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SECTION I.

THE agents which more generally influence chemical, and thence pharmaceutical combinations, are *Attraction* and *Repulsion.*

I. ATTRACTION.

ATTRACTION is the term employed to denote that force which causes bodies to approach towards each other, and which preserves them in a state of union after they come into contact. We are ignorant of the cause of this force, but some of the laws respecting it are sufficiently evident; and from observing the different phænomena to which these give rise, we are inclined to believe that there are different species of attractions, although, perhaps, the difference is more in degree than in kind.

When this force is exerted on masses of matter, at sensible

distances, and in the direct ratio of the quantity of matter, and the inverse one of the square of the distance, it is named *gravitation:* but when its operation is confined to the minute atoms of bodies, and is exerted only when these are near to each other, or in apparent contact, it is denominated *contiguous attraction.* The former preserves the planets in their orbits, and sustains in their places all the parts of the magnificent frame of the universe: the second is the cause of the regular figures of natural bodies, and of the various combinations of matter, which take place in and on the surface of our globe. It is this variety that we are here to examine.

CONTIGUOUS ATTRACTION, operating on particles of the same kind, forms an aggregate or mass; and hence, the power in this instance is named the *attraction of aggregation* or *cohesion:* but acting on dissimilar particles, and producing bodies possessed of new properties, different from those of their components, it constitutes *chemical attraction,* or *affinity.*

a. OF COHESION.

The attraction of *cohesion* is that power which retains together the particles of bodies at insensible distances. According to the degree of force which it exerts, substances assume the solid, the fluid, or the aëriform state. 1. In solid bodies this force is sufficiently powerful to prevent their component particles from being moved with regard to each other, except in a very small degree; and to oppose a considerable resistance to any mechanical power applied to separate them. In the same kinds of bodies, all the circumstances being equal, it is always the same; but in dissimilar bodies it is exceedingly various: from which, and the peculiar arrangement of the particles, arise the different qualities of solids, denominated hardness, softness, malleability, ductility, and elasticity.

The attraction of cohesion in solids is exerted at insensible distances only, and may be weakened or altogether overcome by caloric, or that matter which produces the sensation of heat. If a piece of ice, for example, be brought near a fire, the cohesion of its particles is weakened as the caloric flows into it, till it is changed from the solid state to the fluid, or water; and by continuing and increasing the heat, the particles are still further separated from each other, until the fluid passes into the gaseous form, or becomes steam. This power is also weakened by chemical affinity; as when a solid body is put into a fluid, the affinity between the particles of the fluid and those of the solid is often sufficient to overcome the aggregation of the solid; and its detached particles being uniformly diffused through the fluid, now form a part of it, without altering either its fluidity or transparency. This constitutes the ordinary chemical or pharmaceutical process of *solution,* which is

always favoured by the application of heat, owing to the assistance it affords in overcoming the cohesive attraction, as has been already noticed.

2. In *liquid* bodies this force also operates, but in a less degree than in solids, their particles being at a greater relative distance, and moveable with regard to each other by a very small force; but as their mobility does not change their relative distances, they remain within the sphere of this attraction, and are kept together. The exertion of this power varies in different liquids: it is greater in mercury than in water, and in this than in alcohol. It offers, however, scarcely any resistance to the combination of fluids with other bodies: and hence, the mutual affinity of two bodies is always favoured, when one of them is in the liquid state.

3. This attraction is not exerted over *aëriform* substances; for while these remain at the temperature necessary for the preservation of their aërial state, their particles mutually repel each other, and would recede to an indefinite distance, were they not prevented by the pressure of the surrounding bodies.

One of the most important results of this variety of contiguous attraction, in a pharmaceutical point of view, is the formation of crystals, or the regular and determinate figures assumed by many solids, when nothing opposes the union of their particles according to the laws of aggregation.

The process of crystallization, however, does not take place, unless the particles of the solid become moveable; and hence, in order to obtain any body in a crystalline state, it must first be rendered fluid, either by solution in a liquid, or fusion by heat.

The crystallization of salts is usually effected in the first method. When a salt is much more soluble in hot water than in cold, as is the case, for example, with sulphate of soda, nothing more is required for its crystallization, than to saturate boiling water with it, and set the solution aside to cool. As the caloric is dissipated, the saline particles gradually approach each other, and uniting, form solids of that regular shape which characterizes the crystals of this peculiar salt. But when the salt is almost equally soluble in hot and in cold water, as muriate of soda for instance, its crystallization can only be effected by withdrawing by evaporation a part of the fluid; and the more slowly this takes place, the mutual attraction of the particles is more regularly effected, and the more regular is the shape of the crystals which are obtained. In both cases, however, the affinity of the saline particles at length ceases to act, while the fluid still retains as much saline matter as it can hold dissolved at the temperature of the atmosphere, or is a saturated solution; but, by a further evaporation, it will again yield crystals.

By *fusion*, bodies which are not soluble in water, as glass, sulphur, &c. are enabled to assume the crystalline form. In this case the body is, as it were, dissolved in caloric; and the particles being separated from each other, these, when the cooling is gradual, assume, in aggregating, the regular arrangements which take place in crystallization. This mode of crystallizing substances is never used for pharmaceutical purposes.

