, but it is absorbed in large quantity by water, and forms a liquid acid of considerable strength. Its analysis has not been effected, and its composition is therefore altogether unknown. It appears, however, that in its gaseous form it always contains a quantity of water in intimate combination, amounting to a fourth of its weight, and thus water has an important influence on its acidity; for although the acid itself cannot be obtained free from this water, yet when combinations of it with other acids are procured in this state, the acid powers are completely suspended, and are restored on the addition of a little water. This acid, not directly affording oxygen to bodies, oxidates them only by enabling them to attract oxygen from the water it contains; it thus dissolves metals; and it farther combines with other substances, as the alkalis or earths. It is capable of uniting with an additional proportion of oxygen, forming what is named **Oxymuriatic Acid**, which, although its acid powers are weaker, imparts oxygen more readily to bodies. And, with a still larger proportion of oxygen, it forms a third acid, **Hyper-oxymuriatic Acid**, which gives to the saline com-



pounds in which it exists, the power of acting with much energy on inflammable bodies, in consequence of the very large quantity of oxygen condensed in the combination, and not retained by any great force. An hypothesis suggested by Gay Lussac and Thenard, with regard to the nature of this acid, and these combinations of it with oxygen, has lately been maintained by Sir H. Davy, that oxymuriatic acid, instead of being a compound of muriatic acid and oxygen, as had been supposed, is a simple substance, and like oxygen, an acidifying element; and that muriatic acid is a compound of it with hydrogen. This hypothesis, when proposed, was supported by no conclusive independent evidence, but rested entirely on those facts, which are explained more justly, and with more probability, from the peculiar relation of muriatic acid to that portion of combined water which in common with other acids it contains in its insulated state; and in the progress of the discussion with regard to it, the evidence in support of the common doctrine has been extended and confirmed.

Other acids, less important as pharmaceutic agents, are the Carbonic, Phosphoric, Boracic, and Fluoric.

**CARBONIC ACID**, the product of the complete oxygenation of carbon, existing in the elastic form, and being absorbed by water only in sparing quantity, has no very active chemical power, but is of importance from existing in many natural combinations, particularly of saline and earthy substances belonging to the *Materia Medica*. The characters eminently distinguishing it are its only weakening, not entirely neutralizing the properties of the alkalis, when in combination with them, and its being disengaged rapidly with effervescence by other acids from its saline compounds.

**PHOSPHORIC ACID** has phosphorus for its base; and the affinity between this base and the oxygen with which it is combined, being strong, it scarcely acts on bodies by oxyge-

nating them, but simply by entering into combination with them; nor are these combinations comparatively of much importance. PHOSPHOROUS ACID, in which the proportion of oxygen is smaller, is still less important.

BORACIC ACID exists in the concrete form, and its chemical action is comparatively weak. So powerful is the affinity between its base and oxygen, that it has only been decomposed by the agency of galvanism, or by potassium; the product of its decomposition is a dark olive-coloured substance, inflammable, and which, by combining with oxygen, reproduces boracic acid; this substance Gay Lussac and Thenard considered as the base of the acid; it is infusible, insoluble in water or in alcohol, neither does it decompose water; it attracts oxygen, however, from other acids, and from a number of saline compounds; it burns vividly when heated in oxygen gas, and forms boracic acid; the acid, according to the estimate of these chemists, containing about one third of its weight of oxygen.

FLUORIC ACID, in the state in which, until lately, it has been known to chemists, is elastic, and is not very largely absorbed by water; its chemical action is from these circumstances, therefore, not powerful. It unites, however, easily with the alkalis and earths, and, what peculiarly distinguishes it, is capable of dissolving siliceous earth. It suffers decomposition from the action of potassium, oxygen appearing to be abstracted from it, and a substance of a reddish brown colour is deposited, which burns in oxygen, and reproduces the acid. This substance appears to contain the base of the acid combined with a portion of potash, formed by the oxygenation of the potassium. The experiments of Gay Lussac and Thenard have shewn, that the acid, in the state to which these observations apply, holds dissolved a portion of siliceous earth, derived either from the materials

from which it is procured, or from the glass vessels in which the process is performed; and this silex has a very important influence on its properties. When the acid is procured free from silex, it exists in the liquid state at the temperature of  $60^{\circ}$ ; but it evaporates rapidly, and forms dense vapours when exposed to the air; and the contact of silex causes it instantly to assume the gaseous form; it combines with water with a hissing noise, and the production of much heat; is possessed of high acid powers, and is peculiarly distinguished by the energy of its action on animal matter, instantly destroying it, so that a drop of it allowed to fall on the skin, erodes it with severe pain, and produces deep-seated ulceration. This acid forms, with the boracic, a compound acid, the Fluo-boric, which is also distinguished by very peculiar properties, particularly by its strong attraction to water, and also by its very powerful action on vegetable and animal matter.

There is a series of acids with compound bases, derived from the vegetable and animal system; but those of them entitled to notice will be best considered with the classes of substances with which they are more strictly connected.

The acids combine with the alkalis, the earths, and the metallic oxides; and when the combination is established in the due proportion, the chemical properties of the acid, and of the base with which it is united, are mutually neutralized. Hence these compounds are named NEUTRAL SALTS, and, as an order of chemical agents, they are distinguished by certain common properties. They can always be obtained in the solid state: they are generally, though not universally soluble in water; those of them which are soluble, are capable of assuming a crystalline form, the form being very different in different salts. Those which crystallize from their aqueous solution, always retain a quantity of water in

combination, essential to the crystal, and therefore named their water of crystallization. When heated, the increase of temperature is often sufficient to enable this water to dissolve the real saline matter: this is named the watery fusion of salts; as it evaporates, the salt becomes concrete, and, by a farther increase of heat, is either fused or decomposed. The term Neutral Salt is sometimes restricted to those of which the alkalis are the bases: those formed from the earths are named Earthy Salts; and those from the metallic oxides, Metallic Salts. The nomenclature of the whole series is in the modern chemical language simple, and, at the same time, systematic and precise. They are formed into genera and species, according to the acids, and the bases of which they are composed; the name of the genus is derived from that of the acid, the name of the species from that of the base with which the acid is united. Thus all the salts formed from sulphuric acid are considered as constituting one genus, and are named Sulphates; and the name of each species is expressed, by adding the name of the base, as Sulphate of Soda, Sulphate of Lime, Sulphate of Iron, &c. The acid which sulphur forms in a different degree of oxygenation, the Sulphurous, forms a different order of salts; these are named Sulphites; and in like manner we have Nitrates and Nitrites, Phosphates and Phosphites, &c. Those formed from oxymuriatic acid are named Oxy-muriates. Salts are sometimes formed with an excess of acid, or with an excess of base: the acid being considered as the principle forming the genus, these compounds are distinguished by prefixing to the usual name the epithet *super*, when the acid is predominant, and the epithet *sub* when it is deficient, or when the base is in excess, as Super-sulphate of Potash, Sub-carbonate of Soda, &c. When an acid is combined in one compound with two bases, as sometimes happens, the

names of both bases enter into the name of the Salt, as Tartrate of Potash and Soda. Thus, by this simple system, a facility of nomenclature is afforded; the whole is uniform, and the memory is aided, by the name pointing out the nature of the salt; its adoption in Pharmacy is therefore an important improvement, compared with the arbitrary and unstable nomenclature formerly employed.

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So far the chemical analysis of unorganized substances connected with the *Materia Medica* has been the subject of consideration. It remains to take notice of the analysis of those belonging to the vegetable and animal kingdoms,—a subject of much importance, particularly as it relates to the vegetable part of the *Materia Medica*, and which, from this importance, as well as from the nature of the substances themselves, requires to be considered with more minute details.

These two classes of bodies are distinguished by very obvious chemical characters. In unorganized substances, the principles are few, and are combined generally in very simple states of union; their analysis can be executed with accuracy; even the proportions of their principles can be determined with precision, and they can be again combined so as to form the decomposed substance, thus confirming the analysis by synthesis. But, with regard to the products of organization, while the composition, so far as it relates to the ultimate elements, is more uniform, it is, with regard to the modes in which they are united, much more complicated. They consist of a few common principles; but these, presented to each other in the vessels of the organic being, have been placed under circumstances indefinitely varied, and which art can very imperfectly imitate. Combinations of

the same elements are formed, therefore, greatly diversified, and properties are derived from differences of proportions, or modes of union extremely minute. Hence their accurate analysis is executed with difficulty,—a difficulty increased by the circumstance, that these elements having strong mutual affinities, cannot in general be obtained insulated, but when the compound is decomposed enter into new combinations, liable to be modified by slight variations of circumstances; the proportions therefore can seldom be determined with accuracy, the modes of union in general remain unknown, and the confirmation by synthesis is entirely precluded.

