## CHAP. II.

### OF THE PHARMACEUTICAL OPERATIONS TO WHICH THE ARTICLES OF THE MATERIA MEDICA ARE SUBJECTED.

NATURAL substances, it has been remarked, are not always obtained in that state in which they are best adapted to exhibition as remedies. They are subjected, therefore, to various processes, with the view of preserving them, or of preparing them for use; and to complete this statement of the Principles of Pharmaceutic Chemistry, the nature of these is to be pointed out.

These processes, or at least the greater number, and the most important of them, are chemical, and are dependent therefore on the agencies of those general forces whence chemical changes arise; they are indeed little more than applications of these, under peculiar regulations adapted to different substances. The general facts, therefore, connected with the operation of these forces, are first to be stated, in so far as they have any relation to the present subject.

The force principally productive of chemical action, is that species of attraction exerted between the particles of bodies, which brings them into intimate union. If two substances of different kinds be placed in contact, and with that degree of fluidity which admits of the particles of the one moving to those of the other, it often happens that they unite together, and form a substance in which neither can be any longer recognised, and which is homogeneous, and in general possessed of new properties. This constitutes what, in the language of Chemistry, is named combination, and is conceived to arise from an attraction exerted between the particles of the one body to those of the other. It is this which is denominated Chemical Attraction or Affinity, and which is distinguished from the other species of attraction by the phenomena to which it gives rise, or by the laws it obeys,—from the attraction of gravitation, by not being exerted at sensible distances, or on masses of matter, but only at insensible distances, and on the minute particles of bodies,—from the attraction of aggregation, by being exerted between particles of different kinds, and forming a substance with new properties, while that force operates on particles of a similar nature, and of course unites them into an aggregate in which the same essential properties exist. It is possible that these forces, though thus distinguished, may be the result of the same power modified by the circumstances under which it acts.

The substance formed by chemical combination is named a compound. The substances united are the constituent or component parts or principles of the compound. When these are separated, the process is named decomposition. The most minute parts into which a body can be resolved without decomposition, are named its integrant parts; and it is between these that the force of aggregation is conceived to be exerted. Chemical attraction is exerted between the constituent parts.

The most important phenomenon attending chemical combination is a change of properties. In general, the form, density, colour, taste, and other sensible qualities, as well as the fusibility, volatility, tendency to combination, and other chemical properties in the compound, are more or less different from what they are in either of its constituent parts, and frequently indeed they are wholly dissimilar. There are cases, too, however, where the change is less considerable, as is exemplified in several of the operations of Pharmacy,—the solution of the vegetable proximate principles in water or in alkohol, or the solution of salts in water, in which the body acquires merely the liquid form, with perhaps a slight change of density, but in which no important property is changed, nor any new one acquired.

Chemical attraction is not an invariable force exerted by every body to every other, and always with the same degree of strength. Between many substances, it does not sensibly operate, though this perhaps may be owing to the predominance of external circumstances, by which its operation is influenced, rather than to the absence of all mutual attraction. It is exerted too by each body towards others, with different degrees of strength.

It is not limited in its action to two bodies, but is frequently exerted at the same time between three, four, or a greater number, so as to unite them in one combination. Such compounds are named Ternary, &c. according to the number of their constituent principles; they are abundant among the productions of nature, and can be formed also by the arrangements of art.

This force is exerted too, so as to combine bodies in more than one proportion; and, from the union of two substances in different proportions, compounds are formed frequently as dissimilar in their properties as if they were composed of principles totally different. In some cases, the combination is unlimited with regard to proportions; in others, it is fixed to two or three relative quantities, and there are examples where it can be established in only one proportion. The opinion has been maintained, and is probably just, that the tendency of chemical attraction is to unite bodies indefinitely with regard to proportion, and that determinate proportions are established only by the operation of external forces.

The compounds formed by the exertion of chemical attraction have apparently the same relation to this power as simple bodies have: they have a similar tendency to combination, unite in different proportions, and with different degrees of force; and all these combinations are accompanied by the same phenomena, and appear to observe the same laws. It has been supposed, however, that when compound substances combine together, the combination is the result, not of the mutual attraction between the integrant particles of these compounds, but of the affinities of their ultimate elements modified by the condition in which they exist.