Crystallization is promoted or retarded by various circumstances, to be afterwards noticed. (See *Section* iii.) Its theory is still obscure; but some light has been thrown upon it by the experiments of Haüy. He found that crystals may be mechanically divided, and reduced to certain primitive forms, which are always the same in the same kind of substances, and depend upon the figure and the mode of combination of the integrant particles composing the crystals. The varieties of figure of these particles, notwithstanding the great diversity of crystalline forms, are reducible to three: namely, 1. the parallelopiped, the faces of which are six, and parallel two and two; 2. the triangular prism; and 3. the tetrahedron, or four-sided pyramid: and these particles, therefore, according to the mode in which they unite, which may be either by their faces or their edges, form primitive crystals, which are the nuclei of the secondary crystals. The forms of primitive crystals may be reduced to the following six: 1. the parallelopiped, including the cube, the rhomboid, and all solids terminated by six faces, parallel two and two; 2. the regular tetrahedron; 3. the octahedron with triangular faces; 4. the six-sided prism; 5. the dodecahedron, terminated by rhombs; and 6. the dodecahedron, with isosceles triangular faces. The variations of the forms of secondary crystals are considerable in the same salt, and depend, in general, either on variations in the proportions of the ingredients which compose the integrant particles, or on the properties of the solvent in which the crystals are formed: thus alum crystallizes in octahedrons, but the addition of a little alumina produces cubes; and an excess of this earth prevents crystallization altogether: thus also, muriate of soda, which crystallizes in cubes, when dissolved in water, assumes the regular octahedral form when it is crystallized in urine. Independent, however, of these causes, a variety of secondary forms make their appearance; which the theory of Haüy explains by supposing that, as the matter which envelopes the primitive nucleus to form a secondary crystal is attracted in thin layers, each layer decreasing in size in consequence of one or more rows of integrant particles being abstracted from its primitive edges or angles. The decrements may be on the *edges* of the slices, which correspond with the edges of the primitive nucleus; or on the *angles*, that is, parallel to the

diagonals of the faces of the primitive nucleus; or the decrements may be *intermediate*, parallel to lines situated obliquely between the diagonals and edges of the faces of the primitive nucleus. It would be impossible, however, to give a satisfactory view of this ingenious theory in the narrow compass of this epitome; and therefore I must refer the reader to Haüy's *Traité de Minéralogie*, tomes 1 and 2; to the *Annales de Chimie*, tom. 17; and the 3d volume of the fifth edition of Thomson's *System of Chemistry*.

Such is the attraction of aggregation, and its general effects. It is frequently concerned in modifying pharmaceutical results; but it is a power of much less importance than the next variety of *contiguous attraction*.

b. OF CHEMICAL ATTRACTION, OR AFFINITY.[1]

Chemical attraction or affinity is that power by which dissimilar substances placed under certain circumstances are enabled to unite, and form new aggregates, in which the properties of the component particles are lost or changed. Its action is confined to the minute atoms or particles of bodies, and is exerted only at insensible distances: not indifferently, however, between the particles of all bodies, but electively. The result of its operation is a *combination* of the constituent particles of the substances so intimate that the components cannot be recognised, nor separated by any mechanical force. Thus, lime acts as a powerful caustic when applied to animal matter, and is partially soluble in water; phosphoric acid has an acid taste, and is very soluble in water; but phosphate of lime, the compound produced by the chemical combination of these substances, is inert, insipid, and insoluble in water; and cannot be again resolved into lime and phosphoric acid by any mechanical power.

Chemical combination, therefore, is the result of the affinity of two or more substances for each other. It differs from *Mixture*, in which the substances are only blended without acquiring any new properties, and in which the dissimilar parts are easily discovered, and may be separated by mechanical powers. Chemical compounds can, however, be decomposed, either by exposure to a high temperature, which weakens the force of attraction existing between their principles; or by mixture, under favourable circumstances, with some other chemical agent, which has a more powerful affinity for one of its components than these have for each other: and by these means, which constitute *chemical analysis*, the principles of a compound may be ascertained.

[1] The following observations on affinity may be regarded, in a great degree, as an abridgment of the excellent chapter on this subject in the first volume of *Dr. Murray's System of Chemistry*.

As *analysis* separates compounds into their constituent principles, so *synthesis* may reproduce them by recombining these principles; and when this can be effected, it is the surest proof of the accuracy of any analysis. In many instances, however, this is impossible; and the evidence of the truth of an analysis is to be drawn from other sources.

It is an acknowledged law of chemical affinity, that a compound "does not possess properties merely intermediate between those of its component parts, but has acquired others more or less new." One of the most general changes is that of form. The combination of two gases, for example, may produce a fluid or a solid; that of two fluids may form a solid; and the common process of *solution* presents to us the fact, that by the combination of a solid with a fluid, the solid assumes the fluid form. In the last-mentioned instance the fluid is generally regarded as the active substance; but, nevertheless, the attraction of affinity is reciprocal; and hence, the general mode of expressing the fact, that the fluid dissolves the solid, or is the solvent or menstruum, is, in strict language, erroneous. These terms, however, are more correctly applied, when the properties of the solid, except in form, are scarcely sensibly altered; as, for example, when common salt, muriate of soda, is dissolved in water.