Another character distinguishes these two classes. The composition of unorganized bodies being more simple, is not so liable to be subverted; their constituent principles being few, their affinities operate with more force, and the combination is more permanent. That of organized bodies being more complicated, has characters precisely the reverse. Composed always of several elements, the affinities are more nicely adjusted, and are therefore more easily modified; and their principles having tendencies to enter into numerous forms of combination, slight variations of circumstances subvert the equilibrium. Hence the susceptibility of decomposition by which they are distinguished: they are liable even to spontaneous changes from the reaction of their elements; and when this is favoured by humidity, elevation of temperature, or the action of the air, new combinations are established, whence the original compounds are decomposed.

From the peculiar constitution of the products of organization, there are two kinds of analysis to which they are subject. The object of the one is to discover their ultimate composition; that of the other is less refined, being confined to the investigation of the proximate principles of which they are composed.

It is seldom that a vegetable substance is homogeneous. The seed, for example, the bark, or the leaves of a plant, is not of one uniform composition, but consists of various proximate principles in a state of mixture, or of slight combination, and capable of being easily separated from each other. Now, these are often connected with their medicinal virtues; the virtue residing perhaps not in the entire substance of the leaf, bark, or seed, but in a principle capable of being separated, and which may frequently be employed in its insulated state. Hence the importance of the analysis of the vegetable substances belonging to the *Materia Medica*, so far as relates to their proximate principles; the knowledge it conveys enabling us to employ them with more discrimination, and to submit them to the proper pharmaceutic treatment. An enumeration of their proximate principles, and more particularly of those on which their medicinal powers depend, accordingly always enters into their description as articles of the *Materia Medica*.

This analysis is executed in various modes, adapted to particular cases, according to the principles which form the vegetable substance.

Sometimes it is effected merely by heat. The temperature cannot indeed be elevated very high, as then the proximate principles of the vegetable would be themselves decomposed, and their elements brought into new combinations. But at a heat comparatively moderate, as that of boiling water, this does not happen; and at this temperature several of these principles, such as essential oil, camphor, and some others not very well defined, are volatilized without decomposition, and of course can be obtained pure.

The action of different solvents is of more extensive use in conducting the vegetable analysis. Water dissolves several of their component principles, such as gun and extrac-

tive matter, tannin, saline substances, and some others. These are dissolved in greater or less quantity, and in more or less purity, according to the temperature of the water employed. In general, by raising the water to its boiling point, it is able to dissolve them more completely; but some of them are apt to be volatilized, and others altered in composition, especially if the atmospheric air is not excluded. Of the substances which the water holds dissolved, part are separated as it cools; the gum can be precipitated by alcohol; the saline substances may be crystallized, or can be discovered by evaporating the solution to dryness, and exposing the mass to such a heat as will destroy the inflammable parts; tannin and some others are detected by their chemical tests.

Alcohol is another agent of much importance in executing the vegetable analysis. It dissolves the resin, balsam, camphor, and essential oil: these solutions are decomposed by water, each substance being separated, and discernible by its peculiar qualities. Equal parts of alcohol and water, or proof spirit as it is named, is also often employed as a solvent in the analysis of vegetables. Ether dissolves nearly the same principles as alcohol. And the acids, alkalis, and soluble earths, are sometimes of utility as re-agents, in pointing out the existence of peculiar principles.

Lastly, in the analysis of vegetables, we are often able to procure several of their proximate principles, by mechanical means, particularly by expression. Sometimes too, they exude spontaneously from the growing vegetable, or are obtained by it from incisions made in the branches or trunk.

After we have discovered the proximate principles of a plant, or of any part of it, the next step is to ascertain their composition. This is an investigation attended, however, with much difficulty, as being liable to all the deceptions



arising from a complicated analysis, and incapable of being confirmed by the surer test which synthesis affords.

The composition of these substances with respect to their ultimate principles is nearly uniform. All of them contain carbon and hydrogen, generally if not invariably united with oxygen: some farther contain nitrogen and phosphorus; and in others several of the metals, particularly iron and manganese, exist. Lime, too, and the two fixed alkalis, either pure or more commonly in combination with some of the acids, are not unfrequently constituents of vegetable matter. These latter substances, however, are seldom in any considerable proportion; nor in general do they appear to modify much the properties of the substances in which they exist. Nitrogen, and perhaps lime, when present, appear to have the most important influence, and with the exception of the few compounds of which they form a principal part, it may be said, that the vegetable proximate principles consist of carbon, hydrogen and oxygen; the differences in their properties being produced by differences in the proportions of these principles, and of the modes in which they are combined.

That a difference in the proportions of these elements may give rise to the differences in the properties of the compounds which they form, cannot be doubted; since in many other cases of chemical combinations, where there is no difficulty in the analysis, differences equally important and well marked are produced by this cause. In vegetable substances we accordingly can often trace this as the cause, without being able to point out any other. Thus, fixed and volatile oils have properties in many respects dissimilar: by analysis both are found to consist of carbon and hydrogen, united in different proportions, the volatile oils having more hydrogen in proportion to the carbon than the fixed have; this is a cause sufficient to account for the difference in their proper-

ties; and it accords sufficiently with that difference, for hydrogen being a substance of great rarity and volatility, those compounds in which it predominates, as ether, alkohol and others, are in general light and volatile. The greater volatility, therefore, of the essential, compared with the fixed oils, may be ascribed to its predominance.

In other cases, it is probable that the mode in which the constituent principles of these substances are united, is the cause of the difference in their qualities. This is indeed a cause which can be but imperfectly investigated, either by analysis or synthesis; but it is conceivable *a priori*, and sufficiently confirmed by chemical facts, that a difference in the mode of union may give rise to very important diversities of properties. If a compound, for example, consist of three elements, these may be united in two modes. Their attractions may be reciprocally balanced, and they may form what is named, in strict propriety, a ternary combination; or, from a variation in the circumstances under which the union has been effected, or a difference in the strength of their attractive powers, two of them may be combined, and the compound thus formed may exert an attraction to the third principle, unite with it, and form a new substance. The compounds resulting from these different modes of combination, though composed of the same principles, united perhaps even in the same proportions, would still have properties different from each other. Still greater diversities will be produced where the elements are more numerous, and the possible modes of union are of course more diversified. And when we consider these causes from difference of proportions, and modes of combination, we shall scarcely be surprised at the number of different substances, immense as it is, which nature forms from a few elementary principles.

The proximate principles of vegetables are sometimes ana-

lysed by exposure to heat: their elements enter into new combinations, and from the nature of the products, we discover what the principles were. Thus, if the substance exposed to heat yields a large quantity of acid, we conclude that it contains a considerable quantity of oxygen as a constituent part. If it afford much empyreumatic oil, we infer that it contains a large proportion of hydrogen, this principle being necessary to the constitution of that product. When ammonia or prussic acid is afforded by this kind of analysis, we conclude, for the same reason, that nitrogen has been a constituent principle. And by the same mode are discovered the earths and metals which had been present in it; these remaining after the volatile parts have been expelled. Lastly, from the quantity of charcoal which remains as a residuum, we can form some conclusion as to the quantity of carbon which the vegetable substance contained.

Their analysis is also effected by exposing them to heat with the access of atmospheric air, and collecting the products of the combustion that takes place. From the nature of these products, we can ascertain the proportions in which they were united. Oil, for example, when subjected to this analysis, yields nothing but carbonic acid and water. We conclude therefore that it is composed of carbon and hydrogen, since these principles, united with oxygen, form these products, and since, if any other simple substance had existed in the oil, it would have appeared either pure or in combination with oxygen. We can even determine in this manner the proportion in which the carbon and hydrogen existed in the combination. From knowing what quantity of carbon exists in a given quantity of carbonic acid, and what quantity of hydrogen exists in a given quantity of water, we thus also discover whether any oxygen had existed in the composition of the oil.

Their analysis is also sometimes executed by the agency of the nitric acid, which communicates to them oxygen, and by the product ascertains the nature of their acidifiable base.