In all cases, attraction is much modified, and its results determined by circumstances foreign to the attractive force itself. The operation of these circumstances has been established with more precision by the labours of Berthollet, and been proved to be more important than was formerly believed. They require, therefore, more distinct enumeration, especially as some of them give rise to important results in the processes of Pharmacy.

*1st*, Quantity of matter influences affinity, an increase in the relative quantity of one body with regard to another enabling it to act with more force; or, as the law has been stated, "every substance having a tendency to "enter into combination, acts in the ratio of its affini- "ty and its quantity." Hence an effect can be produced from the mutual action of two bodies, when one is in a certain relative proportion to the other, which will not be obtained when the proportion is changed,—a circumstance of much importance in Pharmacy, requiring, in particular, attention towards insuring the uniform strength of active preparations; and of much influence too on the results of chemical decomposition, rendering it frequently partial, where it was supposed to be complete.

*2d*, COHESION, or the state of a body with regard to the aggregation of its integrant particles, must obviously modify the chemical action of another body upon it, by opposing a resistance which must be overcome before the union of their particles can be effected; hence the cause, that two solid bodies seldom act chemically on each other, and that fluidity promotes chemical action. But besides this obvious effect, cohesion, even when it has been overcome, still modifies the exertion of chemical attraction, by resuming its force whenever the force of that attraction is diminished, and thus sometimes giving rise to new combinations; and sometimes too, when suddenly established in consequence of the affinities becoming effective, it determines the proportions in which bodies combine, by insulating the compound at a certain stage of the combination. It is thus the most powerful cause in placing limits to the exertion of chemical attraction. INSOLUBILITY is merely the result of the force of cohesion, in relation to the liquid which is the medium of chemical action, and its action is of course similar; and great DENSITY, or specific gravity, so far as it influences attraction, operates in nearly the same manner, counteracting it, by withdrawing the substances between which it is to be exerted from the sphere of mutual action.

3*d*, ELASTICITY, or that property of bodies arising from repulsion between their particles, and present to any extent only in those existing in the aëriform state, opposes the exertion of chemical attraction, by enlarging the distances at which these particles are placed. Hence aërial fluids combine in general with difficulty; and hence too, a compound which contains an ingredient which, when insulated, assumes the aërial state, is more easy of decomposition, and the decomposition is more complete, than a compound, the ingredients of which are fixed;

for the tendency to elasticity in the volatile ingredient counteracts the mutual affinity; and when, by the application of heat, or the operation of a superior attraction, any portion of it is displaced, by assuming the elastic form it is withdrawn from the sphere of action, and ceases to oppose any obstacle by its affinity or quantity to the progress of the decomposition. Elasticity too, by counteracting attraction, places limits to the proportions in which bodies combine.

*4th*, The last circumstance influencing attraction is TEMPERATURE, or the state of a body with regard to heat or cold, which sometimes favours, and in other cases subverts combination. The cause of temperature is a peculiar subtle power or principle, (in modern chemical language denominated Caloric), capable of being communicated to bodies, and of being in part at least withdrawn from them. Its immediate tendency is to establish a repulsion between their particles; hence it gives rise to expansion or enlargement of volume, greater in each body according to the quantity of caloric introduced. This progressive augmentation of distance, at which the particles are placed by its action, is accompanied with a proportional diminution in the force of cohesion; if carried, therefore, to a certain extent, that force is so far modified, that the particles become capable of moving easily with regard to each other,—a state which constitutes fluidity; and, if the communication of caloric be continued, the expansion still continuing, the particles are at length placed at such distances, that the attraction is entirely overcome, and they repel each other,—a state which constitutes the aërial or gaseous form. The operation of caloric in influencing chemical attraction, appears to depend on the changes it occasions in the cohesion and elasticity of bodies,—favouring combination by diminishing cohesion, counteracting or subverting it by communicating or increasing elasticity; these effects too being often produced together, and modifying each other.

From the differences of the forces of affinity among bodies, or still more perhaps from the operation of those circumstances by which affinity is modified, its power is often suspended or overcome, and substances which have been combined are separated. This forms what in Chemistry is named Decomposition, and it presents results equally important with those from combination.