Chemical combination produces an alteration of *density* — that of the compound not being the mean of the components, but often different. In the greater number of cases the density is increased; owing probably to a mutual penetration of the components, as there is a diminution of volume; and hence the specific gravity of a compound cannot be determined by calculation from the specific gravity of its ingredients. There are cases of combination, however, in which the density is diminished: and there is an increase of volume in the resulting compound: for instance, when a solid is dissolved by a liquid, the increase of volume acquired by the solid in passing into the fluid state may be greater than the condensation resulting from its union in that state with the liquid; and this happens from the solution of a considerable number of the salts in water.

"The exertion of chemical attraction is accompanied by a *change of temperature*." Thus, if four parts of sulphuric acid and one part of water, both at the temperature of 32°, be mixed together, the temperature of the mixture rises to 300°; and the density of the compound is much greater than the mean of the densities of the components. The heat also which is evolved by combustion, and in fermentation, is the direct consequence of chemical combination. In all cases the increase of temperature is accompanied with an increase of

density, to which, and the change of form suffered by one or both of the components, its production may be ascribed. Thus steam condensed to water parts with a large portion of caloric; and the same effect is produced when water is solidified by being mixed with quicklime. The contrary effect, however, or an absorption of caloric, is also produced by chemical combination, when the density of the compound is less than the mean; as, for instance, when, by solutions of salts in water, or in some other fluids, very intense colds, greater than any natural cold, are artificially produced.[1]

The exertion of chemical affinity is influenced by various circumstances: these, according to Berthollet, are mass, cohesion, insolubility, specific gravity, elasticity, and inflorescence.

1. That *mass* has a considerable share in influencing chemical affinity was first suggested by Berthollet, who states it as a canon, that combinations do not depend altogether on the attraction of affinity, but on the proportions also, of the substances brought into action. Thus, if A and B form a compound, and C be a substance which has a stronger affinity for A than B has, it should be able when mixed with the compound to withdraw A altogether from B, if combination was regulated by affinity only: but this he affirms is not the case in fact; for C does not entirely combine with A, but is shared between it and B, according to the force of the affinity, and the bulk of each. This view of the subject affords a reason why, in pharmaceutical compositions, a small quantity of a substance may be added to a compound, without producing any sensible effect, although, if added in large quantity, decomposition would directly ensue. It follows, also, from it, 1st. that "the chemical action of one substance on another, must diminish as it advances to saturation:" and, 2dly, that a decomposing substance "must oppose a stronger resistance to the decomposing agent, in proportion as the decomposition proceeds, from the increase in the relative quantity of one of its ingredients to the other, which is abstracted:" and, lastly, "that in estimating the relative forces of affinity in bodies, the quantities of them must be taken into account, and ought to be equal." Objections have been advanced to the opinions of Berthollet on this subject, yet, as the opposing theories are not fully established, it is unnecessary to enter into an examination of the objections at the present moment.

2. *Cohesion* has an evident influence in opposing chemical action, and counteracting the exertion of chemical affinity. Thus all aggregates are more slowly acted on by liquids in

[1] See Appendix to Part I. No. I.

which they are soluble, than when their parts are mechanically divided; and this does not happen altogether from the mere circumstance of a larger surface being presented to the fluid; for native oxide of tin, which in the aggregate resists completely the action of any acid, becomes soluble when its aggregation is overcome by mechanical operations; and some other substances are similarly affected. Hence *trituration*, *levigation*, and *granulation* are ranked among pharmaceutical operations, and are of importance "in facilitating chemical action, partly by diminishing aggregation, and partly by increasing the surface on which affinity is exerted." In some instances mechanical division is not sufficient, and recourse must be had to precipitation. Thus liquid potash will not dissolve silica in powder, as it can be obtained by trituration; but when the silica is precipitated from a state of chemical solution, it is readily dissolved in liquid potash.

Owing to the force of cohesion, also, solid bodies seldom act chemically on solids; while fluids readily combine with fluids, and likewise act with energy on solids for which they have an affinity. Fluidity, however, is not indispensable to chemical action; there being many cases in which two solids, in a state of minute mechanical division, act chemically on each other.[1] (See *Section* iii.) When, however, the specific gravities of even two fluids are very materially different, their chemical combination is opposed, to a certain extent, by the force of cohesion of the heavier fluid; and hence, *agitation* is frequently necessary for aiding the operation of affinity.

Cohesion has sometimes a considerable influence in determining the proportion of combinations formed in consequence of new affinities. Thus, if its intensity be sufficient to counterbalance the affinity of the fluid in which the integrant particles resulting from a new combination are formed, it will combine these, and produce crystallizations or precipitations, which, withdrawing the substance thus formed in part from the sphere of action, and opposing a resistance to any further exertion of chemical power, will consequently determine the proportions of the combination.