This mode of analysis by oxygenation has lately been rendered more exact in the execution by a variation introduced by Gay Lussac,—that of employing hyper-oxymuriate of potash as the oxygenating substance; a certain weight of this salt being heated with a portion of the vegetable matter in its driest state; and the products formed by the combination of the oxygen of the salt with the elements of the vegetable substance being collected. His experiments establish the important general results,—that in one class of vegetable products, those which are of the nature of gum or fecula, the oxygen and hydrogen they contain are in that proportion to each other which forms water, there being added to this a certain quantity of carbon;—that in another class, those which are acid, the oxygen is to the hydrogen in a larger proportion than that which forms water;—and that in a third class, composed of those which are oily or inflammable, the hydrogen is in larger proportion. The following table presents these results, and the proportions of the elements of some of the most important vegetable proximate principles, as assigned by this method.

Substances analysed.	Carbon contained in that substance.	Oxygen contained in that substance.	Hydrogen contained in that substance.	Supposing the oxygen and hydrogen in the state of water in the substance.		
				Carbon.	Water.	Oxygen in excess.
Sugar . . . . .	42.47	50.63	6.90	42.47	57.53	0
Gum-arabic . . . . .	42.23	50.84	6.93	42.23	57.77	0
Fecula . . . . .	43.55	49.68	6.77	43.55	56.45	0
Sugar of milk . . . . .	38.825	53.834	7.341	38.825	61.175	0
Oak-wood . . . . .	52.53	41.78	5.69	52.53	47.47	0
Beech-wood . . . . .	51.45	42.73	5.82	51.45	48.55	0
Mucous acid . . . . .	33.69	62.67	3.62	33.69	30.16	36.15
Oxalic acid . . . . .	26.57	70.69	2.74	26.57	22.87	50.56
Tartaric acid . . . . .	24.05	69.32	6.63	24.05	55.24	20.71
Citric acid . . . . .	33.81	59.86	6.33	33.81	52.75	13.44
Acetic acid . . . . .	50.22	44.15	5.63	50.22	46.91	2.87
Resin, common . . . . .	75.94	13.34	10.72	75.94	15.16	Hydrog. in excess. 8.90
Copal . . . . .	76.81	10.61	12.58	76.81	12.05	11.14
Wax . . . . .	81.79	5.54	12.67	81.79	6.30	11.91
Olive oil . . . . .	77.21	9.43	13.36	77.21	10.71	12.08

The ultimate analysis of the vegetable substances belonging to the *Materia Medica* is seldom of utility, since we can scarcely ever discover any relation between the composition and the medicinal powers of the substance analysed. These, in common with all its properties, no doubt depend on that composition; but our modes of analysis are still too limited and imperfect to admit of our tracing the connection between them. The application of chemistry, therefore, to the vegetable substances belonging to the *Materia Medica*, is in a great measure confined to the discrimination of their proximate principles.

The Proximate Principles of vegetables are numerous,

and of very different kinds. They are not all to be met with in every vegetable, or in every period of vegetation: some exist only in certain plants, and that only in their state of vigour and maturity: at other times they are to be found only before they have arrived at that period; some are deposited in particular organs, others are diffused through the whole substance of the vegetable, and mixed in a manner more or less intimate with all its parts: and some are nearly peculiar to certain vegetables, while others are common to almost every plant. Those only require to be pointed out in this sketch, which are particularly connected with medicinal properties.

These principles are the products of vegetation from a common juice or sap, which circulates freely through every part of the vegetable system, being supplied by absorption from the soil, and perhaps from the atmosphere. It varies in its qualities, particularly according to the season, and the progress of the plant to maturity; frequently too it has an intermixture of the proper juices: it always contains the usual elements of vegetable matter, with generally saline substances, having principally lime for their base. By the chemical changes it suffers from the action of the vessels of the plant, aided by the action of the air and of light, its elements pass into various states of combinations, whence the peculiar products of vegetation are formed.

The first transition of the sap appears to be into MUCILAGE, or GUM, one of the proximate principles contained in greatest abundance in vegetables. Gum is the name given to this principle when it is obtained in a concrete state; Mucilage is the name given to it when it is expressed in a liquid state, or extracted by maceration in water. Between these there exist some differences in their relation to reagents, whence a distinction has been established between

them ; but their general properties are the same, and similar differences exist between the different varieties of gum itself.

This principle is found in all young plants, in greater or less quantity ; and is often so abundant in the plant, as to be discharged by spontaneous exudation. It abounds also in their roots, stalks, and leaves, and especially in their seeds. It is an inodorous, insipid, and glutinous substance, soluble in water, in every proportion, and forming with it a thick viscid solution, which by evaporation affords a tenacious mass, that when dried is brittle and again soluble. It is insoluble in alkohol, ether, or oil, and is precipitated from its solution in water by the addition of alkohol. It does not absorb oxygen from the atmosphere ; though its solution becomes sensibly acid by keeping, owing to partial spontaneous decomposition, and the combination of part of the principles of the gum, so as to form acetic acid. Exposed to heat it is neither fusible nor volatile. At a temperature superior to 212, but inferior to that of ignition, it is decomposed ; its principles entering into new combinations : the products are an acid liquor, consisting principally of acetic acid, carbonic acid and carburetted hydrogen gases, with a little ammonia, and a residuum of charcoal containing lime, one ounce of gum, affording 6 grains of lime. This lime is also detected by adding sulphuric acid to a solution of gum. From these products of the analysis, it is evident that the ultimate principles of gum are, oxygen, hydrogen, and carbon, with smaller proportions of nitrogen and lime. Gum is not capable of passing into the vinous fermentation, which appears to be owing to the portion of lime existing in it, as lime has the effect of preventing even sugar from suffering this change.

Gum is not inflammable ; for although, when heated, in contact with atmospheric air, it combines with oxygen, it

emits no flame. The principal products of this combination are carbonic acid and water. By the action of nitric acid it is converted into oxalic, malic, and saccholactic acids. Oxymuriatic acid converts it into citric acid.

Gum is usually obtained either by spontaneous exudation, or by incisions made in the trunks and branches of trees. It is more or less pure as it is obtained from different plants. Its existence in vegetables is detected by boiling gently the vegetable substance with water; the water dissolves the gum, and if much of that principle be present, the solution is glutinous. It may be allowed to remain till the impurities have subsided; if it then be evaporated to the consistence of thin syrup, the addition of three parts of alcohol will separate the whole of the gum in flakes.

Pure gum is not an active substance, considered with respect to its effects on the living system. In medicine it is only used for its lubricating quality; and so little activity does it exert, that it has often been taken for a considerable time as an article of food. From its chemical properties, it is of rather more importance. As a component part of vegetable matter, it renders the other parts more soluble in watery liquors, and may thus favour their action on the stomach. In Pharmacy it is used as a medium to combine balsams, resins and oils with water. If a small quantity of any of these substances be triturated with a little gum or mucilage, on the addition of water they remain suspended in it, forming a white milky-like mixture, retaining all the properties of the balsam or oil. Though pure gum is thus inactive, yet the virtues of many vegetables depend on a gummy matter.

FECULA is a principle approaching in several of its characters to gum. Like it, it is soluble in hot water, and forms a viscid glutinous solution; but it is at once distin-



guished by being perfectly insoluble in cold water. It exists principally in the tuberosc roots and gramineous seeds. It is extracted by beating the dried root or seed with a large quantity of water; the liquid soon becomes milky, from the diffusion of a white powder through it. On being poured from the remaining vegetable matter, and allowed to remain at rest, this powder is deposited, and when washed and dried is the fecula of the plant. It is generally mild and insipid, of a white colour, with a peculiar kind of brilliancy, soft to the touch; but portions of the other principles of the plant sometimes adhere to it, from which it receives colour, smell, and taste. Starch is the fecula of wheat, and is the most abundant part of that grain.

Fecula is insoluble in alcohol. The action of the acids on it is somewhat analogous to that they exert on gum, dissolving it when they are weak or diluted, but decomposing it when they are more concentrated. The alkalis also dissolve it. Exposed to heat, it is charred, and suffers decomposition, affording products which indicate carbon, hydrogen and oxygen to be its constituent principles. A property eminently characteristic of it, and probably depending on its composition, is that of being convertible into saccharine matter, and thence ultimately passing into the vinous fermentation,—a property not belonging to gum or any other principle. This conversion takes place in germination, and is accompanied with an absorption of oxygen, and formation of carbonic acid.

Fecula is a substance highly nutritive, and is usually contained in those plants which serve as food. It is sometimes employed in its pure state in medicine, on account of its nutritive quality, and from being easy of digestion; sago and salop are substances of this kind.