The decomposition may be simple, that is, a compound may be resolved into its constituent parts, each of which is insulated. This is in general effected by the agency of heat. Within a certain range of temperature, the affinity which has combined two bodies continues to operate; but when the temperature is raised, and when the bodies differ in their volatility, or the tendency they have to assume the elastic form, the elasticity of the more volatile one is so far favoured by the elevated temperature, that the mutual affinity is overcome, and it is disengaged. It is generally obtained pure; but the fixed substance, from the influence of quantity on chemical attraction, frequently retains a portion of the other combined with it.

Decomposition is more complicated when it is produced by the introduction of a third substance, which exerts an attraction to one of the ingredients of a compound. When this is effective, the body added combines with this ingredient, forming a new compound, and it is only the other ingredient of the original compound that is obtained insulated. A case still more complicated is, where two compound substances are brought to act on each other, and the principles of the one exert affinities to those of the other; so that an interchange takes place, the two compounds are decomposed, and two new ones are formed. Both these kinds of decomposition are likewise materially modified by the state with regard to temperature. The former case used to be named by chemists single elective attraction; the latter double elective attraction; and both were considered as the results of the relative forces of attraction among the bodies concerned. But there is reason to believe, that they arise from the operation of cohesion, elasticity, and the other forces that influence attraction; and that but for the operation of these forces, three or more bodies presented to each other would enter into simultaneous union, instead of passing into binary combinations.

Galvanism, as well as caloric, influences chemical affinity, and, by the attractive as well as by the repulsive force it exerts, is even more powerful in producing decomposition. It scarcely admits, however, of being applied to any pharmaceutic process.

The OPERATIONS of Pharmacy are generally dependent on these chemical powers; they consist of arrangements of circumstances, with the view either of promoting their exertion, or of obtaining the products of chemical action.

Some preliminary operations are frequently had recourse to of a mechanical nature, to diminish the cohesion of bodies, or enlarge their surface. Such are Pulverization, Trituration, Levigation, Granulation, &c. PULVERIZATION is the term employed where solid bodies are reduced to powder by beating: TRITURATION that where the same effect is produced by continued rubbing. LEVIGATION denotes the operation where the powder is rubbed to a still greater fineness, the rubbing being facilitated by the interposition of a fluid, in which the solid is not soluble. As by any of these operations, the powder must consist of particles of unequal size, the finer are separated from the coarser by sifting or washing. Sifting is passing the powder over a sieve, the interstices of which are so minute as to allow only the finer particles to pass. WASHING or ELUTRIATION, is an operation performed only on substances which are not soluble in water. The powder is diffused through a quantity of that fluid, and the mixture is allowed to remain at rest. The coarser particles quickly subside, and the finer remain suspended. It is then decanted off, the powder is allowed to subside, and is afterwards dried. These methods of reducing bodies to powder, can be applied to very few of the metals, their force of cohesion being too strong. They are mechanically divided by rasping, or by being beat into leaves, or they are granulated,—an operation performed by melting the metal, and when it is cooled down as far as it can be, without becoming solid, pouring it into water: it passes to the solid state, assuming the granular form.

In Pharmacy, these operations are sometimes of importance, besides merely promoting chemical combination, as there are some medicines which act with more certainty, and even with more efficacy, when finely levigated, than when given in a coarse powder.

As means of promoting chemical combination, it is evident, that they can act only indirectly; the bodies being far from being reduced to their minute particles, between which only chemical attraction is exerted. They are therefore employed, merely as preliminary to those operations in which such a division is obtained by chemical means.

Of these, the first is SOLUTION. By this is understood that operation in which a solid body combines with a fluid in such a manner that the compound retains the fluid form, and is transparent. Transparency is the test of perfect solution. When the specific gravity of a solid body differs not greatly from that of a fluid, it may be diffused through it, but the mixture is more or less opaque; and on being kept for some time at rest, the heavier body subsides; while in solution the particles of the solid are permanently suspended by the state of combination in which they exist, and are so minute as not to impair the transparency of the liquid.