3. *Insolubility* must necesarily modify chemical action. If an insoluble compound substance be acted on by any substance tending to combine with one of its principles, this is protected in some degree by the insolubility of the compound withdrawing it from the action of the decomposing substance; and if a compound which is produced in the progress of combination be insoluble, it will be directly precipitated, and thus

[1] Thence the axiom *Corpora non agunt nisi sint soluta*, which was formerly established in chemistry, is not generally true.

fixed in its proportions. In decomposition this is extremely useful; for the insoluble product, being immediately separated, cannot oppose the further action of the decomposing substance, which would be the case were it to remain in solution.

4. *Specific gravity* influences considerably the exertion of affinity, particularly if the substance be of little solubility, by withdrawing it from the sphere of action, and hence retarding its combinations; and in many instances this can be but imperfectly counteracted by agitation.

5. Chemical attraction, as far as the aëriform substances are concerned, is opposed by *elasticity*. Thus, when two gases, having mutual affinities, are mixed together, they very seldom combine, which is ascribed to the distances between the particles of substances existing in the gaseous state: for, as chemical attraction is exerted at insensible distances only, the particles of the two gases, although mingled together, are yet without the sphere of attraction. That this is owing to elasticity, is evident from the circumstance that the vapours which are not elastic more readily combine. Hence, whatever gives density to highly elastic substances, as for example, mechanical pressure, or cold to a certain degree, must favour their chemical combination.

6. *Efflorescence* may also influence chemical affinity; a fact which was first observed by Scheele, who ascertained, that if in a paste composed of several saline substances decomposition is going on, one of the resulting compounds often rises through the mass, and forms an efflorescence on its surface; and its being thus withdrawn from the sphere of action contributes towards forwarding the decomposition.

7. The influence of *temperature* in modifying chemical action is very considerable. An increased temperature, by promoting fusion, and in other respects weakening the attraction of cohesion in solids, favours combination; but opposes it in some cases, as much as it augments elasticity. In both instances its effects are much modified by the degree of its intensity; combinations effected at a lower, being often dissolved at a higher temperature, owing to one or more of the components having its affinity weakened by an increased elasticity. Thus, mercury exposed to air for some time at a temperature equal to its boiling point, combines with the oxygen of the air, and is converted into red oxide of mercury; but if the fire be raised so as to make the retort red hot, this oxide is again decomposed, and running mercury and oxygen gas obtained.

From the influence of the above circumstances on chemical combination, the utility of these pharmaceutical and chemical operations, which diminish aggregation, overcome the effect

of specific gravity, diminish elasticity, and regulate temperature, such as pulverization, trituration, granulation, agitation, and compression, with the proper management of furnaces, is sufficiently obvious.

In that department of pharmacy, also, which regards extemporaneous compositions, it is of importance to attend to the slowness with which chemical action is in many instances produced; for substances, which have mutual affinities for each other, may give no indication of any change when newly mixed, but yet, after some time, may act, and produce even complete changes.

Chemical attraction may be exerted between more than two bodies, so as to bring three or four into one combination; and such compounds are named *ternary*, *quaternary*, *&c.* according to the number of their components. Several examples of these are to be found among the saline preparations (*Part* iii.); and almost all the vegetable substances are compounds of three or more principles.

The forces with which chemical attraction is exerted are different in different bodies. In cases where this attraction is exerted in a superior degree by a third body to either of the components of a compound of two bodies, so as to decompose it, and form a new compound, while at the same time one of the components of the previous compound is set free, the affinity thus exerted has been termed *single elective attraction*. To represent the relative forces of affinity, tables were first constructed by Geoffroy; and afterwards much improved and extended by other chemists, particularly Bergman: but the opinions of Berthollet on this subject have tended very much to lessen their value, although their utility to a certain extent must undoubtedly be acknowledged.[1] When the elective attractions are more complicated, or when two elective affinities are exerted, and two new compounds formed, this is termed *double elective attraction*. In such cases, Mr. Kirwan denominated the attractions which tend to preserve a compound in its original state *quiescent*; while the others which tend to separate the principles of a compound from each other, he termed *divellent attractions*. As an example of double elective attraction, let it be supposed that two compounds, one consisting of potash and sulphuric acid, or *sulphate of potash*, and the other consisting of muriatic acid and lime, or *muriate of lime*, be mixed together, a double decomposition will take place, and

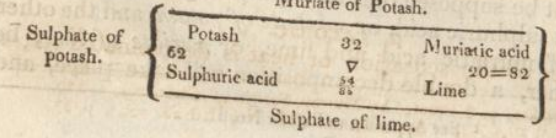
1 See Appendix to Part I. No. II.

two new compounds, *sulphate of lime*, and *muriate of potash* will be formed. In this case, if the attraction between potash and sulphuric acid be 62, and that between lime and muriatic acid be 20, the sum of the quiescent attractions will be 82; but if the attraction between potash and muriatic acid be 32, and that between sulphuric acid and lime be 54, the sum of the divellent attractions will be 86: which, exceeding the former sum of the quiescent, will operate and produce the above-stated decompositions and resulting compounds.[1]

According to the opinions of Bergman, the relative force of the affinities which produce these effects is capable of being measured, and the changes are altogether to be ascribed to the predominance of the affinities of one set of substances over another. But a different and more correct view of the subject has been given by Berthollet, of which we shall now give an outline.