**GLUTEN.** This principle is usually associated with fecu-

la, and is obtained in the process in which the fecula is separated. It then appears as a viscous, elastic, and fibrous-like substance, which, from its close resemblance to the animal product named Gluten, has been denominated Vegetable Gluten. It is obtained from the flour of wheat in greatest abundance: the flour is made into a paste with water, which being compressed by the hand, while a stream of water falls upon it, the fecula is carried off in the state of powder: the mucilaginous and saccharine parts of the grain are dissolved by the water; and there remains a tenacious ductile mass, forming the gluten; it has scarcely any taste, is of a greyish colour, and when dried is semi-transparent, resembling glue in its appearance: it is insoluble in water, and is dissolved in very small quantity by alcohol: by the action of nitrous acid, it is converted into oxalic acid, giving out, at the same time, nitrogen gas: decomposed by heat, it affords a large quantity of ammonia, and it is subject like animal matter to putrefaction. It contains a larger proportion of nitrogen than any other vegetable product does, and it is supposed to render those vegetables in which it is present highly nutritive.

Another principle which has been supposed to exist in vegetables, is that which has been named Albumen, from its resemblance to the animal principle of that name. It is soluble in cold water, its solution being coagulated by heat: it is coagulated also by alcohol, but is dissolved by the alkalis: like gluten, it is liable to putrefaction, and furnishes a large quantity of ammonia by distillation. This principle is found in hemlock, scurvy grass, cresses, and several other plants, and is obtained from the fresh expressed juice of the leaves when they are heated nearly to the boiling point; the albuminous matter coagulating, and separating in the form of flakes. A similar separation takes place on the addition of

spirit of wine. It is contained also in the seeds of other plants, particularly in the different nutritive grains; in the farina of wheat, for instance, it is found dissolved in the water which is employed in separating the fecula from the gluten. This principle has, however, been regarded, and perhaps justly, as a variety of gluten; it differs little from it in chemical properties; and the peculiar physical qualities supposed to be distinctive of gluten are obviously derived from the process by which it is obtained.

**SACCHARINE MATTER.** This exists in many vegetable substances, especially in their fruits and roots, but often intimately united with their mucilaginous and extractive matter. When freed from these, its taste is sweet, without any peculiar flavour; it is soluble in water and in alcohol; is capable of crystallizing; its watery solution enters first into the vinous, and then into the acetous fermentation. By the action of nitric acid, it is converted into oxalic acid; by decomposition by heat, it affords a large quantity of empyreumatic acetic acid, a small quantity of empyreumatic oil, carbonic acid and carburetted hydrogen gases, the residuum being charcoal. It consists, therefore, of carbon, hydrogen and oxygen; and from the large quantity of acid which its analysis yields, it appears to contain more oxygen than any other vegetable substance that is not acid.

Sugar appears to be often formed from the fecula of the vegetable in which it exists. It contains nearly the same principles as fecula does, and the operation of malting throws considerable light on its formation; in this process, the fecula of grain is converted into saccharine matter, oxygen is absorbed, and carbonic acid formed; and this abstraction of carbon, if it constitutes the whole change, of course proves that the sugar, which is the product of the operation, has an increased proportion of hydrogen and oxygen.

In other cases, as in the maturation of fruits, sugar appears to be formed from the acid juice of the fruit, and this is probably effected by an abstraction of oxygen. Saccharine matter has little activity, though there are some varieties of it, in which some weak medicinal powers reside.

OIL is a common proximate principle of vegetable matter; it is of two kinds, expressed or fat oil, and distilled, volatile, or essential oil. These have the common qualities of unctuousity and inflammability; but they also possess peculiar properties, by which they are distinguished as species.

The Expressed, fat, or fixed oils, are thick and unctuous, insipid and inodorous; they congeal on exposure to cold, are lighter than water, and insoluble in that liquid; they are likewise insoluble, except in very minute quantity, in alcohol, and they combine with the alkalis, forming soap. They are not volatilized at the temperature of  $212^{\circ}$ : some require to be raised to  $600^{\circ}$  to make them boil, and the condensed oil is changed in its properties. At a temperature somewhat higher, they are decomposed in close vessels, and burn when the atmospheric air is admitted. They also slowly absorb oxygen at a low temperature; a small quantity of an acid is formed, which renders them rancid; by longer exposure to the air, they are inspissated, and even become at length concrete. Those oils in particular which have been expressed with the aid of heat, and which are named drying oils, suffer this last change, and are ultimately converted into a resinous matter.

Expressed oils consist chiefly of carbon and hydrogen, as is established by the products of their decomposition by heat, which are chiefly carburetted hydrogen and carbonic acid. The products of their combustion are water and carbonic acid.

These oils are generally contained in the seeds and fruit

of vegetables, and only at the period of their maturity. They are extracted by expression, or by decoction with water; they are frequently impregnated with part of the extractive, mucilaginous or resinous particles, which the seed or fruit contains; from which they derive colour, and in many cases a peculiar taste and odour, and even perhaps certain medicinal powers. In general, however, they have little activity as medicines. They are mild and emollient, and are used principally for these virtues. They are rendered miscible with water by the medium of gum or sugar, or by the addition of a small quantity of any of the alkalis.

Volatile or Essential oils have characteristic properties different from those of expressed oils. They are volatile at a low temperature, and are entirely and quickly converted into vapour at the heat of boiling water, without being decomposed; they are soluble in a small proportion in water, and hence the impregnation which water receives from many vegetables by distillation. In alkohol, they are completely soluble; but they do not combine with the alkalis with facility; they are in general odoriferous, pungent, and even acrid; they are more highly inflammable than the fixed oils, and by exposure to the atmosphere they slowly absorb oxygen, are thickened and coloured, lose much of their smell and pungency, and are at length converted into substances of a resinous nature. This change is partly owing to the volatilization of the oil, but principally to the oxygen absorbed combining with a portion of their hydrogen.

These oils, from their analysis by heat, or by combustion, appear to consist principally of carbon and hydrogen. They differ from the fixed oils in containing a larger proportion of hydrogen; hence they are more volatile, and more inflammable, and by combustion afford a larger quantity of aqueous vapour.

Volatile oils are less abundant in the products of vegetation than some other principles; they do not exist indeed in any considerable quantity but in the aromatic plants; in some plants, the oil is confined to the flowers, fruit, leaves, or bark; sometimes it is contained in several of these parts, and in a few instances it is found diffused through every part. The quantity varies, not only according to the age, but also according to the vigour of the plant; hence it is much influenced by climate, soil, and season. It is remarkable, that some of the most odoriferous flowers, as the rose or jessamine, yield scarcely any essential oil, though they lose their flavour by a gentle heat.

Some of these oils, being contained in distinct vesicles, may be obtained by simple pressure. In this manner, essential oils can be obtained from orange or lemon rind. More usually, they are procured by distillation; the vegetable is boiled in water; the essential oil is volatilized with the aqueous vapour; both are condensed in close vessels; the water has the taste and flavour of the plant, from having dissolved a small part of the oil; the greater part of it, however, is collected pure, either swimming on the surface of the water, when the oil is lighter, as is generally the case, or, in a few cases, when it is heavier, having fallen to the bottom.

The essential oils of vegetables are not without some degree of medicinal activity. They have always the odour, and generally the taste of the vegetable from which they are obtained, accompanied with more or less pungency. Some of them, however, are less pungent and less acrid than the vegetable matter from which they are procured, these qualities residing in the resin, or some of the other proximate principles.

A proximate principle, found in some vegetables similar in

many of its properties to essential oil, is CAMPHOR. It is a solid substance of a white colour, semi-transparent, having a strong peculiar smell, and a penetrating taste; tenacious, and slightly unctuous to the touch. It is very sparingly soluble in water, but is abundantly soluble in alcohol, ether, and oils; from these solutions it is precipitated by the addition of water. It evaporates entirely, though slowly, at the common temperature of the atmosphere; at a higher temperature, in close vessels, it is sublimed without alteration; it is also highly inflammable, the products of the combustion being carbonic acid, and a quantity of what is named camphoric acid. It is acted on by the more powerful acids, sulphuric acid charring it and forming a portion of tannin; nitric acid dissolving it, and decomposing a portion of it, converting it into an acid; muriatic, fluoric, acetic and carbonic acid dissolving it, without materially changing its composition, as the greater part can be precipitated by water. Nitric acid, repeatedly distilled from it, converts it into a concrete acid, named camphoric acid, which appears to be different from any known acid, though it approaches in many of its properties to the benzoic.