The liquid has, in this case, been regarded as the body exerting the active power, and has been named the Solvent or Menstruum; the solid is considered as the body dissolved. The attraction, however, whence the solution proceeds, is reciprocal, and the form generally proceeds from the larger quantity of the liquid employed, and from the absence of cohesion being more favourable to the combination proceeding to a greater extent.

In general, the solution of a solid in a liquid can be effected only in a certain quantity. This limitation of solution is named Saturation; and when the point is reached, the liquid is said to be saturated with the solid. As the fluid approaches to saturation, the solution proceeds more slowly. When a fluid is saturated with one body, this does not prevent its dissolving a portion of another; and in this way three, four or five bodies may be retained in solution at the same time by one fluid. In these cases, the fluid does not dissolve so large a proportion of any of these substances, as if it had been perfectly pure, though sometimes the whole proportion of solid matter dissolved is increased from the mutual affinities the bodies exert. Neither is the solvent power always thus limited, there being many cases where a solid may be dissolved in a fluid to any extent. Gum or sugar, for example, will dissolve in water, and form a perfect solution in every proportion.

An increase of temperature, in general, favours solution, the solution proceeding more rapidly at a high than at a low temperature; and in those cases in which a certain quantity only of the solid can be combined with the fluid, a larger quantity is taken up when the temperature is increased. The quantity dissolved is not in every case promoted alike by an increase of temperature; water, for example, having its solvent power, with regard to nitre, greatly increased by augmentation of temperature, while sea salt is dissolved in nearly as great a quantity by water at a low as at a high temperature. This difference in these salts, and in many others, depends on the difference in the degree of their fusibility by heat; those which are most easily fused having their solubility in water most largely increased by increase of temperature. All these facts, indeed, with regard to solution, are explained, by considering this operation as depending on chemical affinity overcoming cohesion in the body dissolved.

Agitation favours solution, by bringing successively the different parts of the liquid into contact with the solid, and thus preventing the diminished effect which arises from the approach to saturation in the portion immediately covering the solid. The mechanical division of a solid too, is favourable to its solution, principally by enlarging the surface which is acted on.

Solution is an operation frequently had recourse to in pharmaceutical chemistry, the active principles of many bodies being dissolved by their proper solvents. Salts are dissolved in water, as are also gum, extract, and other vegetable products. Products of a different kind, as resin, camphor, and essential oils, are dissolved in alkohol and wine; and metals are rendered soluble and active by the different acids. Solutions in water, alkohol, or wine, possess the sensible qualities and medical virtues of the substance dissolved. Acid and alkaline liquors change the properties of the bodies which they dissolve. In Pharmacy, the operation receives different appellations, according to the nature of the solvent, of the substance dissolved, and of the manner in which it is performed. When a fluid is poured on any vegetable matter, so as to dissolve only some of its principles, the operation is named EXTRACTION, and the part dissolved is said to be extracted. If it is performed without heat, it is termed MACERATION; if with a moderate heat, DIGESTION; if the fluid is poured boiling hot on the substance, and they are kept in a covered vessel till cold, this is denominated INFUSION. DECOCTION is the term given to the operation when the substances are boiled together. It is evident, that these are all instances of solution, varied only by particular circumstances; and I have already stated, under the analysis of the vegetable part of the Materia Medica, the advantages belonging to each. LIXIVIATION is the term applied to solution performed on saline substances where the soluble matter is separated, by the action of the solvent, from other substances that are insoluble; and the solution obtained in this case is named a LEY.

The other principal method by which that fluidity necessary to chemical action is communicated, is FUSION. It requires, merely with regard to each substance, the necessary degree of heat; and where this is high, it is performed usually in crucibles of earthen ware, or sometimes of black lead, or on a large scale in iron pots.

Chemical combination is frequently promoted by an elevation of temperature, though the heat may not be so high as to produce fusion, but only to diminish cohesion to a certain extent. CALCINATION, as it used to be named, or metallic oxidation, is an example f this; a metal being heated to a high temperature, so as to enable it to combine with the oxygen of the air. DEFLAGRATION is a similar operation, an inflammable or metallic substance being exposed to a red heat in mixture with nitre: the acid of the nitre yields its oxygen; which being thus afforded in large quantity and nearly pure, the oxidation takes place with rapidity, and generally to its *maximum*.