The changes produced by the predominance of certain affinities over others, according to the theory of Bergman, are ascribed by Berthollet to those circumstances which influence attraction, and limit combination. If four substances, for example, be presented to each other, two of which have a greater tendency to cohesion than the other two, so as to form by their union an insoluble compound, instead of one compound being formed by the union of the four, in which the affinities are balanced, this will be averted by the force of cohesion, and the two which form the insoluble compound will unite, and be separated by precipitation or crystallization, leaving the other two in combination in the fluid which has been the medium of action. "If even these four substances were previously in the reverse binary combinations, on presenting them to each other, the affinities within the sphere of action must be reciprocally exerted; and the same extraneous forces will cause an exchange of principles, or the phœnomena which have been ascribed to elective affinities will be produced." To avoid the term elective attraction, Berthollet denominates cases of this kind *complex affinity*. The explanation of single elective attraction, or where three substances are presented to each other, is pre-

[1] To represent this effect of double elective affinity more clearly, diagrams are used, the idea of which first occurred to Dr. Cullen. Thus the above operations would be represented in the following manner: The inverted triangle in the centre denotes water, or that the decomposition was effected in the humid way.



cisely the same; the union which takes place between two of them being determined by the tendency to cohesion, or the disposition of the combination of two of them to form a compound of little solubility.

Elasticity likewise has a considerable influence in determining decompositions where the application of heat is necessary; and, according to Berthollet, the decomposition of a compound body, of which one of the ingredients has a great tendency to assume the elastic form, is to be ascribed to the disposition it has to escape from its combination, when aided by the intervention of even a weaker affinity.

In complex affinities the same cause determines the union of substances disposed to assume the elastic form, and separates them as a volatile compound. "If, therefore," says he, "it be desired to know the result of the exposure of two salts to the action of heat, it is only necessary to consider which of the two bases, and which of the two acids have the greater volatility, if there be a difference: for the more volatile base and acid will escape and enter into combination, and the fixed base and fixed acid will remain behind, and combine with one another."[1] Tables representing the forces of affinity have been constructed; but, as Dr. Henry has justly remarked, "one great obstacle to the construction of such tables, is the difficulty of ascertaining, with precision, the quantities of bodies required for neutralization."[2]

A knowledge of the doctrines of affinity is of the utmost importance in pharmacy; and, as the foregoing sketch presents little more than an outline, I must refer those who would wish to investigate the subject to Thomson's and Murray's Systems of Chemistry, Bergman's Dissertation on Elective Attraction, and Berthollet's Researches into the Laws of Chemical Affinity.

II. REPULSION.

REPULSION is that force which separates the particles of bodies from each other, and consequently counteracts or modifies the attractions by which they are combined and preserved together in masses. It is supposed to depend on the operation of one or more of the three following powers; *Caloric*, *Light*, *Electricity*.

a. CALORIC.

The cause of the sensation of heat is denominated *caloric*.

1 *Researches*, p. 3. quoted by Murray, *System of Chemistry*, i. 120.
2 Henry's *Elements of Experimental Chemistry*, 7th ed. vol. i. p. 57.

Philosophers are not completely agreed whether it is a property only of bodies, such as a vibration of their particles[1], or a peculiar substance; but the latter opinion is the one more generally adopted.

Under this opinion caloric is regarded as a very subtile elastic fluid, which penetrates more or less all bodies, passing readily from one to another; and is every where diffused. Its particles are supposed mutually to repel each other; and bodies into which it enters in any sensible quantity are increased in bulk, and undergo other changes of form. It is radiated in the same manner as light, and in this state forms a part of the solar ray.[2] The rays are refrangible, and capable of reflection. It has no ascertainable gravity; and neither the addition nor the abstraction of it alters sensibly the weight of bodies.[3] It exists in two different states; in a free state, in which it is merely loosely mingled as it were, with other bodies; and, in a latent state, or one of intimate combination.

Regarding it as matter, the sources whence it may be obtained, the laws which regulate its motion and distribution, and its effects, require to be noticed.

Sources of Caloric.

The known sources of caloric are the *sun*, *combustion*, *percussion*, *friction*, and *mixture*.

a. The *sun* is an apparent source of caloric; but, the direct action of the sun's rays upon bodies seldom produces a temperature exceeding 120°. When these, however, are concentrated by means of a concave mirror, or a lens; or when means are taken to prevent the communicated heat from being carried off by the surrounding bodies, a much higher temperature can be produced. This source of caloric is not resorted to for pharmaceutical purposes.

b. Combustion is a source of caloric highly interesting on account of its utility.

When a combustible is heated to a certain degree, it is consumed, emitting rapidly light and caloric, until the whole substance has suffered a change of properties.