By peculiar arrangements, which impede its volatilization, camphor may be decomposed by heat. This is effected by mixing it intimately with six parts of pure clay, making the mixture into balls by the addition of water, and when these are dry, subjecting them to a strong heat, suddenly raised. A volatile oil, fragrant and pungent, of a golden yellow colour, amounting to one-third of the weight of the camphor, distils over; a quantity of charcoal, about  $\frac{1}{4}$ th of the weight of the camphor, remains; the remaining products of the decomposition are, carburetted hydrogen, carbonic acid gas, and camphoric acid. From the result of this analysis, camphor appears to differ from the essential oils, principally in

containing a much larger proportion of carbon, since, by its decomposition by heat, it is resolved principally into charcoal, or compounds of carbon, and into an oil, which has all the properties of an essential oil, being odorous and pungent, volatile and inflammable, soluble in alkohol, and precipitated from it by the addition of water.

Camphor is found in distinct vesicles, in the wood and bark of certain vegetables. It is also contained in many essential oils, as those of lavender, sage and others, from which it is deposited on long keeping. A substance analogous to it in many of its properties, is capable of being artificially formed, by the action of muriatic acid on oil of turpentine.

The same relation which camphor bears to the volatile, Wax seems to have to the fixed oils. This substance, though formed by the bee, is also a product of vegetation; it is yielded by the leaves and fruit, and it is sometimes intimately mixed with the resin, gum, or extractive matter of plants. It is insoluble in water, and is soluble in very small quantity with the aid of heat in alkohol. It combines with the fixed alkalis, though with some difficulty. It unites easily with the expressed oils. It melts at a moderate heat. By distillation in close vessels it affords an acid, and a considerable quantity of thick oil, a small quantity of charcoal being the residuum.

RESIN. This principle is in some measure connected with essential oil, and in plants is often united with it, as well as with other principles. Some vegetables, however, exude juices which concrete into a matter entirely resinous, and it is from these that the characters of the substances belonging to this genus are taken. The distinguishing properties of a resin are its existing in a solid state, being insoluble in water, but soluble in alkohol, ether, and oils; the solution in ether or alkohol is decomposed by water; resins are in general



odorous and sapid, though neither of these qualities is essential to a pure resin; they are inflammable, and burn with much smoke; at a temperature nearly that of boiling water they melt; but they cannot be volatilized without being decomposed. In close vessels the products of their decomposition by heat are water, empyreumatic acetic acid, an empyreumatic oil, and a residuum of charcoal, indicating carbon, hydrogen, and oxygen, to be their ultimate principles. At the common temperature of the atmosphere, they do not combine with oxygen; neither are they acted on by water; the solutions of them in alkohol are therefore employed under the form of varnishes, to preserve other bodies from alteration by exposure to the air. They are dissolved by the fixed alkalis, likewise by some of the acids, especially the acetic: the stronger acids decompose them.

The existence of resin in a vegetable is discovered by infusing it in alkohol; this dissolves the resin if any is present, and it can then be precipitated from the solution by the addition of water. The method of estimating the quantity of resin in any vegetable, is by ascertaining the increase of weight which alkohol acquires from it by digestion, or the alkohol may be evaporated by a moderate heat, and the resin obtained pure.

Resins are in general more active than gums, with respect to their medicinal powers. The purest resins are indeed nearly inert, but there are many vegetable substances which act powerfully on the system, that appear to consist principally of resinous matter, and it is in this resinous part that their powers reside. The proper solvent or menstruum of resin is alkohol; by this it can be extracted from some of the other constituent parts of vegetables: there are others, however, which are soluble in the same fluid, and therefore it is difficult to obtain the resin pure. Though resin is inso-

soluble by itself in water, yet part of it can be taken up, and kept suspended by the medium of gum.

These two principles, Gum and Resin, are often naturally mixed in vegetables, forming what are named GUM-RESINS, and some of the most active articles of the *Materia Medica* are natural compositions of this kind. Their chemical properties are derived from the two principles of which they consist: thus, they are only partially soluble either in water or in alcohol; they are soluble in alkaline liquors; they are not fusible by heat, they only soften, and if the heat is raised higher are decomposed, affording a little ammonia with the usual products, probably derived from the gum they contain. The proportions of gum and resin, thus mixed, are in different substances of this family very various; but they are generally such, that a mixture of equal parts of water and alcohol dissolves the gum-resin. This is their proper solvent; it also dissolves some other vegetable principles, particularly extract, and hence it is the menstruum most generally used in Pharmacy to extract the active matter of vegetables.

BALSAMS are resinous juices, with an intermixture generally of essential oil, and containing always a portion of the acid named Benzoic Acid. They are usually thick and tenacious, becoming by age concrete. They are odorous and pungent, principally from the essential oil they contain.

A principle of considerable importance in its pharmaceutic relations, which is supposed to constitute the active matter of many vegetables, is what has been named by the French Chemists, by whom its characters were first established, EXTRACT, or Extractive Matter. Its leading character is, that it is soluble equally in pure water and in alcohol; and hence a solution of it in the one fluid is not precipitated by the addition of the other. By this property it is distinguished

both from gum and resin, the one being insoluble in water, the other in alkohol. The compound of the two, or gum-resin, is indeed partly soluble in either of these fluids, but it never is completely so, since if it contain as much gum as renders it soluble in water, it is only partially dissolved by alkohol; and if it consist principally of resin, so as to be completely dissolved by alkohol, it is imperfectly dissolved by water. If a gum-resin be digested with alkohol, the tincture it affords is decomposed by water, and, *vice versa*, its watery solution is decomposed by alkohol.

There is another character by which extractive matter is distinguished, that of suffering decomposition when exposed in a humid state to the atmospheric air; this takes place even at natural temperatures, and with still more rapidity when the temperature is raised, as when the extractive matter is boiled in water: it then becomes insoluble and comparatively inert. This change Fourcroy ascribed to the fixation of oxygen. According to T. Saussure, oxygen is indeed absorbed, but carbonic acid is at the same time formed; he supposes, too, that part of the oxygen and hydrogen of the extractive matter combine and form water, and that the inert insoluble precipitate has therefore an increased proportion of carbon. It is from this cause apparently that the medicinal powers of many vegetables are injured by decoction in water with the admission of air, and not, as was at one time believed, from the dissipation of any volatile active principles; many plants indeed which sustain injury from this operation, containing no such principles.

By oxymuriatic acid, extract is converted into a concrete substance of a yellow colour, insoluble in water, probably from a similar change. It exerts affinities to argil and to metallic oxides, and is hence acted on by a number of metallic salts. Muriate of tin, at the maximum of oxidation,

precipitates it copiously, and forms therefore a delicate test of it, which is liable however to the fallacy that it likewise precipitates some other vegetable principles. By heat it is decomposed, affording empyreumatic oil and acid, with a portion of ammonia; and in this, as well as in its spontaneous decomposition, when the re-action of its elements is favoured by humidity, it leaves as a residuum carbonates of potash and lime.

This principle is supposed to be the base of what are named the Extracts of Plants;—preparations formed by boiling vegetables in water, and evaporating the clear liquor to a thick consistence. As procured in this way, it must generally have an intermixture, greater or less, of those principles, which are soluble in water; and from being so liable to decomposition, it must be injured during the evaporation. It is the basis, too, though in a similar state of intermixture and partial decomposition, of what are named the inspissated juices of plants. It exists also in the seeds, leaves, bark, and wood.

Though the characters of this principle appear to be distinctive, there is still some ambiguity with regard to it, particularly from the circumstance, that these characters are not uniform; a principle existing in some vegetables which has some of these distinctive properties, without the others; as, for example, in Peruvian bark, the active matter of which is rendered inert and insoluble by decoction in water, and so far has one of the peculiar properties of extract; while it has not the other, that of equal solubility in alcohol and water, but is more soluble in the former than in the latter. Nor is there any certainty that this extractive matter has been obtained pure and insulated; and it is therefore possible that it may consist of some of the other principles in a state

of mixture, their properties being modified by their reciprocal action.