When chemical action has been exerted, other operations are sometimes required to obtain the product, or sometimes this product is formed and collected in the operation itself.

By EVAPORATION, or dissipating a liquid by the application of heat, a solid substance which has been dissolved in it is recovered, and this operation is one frequently performed in Pharmacy. When performed on a small scale, vessels of glass, or of earthen ware, are generally employed, and the heat is applied either by the medium of sand, or, if it is required to be more moderate, the vessel is placed over water which is kept boiling, forming what is named the Water Bath, or *Balneum Mariæ*. When performed on a larger scale, shallow iron pots or leaden troughs are used, to which the fire is directly applied; and experiments have shewn that the operation is conducted more economically when the liquor is kept boiling strongly, than when it is evaporated more slowly by a more gentle heat. There is, on the other hand, however, some loss, from part of the dissolved substance being carried off when the heat is high, by its affinity to the liquid evaporating; and in many cases in Pharmacy, particularly in the evaporation of vegetable infusions or tinctures, the flavour, and even the more active qualities of the dissolved substance, are liable to be injured, especially towards the end of the operation, by a strong heat.

When the object is to obtain the volatile matter by evaporation, the process is of course conducted in close vessels adapted to condense the vapour and collect the liquid. This forms the operation of DISTILLATION, which, with regard to different substances, requires to be conducted in various modes.

When a volatile principle is to be obtained from vegetable substances by this process, the difficulty is to apply the heat sufficiently without raising it too high. The mode generally employed is to heat the vegetable matter with water, and the distillation is then usually performed in the common still. At the heat of boiling water, the essential oil of plants, which is the chief volatile principle they contain, is volatilized; it rises with the watery vapour; is condensed; if little water has been employed, the greater part of the oil is obtained apart; if much has been used, it retains it dissolved, acquiring taste and flavour, and thus forming the distilled water of plants. If alkohol, pure or diluted, has been the medium of distillation, it always retains the oil in solution, and forms what are named Distilled Spirits. The still in which the operation is performed with these views is of copper or iron; it consists of a body and head, the former designed to contain the materials, and to which the fire is applied, the latter to receive the vapour; there issues from it a tube, which is connected with a spiral tube, placed in a vessel, named the refrigeratory, filled with cold water. The vapour, in its progress through the tube, is condensed, and the liquid drops from the extremity of it.

When metallic matter would be acted on, by the materials or the product of distillation, vessels of glass or earthen ware are employed; the retort, which is generally used, being connected with a single receiver, or with a range of receivers, according as the vapour is more or less easily condensed; or, if the product is a permanently elastic fluid, which cannot be condensed but by passing it through water, a series of bottles connected by tubes, on the principle of Woolfe's apparatus, is used. When the product obtained by distillation is not perfectly pure, it can be frequently purified by a second distillation; the process is then named *Rectification:* when it is freed from any superfluous water combined with it, the operation is named *Dephlegmation* or *Concentration.*

When the product of volatilization is condensed, not in the liquid, but in the solid form, the process is named SUBLIMATION, and the product a Sublimate. As the condensation takes place with much more facility, a more simple apparatus is employed, consisting usually of a conical bottle or flask with a round bottom, thin and equal, named a Cucurbit, in which the materials are contained, heat being applied by the medium of a sand bath. The vapour condenses in the upper part of the flask, forming a cake, which adheres to it, the orifice being lightly closed to prevent any part from being lost; or a globular head, with a groove at its under edge, and a tube to convey off any liquid that may be condensed, (a Capital as it is named), being applied.

When a solid substance is thrown down from a liquid by chemical action, it forms the operation of PRECIPITATION, and the matter thrown down is named a Precipitate. Frequently the substance precipitated is one which had been dissolved in the liquid, and which is separated by a substance added, combining with the liquid, and weakening its attraction to the one which it held in solution. Or sometimes it arises from a compound being formed by the union of one body with another, which is insoluble in the liquid that is the medium of action. The precipitate is allowed to subside, is usually washed with water, and is dried. From the law of chemical attraction, that quantity influences the force of affinity, it often happens that the precipitate either retains in combination a portion of the substance by which it had been dissolved, or attracts a portion of the substance by which it is thrown down, and this sometimes proves a source of impurity, or of peculiar powers in medicinal preparations.