The true nature of this process was first explained by Lavoisier, who laid it down as a chemical axiom, that "in every case of combustion, oxygen combines with the burning body." His explanation of combustion depends on two laws: 1st. That when a cumbustible body is heated to a certain temperature it immediately begins to attract and combine with the oxygen of the atmospheric air. 2d. This oxygen being in a state

[1] The idea of caloric being motion or vibration, originated with Lord Bacon.
[2] *Philosophical Trans.* 1807. [3] Ib. 1799, p. 179.

of gas, and combined with light and caloric, is decomposed during its union with the combustible, and its caloric and light are set free in a sensible form; while the oxygen itself remains combined with the combustible. The truth of this theory is generally supposed to be proved by the facts, that combustion does not go on unless oxygen be present: and it is more brilliant in oxygen gas than in common air. The products of combustion are always heavier than the body consumed; and this increase of weight is exactly equal to the quantity of oxygen which the air loses. Every combination of oxygen, however, with bodies does not produce the phænomena of combustion. Brugnatelli has endeavoured to explain this by supposing that oxygen combines with bodies in two states: "1. retaining the greater part of the caloric and light with which it is combined when in the state of gas; and, 2. after having let go all the caloric and light with which it was combined."

The above theory of combustion is however liable to some objections; for instance, the emission of caloric and light is not proportional to the quantity of oxygen that combines with the combustible: and the quantity of light that appears depends altogether upon the combustible. Under the supposition, therefore, that the caloric is obtained from the oxygen of the substances supporting combustion, while the light is derived from the combustibles, the process has been regarded as a case of "double decomposition; the oxygen and combustible dividing themselves into two portions, which combine in pairs; the one compound is the *product*," or the combustible base united with oxygen, "the other is the *fire*," or the caloric and light, "which escapes."[1]

The caloric set free by the burning or combustion of coal, charcoal, carbonated hydrogen gas, oil, wax, and tallow, is applied to the purposes of life, and is of the first importance in the practice of pharmacy: thence endeavours have been made to ascertain the quantity of caloric evolved during the burning of different combustibles, and several experiments have been instituted by the most able chemists at different times for this purpose. The following table exhibits the quantity of caloric evolved by the combustion of different substances, the estimate being formed from the quantity of ice melted during the burning of one pound of each of the substances.[2]

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1 *Thomson's Chemistry*, 4th edit. i. 607.
2 *Thomson's Chemistry*, i. 610.

Substances burnt, 1 lb.	Oxygen consumed in lbs.	Ice melted in lbs.		
		Lavoisier.	Crawford.	Dalton.
Hydrogen	6	295	480	320
Carburetted hydrogen	4			85
Olefiant gas	3·5			88
Carbonic oxide	0·58			25
Oil	3·5	148	89	104
Wax	3·5	133	97	104
Tallow	3·5			104
Oil of turpentine				60
Alcohol				58
Æther	3·			62
Phosphorus	1·5	100		60
Charcoal	2·8	96·5	69	40
Sulphur	1·36			20
Camphor				70
Caoutchouc				42

From this table it appears that hydrogen gas would form the best fuel, where a high temperature is required.

c. Percussion, as far as it applies to solid bodies, is another source of caloric. Smiths, for instance, are in the habit of kindling their fires by means of an iron rod, which is smartly and quickly hammered until it becomes red-hot; and sparks are produced by the collision of hard bodies, particularly of flint with steel. This effect appears to arise from condensation, or forcing the integrant particles of the bodies closer together, so as to dislodge the latent caloric they contain, and give it out in the form of sensible caloric. The specific gravity of iron is increased ·052 by being hammered; and it becomes so hard and brittle that it cannot again be heated by percussion, until it has been exposed for some time to a red heat in the forge. By the collision of flint and steel the oxidizement of the steel is also effected, the sparks being small incandescent pieces of oxidized iron.

d. Friction is also a source of caloric. It is a well known fact, that a considerable quantity of free caloric is disengaged when two substances are smartly rubbed together; but the real source of the caloric thus evolved, still remains unknown.

e. Finally, *mixture*, or the chemical union of two substances, in many cases evolves caloric. This always takes place when the density or specific gravity of the mixture is greater than the mean of the substances mixed; as in the mixture of alcohol and water, or of sulphuric acid and water; and much caloric is also evolved when water is thrown upon quicklime, owing

to the solidification of the water when it unites with the lime. The caloric which is evolved in these, and other instances of mixture, is the latent caloric, which is the cause of the fluidity of the components; for as the compound is less fluid, and consequently requires the presence of a smaller quantity of combined caloric, the superabundance which the more fluid components contained must be necessarily set free.

Such are the sources from which caloric is obtained: combustion is the most important of these; and the knowledge of the laws by which it is regulated, and the modes of conducting it, is of the first consequence in the practice of pharmacy. (See *Furnaces.*)

Distribution and Effects of free Caloric.

From whatever source caloric is obtained, it passes from bodies in which it is accumulated in a free state into bodies which contain less of it, until both are brought to an equilibrium. "The state of a body, with regard to its power of producing the different effects arising from the presence of caloric, is termed its *temperature:*" and this depends on the quantity of sensible caloric contained in it. Thus, when a vessel containing water is placed on the fire, a quantity of caloric passing from the fire into the water, its temperature is raised, or it is made sensibly hotter; and if the water thus heated be taken from the fire and placed in a cold place, the sensible caloric accumulated in it, passes from it into the air and surrounding bodies, until it becomes as cold as they are, or its temperature be lowered to an equilibrium with theirs. The caloric which passes from hot bodies during their cooling is carried off; 1st, by the conducting power of the surrounding medium, which "diminishes as the temperature of the hot body approaches to that of the medium;" 2dly, by radiation; 3dly, by currents, or the repeated change of the portion of medium immediately in contact with the hot body; produced by the change of density occasioned by the caloric it receives from the hot body enabling it to rise and give place to a new portion, which, being heated, is also displaced in its turn, and so on till the temperature of the hot body approaches to that of the medium. By accelerating these changes the rate of cooling is proportionably quickened; and hence the cooling effect of winds, and artificial currents of air.