**TANNIN.** The important medicinal property of astringency, appeared from some chemical facts to be dependent in vegetable substances on a peculiar principle, as it is discoverable in them by a chemical test, that of striking a deep purple colour with the salts of iron. This effect is exhibited by all the powerful vegetable astringents, and in a degree nearly proportional to their astringency. A peculiar acid having been discovered to exist in these astringents, afterwards named Gallic Acid, it was supposed to be the principle on which this property depends. But subsequent experiments have proved, that the astringency resides in a principle of a different nature, which, from being the agent chiefly concerned in the operation of tanning, has obtained the name of Tan or Tannin.

This principle exists in all the powerful vegetable astringents; it is extracted by maceration with water, and is detected in the infusion by a peculiar test, that of the animal principle denominated Gelatin. If a solution of gelatin is added to the infusion, it becomes turbid, and a precipitate is thrown down, composed of the tannin and gelatin in combination. We have no very perfect process for obtaining tannin in an insulated state; but the most simple is precipitating it from the infusion of a vegetable astringent by lime-water, and afterwards submitting the compound of lime and tannin, which is formed, to the action of dilute muriatic acid, which abstracts the lime, and leaves the tannin.

Tannin evaporated from its solution is loose and friable, of a brown colour, has a resinous fracture, a peculiar odour, and a taste rough and bitter. It is soluble in water, either cold or warm, and in alcohol not very highly rectified. It appears to suffer decomposition from exposure to the air in a

humid state. By the acids, it is precipitated from its watery solution, and by some of them is decomposed. It unites with the alkalis, forming soluble compounds; with the earths it forms compounds of sparing solubility; it exerts affinities to the metallic oxides, and it is principally from its action that infusions of vegetable astringents produce dark-coloured precipitates with metallic salts. Exposed to heat, it affords an acid liquid, an oil, and a considerable quantity of carbonic acid, leaving a spongy charcoal.

Its action on animal gelatin is its most important property in relation to the object of the present outline, as on this probably depends its astringent power; it combines with it, forming an insoluble precipitate, whence it corrugates and renders more dense the animal fibre of which gelatin constitutes a principal part. It exists in all the powerful vegetable astringents, mixed with extractive matter, mucilage, gallic acid, and other principles. It has also been established, that a product very analogous to it is capable of being artificially formed, principally by the action of sulphuric and nitric acids on vegetable substances which abound in carbonaceous matter.

**VEGETABLE ACIDS.** The acid found in the juice and other parts of plants, is not always the same. Not less than seven acids, different from each other, are of vegetable origin,—the Gallic, Oxalic, Malic, Citric, Tartaric, Benzoic, and Acetic. To these may be added the Prussic, though this is more peculiarly formed from animal matter.

**GALLIC ACID.** The existence of this acid in some of the more powerful astringents, particularly in the gall nut, can be discovered by their watery infusion reddening the infusion of litmus. If the concentrated infusion be left exposed to the air for some months, this acid is deposited in the state of a crystalline deposit, mixed with mucous flakes, from which it may be purified. It may also be obtained by sub-

limation from the gall nut, or even by distillation with water, though it is doubtful whether, as procured by these or other processes, it is altogether free from tannin; that by sublimation appears to be most so. By crystallization it is obtained in slender prisms of a white colour; its taste is sour, and it reddens the vegetable colours; it is soluble in 24 parts of cold, and in less than 2 parts of boiling water; it is also soluble in alcohol. It suffers decomposition from heat, and the process indicates a large quantity of carbon in its composition. It combines with the alkalis and earths, and also with the metallic oxides, forming with the latter in general coloured precipitates; it is doubtful, however, whether these colours are not in a great measure derived from the action of tannin adhering to it.

Gallic acid was at one time supposed to be the principle of astringency, from being contained in the vegetable astringents, and giving a dark colour with the salts of iron, the chemical test by which astringency appears to be indicated. It is doubtful, however, as has just been remarked, whether this latter property does not arise from the presence of tannin: the colour it does produce is less deep too, than that which the infusion itself strikes; and the acid in its insulated state has no astringency. Tannin is much rather to be considered as the astringent principle, and it exists accordingly in some of the more powerful vegetable astringents, as in catechu or kino, with scarcely any trace of gallic acid.

MALIC ACID is contained in the juice of unripe apples and other fruits; it is uncrystallizable, forming when evaporated merely a thick liquor, which, if the heat be continued, becomes charred. By this and by the properties of the salts which it forms, it is principally distinguished from the other vegetable acids. By nitric acid it is converted into oxalic acid.

**CITRIC ACID** often accompanies the malic acid in the juices of unripe fruits, and it exists in a purer form in the juice of the lemon and lime: from these it is usually extracted, the mucilaginous matter of the juice being separated by alcohol. It crystallizes in rhomboidal prisms; which, when it is pure, are colourless; its taste is extremely sour: it is abundantly soluble in water; its solution undergoes spontaneous decomposition, but the crystallized salt can be preserved without injury. The more powerful acids decompose it, converting it principally into acetic acid.

**OXALIC ACID** exists in the juice of the sorrel (*oxalis acetosella*) and some other plants, combined with a portion of potash, not sufficient to neutralize it. It can also be artificially formed by subjecting fecula, gum, or sugar to the action of nitric acid. It crystallizes in slender prisms of a white colour; its taste is extremely sour; it is soluble in twice its weight of cold water, and an equal weight of boiling water; it is also soluble in alcohol. It is decomposed by the more powerful acids: in its decomposition by heat, it affords little empyreumatic oil; hence it appears to contain only a small portion of hydrogen; and as some of the other vegetable acids are converted into it by the action of nitric acid, there is probably a large proportion of oxygen in its composition. The test by which it is peculiarly distinguished, is the insoluble precipitate it forms with lime, an earth to which its affinity is such that it attracts it from all the other acids.

**TARTARIC ACID.** This acid, as it exists in vegetables, is usually combined with potash, in such a proportion, however, as to leave an excess of acid in the combination. This forms the super-tartrate of potash, which is contained in a number of vegetable fruits. It is deposited from the juice of the grape in its conversion into wine, or in the slow fer-



mentation which the wine suffers when kept. The acid procured from this salt is in tabular crystals, transparent; they are very soluble in water, the solution when concentrated being of an oily consistence. It is decomposed by heat, affording a large quantity of liquid acid little changed, with much carbonic acid gas. By nitric acid repeatedly distilled from it, it is converted into oxalic acid. This acid is an important one in pharmacy, from the numerous combinations of it applied to medicinal use.

**BENZOIC ACID** is obtained from the vegetable balsams, generally by the process of sublimation. It condenses in slender crystals, white and brilliant. It is volatile, and its vapour is inflammable; it is very sparingly soluble in cold water, but abundantly in hot water; the solution on cooling depositing nearly the whole of the acid in prismatic crystals: it is also soluble in alcohol, from which it is precipitated by cold water; it is pungent, but not very acid to the taste; in its usual state its smell is fragrant, especially when it is heated; but this odour has been supposed to arise from a minute portion of the oil of the balsam adhering to it; as by repeated combinations with an alkaline base, and precipitation by an acid, it is obtained at length inodorous. It is not easily decomposed by the action of the more powerful acids. Decomposed by heat, it affords a larger quantity of empyreumatic oil than any other vegetable acid, whence hydrogen is supposed to predominate in its composition.

**ACETIC ACID.** This acid is more exclusively the product of fermentation; it exists likewise, however, ready formed in the sap of the vine, and, combined with alkalis and earths, in the sap of plants. In its pure and concentrated state, in which state it can be procured only by artificial processes, it is a very powerful acid, highly pungent and fragrant, volatile and inflammable. It is distinguished by the peculiar

action it exerts on some of the other proximate principles of plants,—essential oil, resin, gum-resin, camphor, gluten, and caoutchouc, which it dissolves without decomposing. Hence, even in its diluted state, under the form of distilled vinegar, it is sometimes used as a solvent in pharmaceutic processes; though it is seldom that it can be employed to advantage, as it is liable to modify the powers of the substances it dissolves.

**PRUSSIC ACID.** The substance to which this name is given, is formed from some varieties of animal matter by artificial processes. It had often been remarked, that its odour is similar to that of the peach blossom, and that the same odour is perceptible in the distilled water of the cherry laurel, and of the bitter almond. This led to experiments on these; whence the fact, rather singular, has been discovered, that all of them contain this acid. The fact, not less important, has been established, that the narcotic property possessed by these distilled waters, depends on the prussic acid. In its insulated state, this substance is volatile, so that it escapes even from its watery solution under exposure to the air. It has no sensible sourness, and does not redden even the more delicate vegetable colours. The character of acidity is therefore given to it, rather from its powers in the combinations it forms, especially those with the metallic oxides, than from its properties in its insulated state,—these compounds being strictly analogous to other saline combinations.