When a substance, in passing to the solid state, assumes a regular geometric form, the process is named CRYSTALLIZATION, and these figured masses are denominated Crystals. Their forms are various, though nearly constant with regard to each substance; they are usually transparent, hard, and have a regular internal structure. The crystallization may happen in two ways, from a state of solution. If a saturated solution has been prepared with the aid of heat, the increased quantity of the solid, which the heat has enabled the liquid to dissolve, separates as the temperature falls; and the attraction of cohesion being thus slowly exerted between the particles, unites them so as to form crystals. Or, if a portion of the solvent be withdrawn by evaporation, and especially by slow evaporation, the particles of the solid unite slowly, and with a similar result.

In both these kinds of crystallization from a watery solution, the crystallized substance always retains a quantity of water, and frequently even a considerable proportion, in its composition. It is essential to the constitution of the crystal, its transparency, structure and form, and is hence named the Water of Crystallization. Some crystals lose it from mere exposure to the air, when they are said to effloresce; others attract water, and become humid, or deliquesce.

Crystallization is promoted by the mechanical action of the air; likewise by affording a nucleus, whence it may commence, and especially a crystal of the substance dissolved; and with regard to a few substances, their affinity to the solvent requires to be diminished by the addition of another substance to enable them to crystallize.

In Pharmacy, crystallization is of importance, by enabling us to obtain substances, especially those belonging to the class of salts, in a pure form; different salts, even when present in the same solution, being thus separated by their different tendencies to crystallization, according as they are more or less soluble in the solvent, or have their solubility more or less promoted by heat, and each salt, when it does crystallize, being in general pure.

These are the principal operations of Pharmacy. Connected with this subject, there remain to be noticed the weights and measures which are usually employed. The division according to what is named Troy weight, is that ordered in the Pharmacopœias. Its parts, with the symbols by which they are denoted, and their relative proportions, are represented in the following table:

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| A pound | (libra), | ℔ | contains | 12 ounces. |
| An ounce | (uncia), | ℥ | contains | 8 drachms. |
| A drachm | (drachma), | ʒ | contains | 3 scruples. |
| A scruple | (scrupulus), | ℈ | contains | 20 grains (grana) gr. |

Measures have been subdivided in a similar manner, being made to correspond to the specific gravity of water. As the specific gravities of liquids vary, however, considerably, a source of error is introduced in applying the standard measure to different liquids, unless the due allowance be made for the difference in specific gravity. This it is to be presumed will often be neglected, and hence the Edinburgh College have rejected the use of measures, and given the proportions of every liquid by weight. The use of measures, however, in apportioning liquids, being more easy and convenient, will probably always be retained; and the London College have therefore, in the late edition of their Pharmacopœia, sanctioned their use. They adopt measures subdivided from the wine gallon, as represented with their symbols in the following table:

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| A gallon | (congius), | | contains | 8 pints. |
| A pint | (octarius,) | O | contains | 16 fluidounces. |
| A fluidounce | (fluiduncia), | f℥ | contains | 8 fluidrachms. |
| A fluidrachm | (fluidrachma), | fʒ | contains | 60 minims; (minima,) ♏. |

This last measure is one newly introduced. In apportioning liquids into very small quantities, the quantity has been usually estimated by drops (gutta, gtt.) allowed to fall from the edge of the mouth of a bottle; but the size of the drop is liable to vary much, not only according to the mobility and specific gravity of the liquid, a circumstance of little importance, since with regard to each substance it remains the same, but also according to the thickness of the edge and degree of inclination. The London College have therefore substituted this division of minims, which are measured in a slender graduated glass tube. The measures of a table and of a tea spoonful are sometimes used in extemporaneous prescription, and, though not very accurate, may be admitted where a small difference in the dose is not important. The one is understood to be equal to half an ounce by measure, the other to about one drachm.