The temperatures of bodies can be comparatively ascertained to a certain extent by the sensations they induce. Thus, a body containing much sensible caloric feels warm or hot to the touch, owing to its caloric flowing into the hand; and one containing less gives the sensation of cold, owing to the abstraction of caloric from the hand. But this mode of judging of temperature is very limited, and depends on the state of the

sentient organ, and many other external circumstances, which prevent confidence from being placed on it as a comparative measure of temperature: and therefore instruments have been invented to measure the degrees of temperature of different bodies; the properties of which depend on the *expansion* or increase of bulk which bodies suffer when caloric enters into them.

The thermometer is a most useful and important instrument of this kind. It is a hollow glass tube, having at one end a hollow globe or bulb; the hollow of the tube being perfectly cylindrical, and of a small bore, and the bulb of a proportional size. The bulb, and a portion of the tube, after the air is expelled, by holding the bulb over the flame of a lamp, are filled with mercury or coloured alcohol, by immersing the open end of the tube in either of these fluids, and the tube is then hermetically sealed at the extremity.[1] When the bulb of this instrument is applied to a hot body, the mercury, or the fluid it contains, rises in the tube, and continues to do so until the thermometer acquire the same degree of temperature as the hot body, when the mercury becomes stationary, and the point to which it rises indicates the temperature of the hot body. In the same manner when the bulb is applied to a cold body, the mercury contracts and falls in the tube. The quantity which it thus rises or falls, indicating the proportion of increase or diminution of temperature, is ascertained by a scale which divides the tube into a number of equal parts or degrees.

For ordinary purposes, mercury is the liquid best adapted for thermometers; its expansion being most equable; but alcohol is used when great degrees of cold are to be measured.

The thermometer commonly employed in this country is that of Fahrenheit[2]: but as three other thermometers are used on the continent, it may be proper to notice all of them, and point out the circumstances in which their scales differ.

Fahrenheit, in forming his thermometer, began the scale at the temperature produced by a mixture of snow and sea salt acting on each other; and divided the space between this and the point indicated by the temperature of boiling water into 212 equal parts or degrees; 212° being marked as the boiling point. The part of the scale indicated by the freezing of water, he found to be 32 degrees from its beginning; therefore 32° is marked as the freezing point: and the space between which and the boiling point is equal to 180°. The scale may be extended above this point and also below its

[1] Thermometers of great accuracy may be purchased; but those who may wish to construct them for themselves, will find ample instructions for their guidance, in the third chapter of *Henry's Elements of Experimental Chemistry*.

[2] Fahrenheit was a German artist.

commencement, the degrees downwards being marked inversely with the same numbers as the ascending scale.

The scale of the thermometer of Celsius, which has been used in France since the revolution, begins at the freezing point of water, which is consequently marked 0, and the space between that and the boiling point is divided into 100 equal degrees; hence it has been named the *Centigrade Thermometer*. Each degree of this scale is $\frac{4}{5}$ths more than a degree of Fahrenheit's, or one of the latter is equal to $\frac{5}{9}$ths of a degree of the centigrade scale. To find, therefore, the degrees of Fahrenheit's scale, corresponding to those of the centrigade, the given number of the latter must be multiplied by 9, and divided by 5, adding 32 to the quotient: the sum expresses the degree on ths scale of Fahrenheit.

Reaumur's thermometer, which is still used in Italy and Spain, also commences at the freezing point, which is marked 0; and between this and the boiling point it is divided into 80 degree. Each degree is therefore $\frac{5}{4}$ths more than one of Fahrenheit's; and to reduce those of Reaumur to Fahrenheit's, the given number of the former must be multiplied by 9, and divided by 4, adding 32 to the quotient.[1]

[1] *TABLE showing the degrees of Reaumur's and Fahrenheit's thermometers corresponding with those of the centrigrade thermometer.*