Several of the vegetable acids, particularly the citric, malic, and tartaric, exist in the same vegetable, and in proportions varying according to the stage of vegetation, whence it is probable that they are mutually convertible. They are seldom pure, but generally in combination with saccharine, mucilaginous, and extractive matter. Combined with alkali-

line and earthy bases, they form what have been named the essential salts of plants.

The last of the proper proximate principles of vegetables is **LIGNIN**, or wood; the substance which, composing the vessels of the plant, is the basis through which the other principles are diffused, or to which they are attached, and which is the basis therefore of all the parts of vegetables, with the exception of their secreted juices. It is, when freed from the principles diffused through it, insipid, inert, and insoluble, liable in a humid state to slow spontaneous decomposition, inflammable, and is decomposed by heat, leaving a large residuum of charcoal, which indicates carbon to be its predominant ingredient, whence probably arises its solidity and comparative chemical inactivity. Being insoluble in water, or in alcohol, it forms the greater part of the residuum, when the active matter of vegetable substances has been abstracted by maceration in these solvents.

Besides the principles which can thus be obtained in a distinct form from vegetables by analysis, there are others of a more subtle nature, the existence of which has been supposed to be established by some facts, though they are scarcely capable of being exhibited in an insulated state; such are the **Aroma** or **Spiritus Rector** of plants, the **Acrid Principle**, the **Bitter Principle**, and the **Narcotic Principle**.

The **AROMA** is the principle in which the odour of plants has been supposed to reside. This quality is generally found in the essential oil; but there are some vegetables, having a strong odour, which yield little or no essential oil, such as the jessamine, the violet, or the rose; or, if this oil be procured from them in small quantity, it has not that strength of odour which, considering their fragrance, and the smallness of its quantity, might be expected from them. They exhale this odour, however, when exposed to the air; it is

at length dissipated ; or it is communicated to water by distillation at a very gentle heat. Hence it has been concluded, that a principle more subtle than the essential oil exists in which the odour resides, and that it is even this principle which communicates odour to the oil.

These facts, however, are inconclusive. The property of odour may belong to any of the proximate principles of vegetables, and does belong to principles of very different kinds ; it exists in other bodies in which we cannot suppose the existence of any common principle ; nor is there any reason to assume the existence of such a principle in plants : and all the facts considered as favourable to the opinion, are accounted for on the supposition that essential oil is the more common principle of odour, and is capable of being volatilized in small quantity at a low temperature, and of thus being diffused through the atmosphere, or communicated to water.

The existence of an Acrid Principle has been inferred from an acrimony residing in some plants, which they lose on drying, while their other active powers remain ; and from this acrimony being in some cases transferred to water or alcohol by distillation. It is not very certain, however, if this quality is not in such cases connected with some of the known proximate principles ; nor has this acrid principle, if it do exist, been obtained so as to submit it to chemical examination.

**BITTER PRINCIPLE.** A principle of bitterness has been supposed to exist in some vegetables. It is obvious, however, that this quality may belong to any of the known proximate principles ; and the characters which have been assigned to this principle as it exists in some of the purest vegetable bitters, particularly in gentian or quassia, such as equal solubility in water and in alcohol, and being precipitated by cer-

tain re-agents, rather prove it in these cases at least to be a variety of extractive matter.

A Narcotic Principle has been supposed to exist, from the narcotic power of some vegetables being impaired by age, without any apparent loss of matter, and from its being rendered inert by decoction, though no volatile matter is collected possessed of the quality. But such facts are rather favourable to the conclusion, that the loss of power is owing to chemical changes in one or other of the known principles, probably the extract, in which the narcotic quality may be supposed to reside. In submitting opium to analysis, it has been affirmed, that a crystalline matter is obtained, which proves narcotic, and has been supposed to be the principle on which that quality possessed by the opium depends. But it does not, admitting its existence, appear to be possessed of the narcotic property in that high degree we should expect, were it the principle on which that property is dependent, nor is there any proof that it exists in any other narcotic.

The existence of all these principles, therefore, is problematical; and the qualities assigned to them may, with more probability, be referred to modifications of composition in the known vegetable principles, which are probably too subtle to be determined by chemical analysis.

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ALCOHOL, and the ETHERS formed from Alkohol by the action of acids, cannot strictly be regarded as vegetable products; yet they have a relation to these, as their chemical constitution is similar, and they cannot be formed but by changes produced in vegetable matter. As important, medicinal, and pharmaceutic agents, they are entitled to notice.

ALCOHOL is formed by the process of fermentation from saccharine matter, or from fecula, the latter being previously subjected, partially at least, to the operation of malting, by which it is converted into the former. The fermented liquor being distilled, affords alkohol diluted with water, and with some impregnation of odour from the fermented substance. From this pure alkohol is procured by repeated distillation, the abstraction of the water from it being aided by the action of potash, or sub-carbonate of potash.

Alkohol is a colourless transparent fluid, having a specific gravity, according to its state of concentration, from 0.835 to 0.800; it is fragrant and pungent, and in its action on the living system exerts a high degree of stimulant and narcotic power; it is volatile and inflammable, affording, during its combustion, water and carbonic acid, the quantity of water exceeding even the weight of the alkohol. It contains, therefore, much hydrogen in its composition, with which carbon is combined, and perhaps also a portion of oxygen. It combines with water in every proportion, and, in consequence of the affinity between these fluids, they mutually precipitate substances which either has dissolved, that are insoluble in the other. It is decomposed by the acids, affording, as the principal product, the different ethers. As a pharmaceutic agent, it is of much importance from the solvent power it exerts on a number of the vegetable proximate principles,—essential oil, camphor, extract, and others, and from its property too of counteracting the spontaneous changes to which vegetable matter is liable.

ETHER. The name Ether is given to a peculiar product obtained by the action of the more powerful acids on alkohol, the product differing in its properties according to the acid employed in its formation, but in general being extremely light, volatile, and inflammable. Sulphuric ether, formed by

the action of sulphuric acid on alkohol, has a specific gravity not greater, when it is pure, than 0.716 ; it is so volatile as to evaporate rapidly at the common temperature of the atmosphere ; in burning it affords water and carbonic acid : its odour is fragrant and penetrating ; its taste pungent ; it is soluble in water only in limited proportion, about one part in ten. It exerts on the vegetable principles the same solvent action nearly as alkohol, except on extract, which it has been said to precipitate,—an effect, however, I have not been able to obtain from it. Nitric ether is equally light and even more volatile ; it is inflammable ; it is soluble in water in limited quantity, but combines with alkohol in every proportion : its odour is strong and penetrating. Muriatic ether is more volatile than either ; it exists in the state of gas, under the atmospheric pressure, at  $60^{\circ}$  ; at  $50^{\circ}$  it becomes liquid, and its specific gravity is not less than 0.874 ; it is transparent, colourless, odorous, and pungent. Acetic ether is moderately light, volatile, and inflammable, soluble in water in limited quantity, and has an odour ethereal, but approaching also to that of vinegar. All these ethers appear to differ from alkohol, principally in having a larger proportion of hydrogen in their composition, to which probably their greater levity and volatility are to be ascribed ; and they generally contain a portion of the acid by the action of which they have been formed, which, in some of them at least, appears essential to their chemical constitution.

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HAVING pointed out the distinguishing properties, and the general pharmaceutic relations of the Proximate Principles of Vegetables, it may be proposed as a question important in relation to the object of the present outline,—Do these

principles usually exist in the vegetable in a state of chemical combination, whence some modification of their powers may result, or are they more generally mechanically mixed?

The latter appears to be generally the case. These principles can often be observed existing apart from each other, and even placed in separate vesicles; they can in many cases be separated by mechanical means; and even where they are more intimately mixed, that change of properties does not take place, which we must have expected were they chemically united, the virtues of each principle being discernible in the entire mixture, weakened, but not changed. It seems to follow, therefore, that the virtues of vegetable substances do not depend on chemical combinations of their proximate principles, but rather on the peculiar ultimate composition of one or other of these principles. Hence also it is evident, that in separating the proximate principles of any vegetable, we cannot expect to alter or improve its virtues, farther than in concentrating them by a separation from what is inert, or in separating principles which are possessed of different or even opposite powers. The attainment even of these ends, however, is, in innumerable cases, of importance in their exhibition as medicines.

From this enumeration of the Proximate Principles of Vegetables, may be explained the rationale of those pharmaceutical processes to which plants are usually subjected.

Vegetable matter being liable to decomposition when in a humid state, from the re-action of its elements, and their entering into new combinations, Exsiccation is an operation to which they are generally subjected, to preserve them without injury. It is performed either by the action of a current of air, or by exposure to heat, care being taken that the heat shall not be such as to dissipate any of their volatile principles, or cause any chemical change.



Inspissation is an operation performed on the expressed juices of plants, with the same view, the dissipating the watery portion of the juice, and thus communicating to it a thick or solid consistence, rendering it less liable to those spontaneous chemical changes which it would otherwise undergo. It is performed by the application of a gentle heat.

By infusion of vegetable matter in water, the fluid is impregnated with the gum, sugar, extract, tannin, saline substances, part of the essential oil, and part also of the resinous principle. The aroma of the plant is generally first taken up: by longer infusion the water is loaded with the colouring, astringent, and gummy parts: these are also most abundantly dissolved when the temperature is high. Hence an infusion differs according as the water has stood longer or shorter on the materials, and according as it has been promoted or not by heat. An infusion made in the cold is in general more grateful, while one made with heat, or by keeping the fluid long upon the materials, is more strongly impregnated with active matter.

By Decoction or boiling, the solvent power of the water is still farther increased; and hence the liquor always appears darker coloured, and it is more loaded with those principles of the vegetable which it can hold dissolved. Those, however, which are volatile, particularly the essential oil, are entirely dissipated; and therefore it is an improper process for vegetables, the virtues of which depend, wholly or partially, on these principles. Even some of the fixed principles of vegetables are injured by long decoction. The extractive matter, for instance, gradually absorbs oxygen from the atmosphere, and is converted into a substance nearly insipid and inert. Opium, Peruvian bark, and many other vegetables, are injured in this manner by decoction, especially if the atmospheric air is freely admitted; and these two circum-

stances, the dissipation of the volatile matter, and the oxygenation of the extractive, considerably limit the application of this process. It is still used, however, with advantage, to extract the mucilaginous parts of vegetables, their bitterness, and several others of their peculiar qualities.

Alcohol may be applied to vegetables to dissolve those principles which are not soluble in water, such are their essential oil, camphor, and resin; and as these are often the principles on which the virtues of vegetables depend, these solutions, or Tinctures as they are termed, are often active preparations.

Equal parts of alcohol and water, in general, extract still more completely the active matter of plants, as we thus obtain a solution of all those substances which are separately soluble in either of these fluids.

When, by the action of one or both of these fluids, a solution of the active principles of a vegetable is obtained, it may be evaporated to the consistence of a thick tenacious mass. This forms what is termed an Extract: it is named an Aqueous Extract when obtained from the aqueous infusion or decoction of a plant, and Spiritous when alcohol has been the solvent. The design of this preparation is to obtain the active matter of the vegetable in a small bulk, and in such a state that it may be preserved without suffering any alteration. It is evident, that it is a process which can be properly applied to such plants only as have their virtues dependent on some of their fixed principles, and even these are often injured by the heat applied, and the free access of the atmospheric air.

Distillation is another process applied to vegetable substances, by which we obtain some of their active principles, particularly their essential oil. If the vegetable matter be heated with a large portion of water, the oil is volatilized

with the aqueous vapour: it separates from the water on being allowed to remain at rest; a part of it, however, is also dissolved, and communicates a considerable degree of flavour, and often also of pungency. This forms what are named *Distilled Waters*. If alcohol be used instead of water, the essential oil is entirely dissolved in it, and we thus obtain what are termed *Distilled Spirits*.

By such processes we extract the active matter of vegetables from the inert matter with which it is more or less mixed, and are thus enabled to administer many remedies under a variety of forms, suited to particular circumstances. A single example will shew the utility of investigations of this kind, respecting the component principles of vegetable products, and their relations to the more important chemical agents. Peruvian bark is one of the most important remedies in the *Materia Medica*. It is not always, however, practicable to exhibit it in substance with advantage, as where the stomach is uncommonly irritable, or where, from the nature of the disease, it is necessary to give it in large doses, frequently repeated, it is liable to occasion sickness and other uneasy sensations, and even to be rejected by vomiting. Such inconveniences are attempted to be obviated, by giving it in the different forms of infusion, decoction, tincture or extract, as any of these may be best suited to the case. Our knowledge of its constituent parts can only lead us to the proper application of these processes. From an accurate analysis of this bark, it has been proved that seven parts out of eight consist of woody fibre, or of a matter inert and insoluble, which cannot act on the system, and which affects the stomach only by its weight and insolubility. The remaining eighth part is that in which the activity of the medicine resides: it is therefore evident, that if this be extracted, without injuring its activity, the medicine could

be exhibited with much more advantage. This is in part accomplished by the preparations of it that have been mentioned; but even these do not convey it in all its force. If the bark be infused or boiled in a certain quantity of water, the infusion or decoction is not nearly equal in efficacy to the whole quantity operated on. It is therefore evident, that during either of these operations, the active matter has not been entirely extracted, or has suffered some change. And here Chemistry farther elucidates the peculiar nature of this substance, and the changes produced in it by these processes. It has been found, that the matter on which the power of this bark depends is liable to oxygenation, and that, during the infusion, and particularly the decoction of that drug, it suffers this change from the action of atmospheric air, and is converted into a substance insipid and inert. This leads to the improvement of the preparations of this medicine; and experiments instituted for the purpose have accordingly proved, that, while by long boiling the virtues of the bark are nearly destroyed, they are extracted with less loss by a few minutes' decoction in covered vessels. The same investigations have pointed out the nature of the action of some other substances on bark, formerly not well understood. Thus, it had been found by experience, that the alkalis, and more particularly magnesia, enable water to extract the virtues of bark more completely by infusion,—a circumstance elucidated by the fact afterwards discovered, that the extractive matter of the bark, to which its activity is owing, combines with facility with these substances, and forms soluble compounds.

Similar examples might be given from other important vegetable remedies, which would sufficiently prove the utility to be derived from the analysis of the substances belonging to the vegetable kingdom, and that indeed researches of this

kind are absolutely necessary for their proper preparation as medicines.

The account of the analysis of animal substances, and of their proximate principles, would, to the same extent at least, be foreign to the objects of this sketch, as so few of these substances are employed in medicine; and of those which are used, the composition, and consequently the pharmaceutical treatment, are in a great measure peculiar to each.

Their general chemical characters are similar to those of vegetable principles.—Composed of a few ultimate elements, the differences in their properties arise in a great measure from the different proportions, or the different modes in which these are combined. And these elements having powerful reciprocal attractions, and being disposed to enter into combinations almost indefinitely diversified, these substances are extremely susceptible of decomposition, from the re-action of their elements, favoured by humidity, by the action of the air, or by elevation of temperature. They are even more liable to this than vegetable substances; for the elements existing in simultaneous combination are more numerous, their affinities are therefore more nicely adjusted, and of course the equilibrium is more easily subverted.

Along with carbon, hydrogen, and oxygen, which are the chief constituent principles of vegetable matter, nitrogen, and frequently sulphur and phosphorus, enter into the composition of animal substances. Hence, when decomposed by heat, they afford products composed of these, of which ammonia is always the principal; and the re-action of these principles, and the evolution of the products arising from this, seem principally to form the series of changes which constitute putrefaction, the species of spontaneous decomposition to which animal matter is more peculiarly subject.

Like vegetable substances, the animal products consist of various proximate principles, and some analogy may be traced between several of the vegetable and animal proximate principles. Animal fat has a strict connection in properties and composition with fixed oil; animal mucus resembles vegetable mucilage; fecula has a similar relation to gelatin; vegetable and animal gluten are nearly if not entirely the same: a substance similar to saccharine matter exists in milk, and in some of the other animal secretions: in the bile is found a principle strictly analogous to resin; and benzoic, oxalic, and acetic acids are common to both. Hence, generally speaking, the few animal substances belonging to the *Materia Medica* are acted on by the usual solvents in nearly the same manner as vegetable substances, and are submitted to similar pharmaceutic processes. The results of these are similar officinal preparations. Thus, by the action of alcohol, the active matter of musk, castor, and cantharides is extracted, and tinctures of these are employed. In other cases water is the proper solvent, particularly of those which consist of gelatin; but such solutions being very liable to decomposition, must always be of extemporaneous preparation.