Cent.	Reau.	Fahr.	Cent.	Reau.	Fahr.	Cent.	Reau.	Fahr.	Cent.	Reau.	Fahr.
100	80·	212·	68	54·4	154·4	36	28·8	96·8	5	4·	41.
99	79·2	210·2	67	53·6	152·6	35	28·	95·	4	3·2	39·2
98	78·4	208·4	66	52·8	150·8	34	27·2	93·2	3	2·4	37·4
97	77·6	206·6	65	52·	149·	33	26·4	91·4	2	1·6	35·6
96	76·8	204·8	64	51·2	147·2	32	25·6	89·6	1	0·8	33·8
95	76·	203·	63.	50·4	145·4	31	24·8	87·8	0	0·	32·
94	75·2	201·2	62	49·6	143·6	30	24·	86·	1	0·8	30·2
93	74·4	199·4	61	48·8	141·8	29	23·2	84·2	2	1·6	28·4
92	73·6	197·6	60	48.	140·	28	22·4	82·4	3	2·4	26·6
91	72·8	195·8	59	47·2	138·2	27	21·6	80·6	4	3·2	24·8
90	72·	194·	58	46·4	136·4	26	20·8	78·8	5	4·	23·
89	71·2	192·2	57	45·6	134·6	25	20·	77·	6	4·8	21·2
88	70·4	190·4	56	44·8	132·8	24	19·2	75.2	7	5·6	19·4
87	69·6	188·6	55	44.	131·	23	18·4	73·4	8	6·4	17·6
86	68·8	186·8	54	43·2	129·2	22	17.6	71·6	9	7·2	15·8
85	68·	185·	53	42·4	127·4	21	16·8	69·8	10	8·	14·
84	67·2	183·2	52	41·6	125·6	20	16.	68·	11	8·8	12·2
83	66·4	181·4	51	40·8	123·8	19	15·2	66·2	12	9·6	10·4
82	65·6	179·6	50	40·	122·	18	14·4	64·4	13	10·4	8·6
81	64·8	177·8	49	39·2	120·2	17	13·6	62·6	14	11·2	6·8
80	64·	176·	48	38·4	118·4	16	12·8	60·8	15	12·	5·
79	63·2	174·2	47	37·6	116·6	15	12·	59·	16	12·8	3·2
78	62·4	172·4	46	36·8	114·8	14	11·2	57·2	17	13·6	1·4
77	61·6	170·6	45	36·	113·	13	10·4	55·4	18	14·4	0·4
76	60·8	168·8	44	35·2	111·2	12	9·6	53·6	19	15·2	2·2
75	60·	167·	43	34·4	109·4	11	8·8	51·8	20	16·	4·
74	59·2	165·2	42	33·6	107·6	10	8·	50·	21	16·8	5·8
73	58·4	163·4	41	32·8	105·8	9	7·2	48·2	22	17·6	7·6
72	57·6	161·6	40	32·	104·	8	6·4	46·4	23	18·4	9·4
71	56·8	159·8	39	31·2	102·2	7	5·6	44·6	24	19·2	11·2
70	56·	158·	38	30·4	100·4	6	4.8	42·8	25	20·	13·
69	55·2	156·2	37	29·6	98·6						

In De Lisle's thermometer, which is used only in Russia, the space between the boiling and freezing points is divided into 150 degrees; the gradation beginning at the boiling point, which is marked 0; and increasing inversely to the freezing point, which is marked 150°. It is seldom mentioned by authors.

These instruments are well adapted for determining the variations of temperature which bodies undergo; but a certain degree of fallacy attends the observations made by them, which is chiefly owing to the expansion of mercury increasing with the temperature. Thus, the medium degree of heat between the freezing and boiling points, although marked on the scale 122°, yet, is actually 118·8° 1′ only; the temperature which is equal to raise the mercury in the tube 86 degrees in the first

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TABLE exhibiting the degrees of the centrigade and Fahrenheit's thermometers corresponding to those of Reaumur's thermometer.

Reau.	Cent.	Fahr.	Reau.	Cent.	Fahr.	Reau.	Cent.	Fahr.
80	100·	212·	46	57·5	135·5	12	15·	59·
79	98.75	209·75	45	56·25	133·25	11	13·75	56·75
78	97·5	207·5	44	55·	131·	10	12·5	54·5
77	96·25	205·25	43	53·75	128·75	9	11·25	52·25
76	95·	203·	42	52·5	126·5	8	10·	50·
75	93·75	200·75	41	51·25	124·25	7	8 75	47·75
74	92·5	198·5	40	50·	122·	6	7·5	45·5
73	91·25	196·25	39	48·75	119·75	5	6·25	43·25
72	90·	194·	38	47·5	117·5	4	5·	41·
71	88·75	191·75	37	46·25	115.25	3	3·75	38·75
70	87·5	189·5	36	45·	113·	2	2·5	36·5
69	86·25	187·25	35	43·75	110·75	1	1·25	34·25
68	85·	185·	34	42·5	108·5	0	o	32·
67	83·75	182·75	33	41.25	106·25	1	1·25	29·75
66	82·5	180·5	32	40·	104·	2	2·5	27·5
65	81·25	178·25	31	38·75	101·75	3	3·75	25·25
64	80·	176.	30	37·5	99·5	4	5·5	23·
63	78·75	173·75	29	36·25	97·25	5	6·25	20·75
62	77·5	171·5	28	35·	95·	6	7·5	18·5
61	76·25	169·25	27	33·75	92·75	7	8·75	16·25
60	75·	167·	26	32·5	90·5	8	10.	14·
59	73·75	164·75	25	31·25	88·25	9	11·25	11·75
58	72·5	162·5	24	30·	86·	10	12·5	9·5
57	71·25	160·25	23	28·75	83·75	11	13·75	7·25
56	70·	158·	22	27·5	81·5	12	15·	5·
55	68·75	155·75	21	26·25	79·25	13	16·25	2·75
54	67·5	153·5	20	25·	77·	14	17·5	0·5
53	66·25	151·25	19	23·75	74·75	15	18·75	1·75
52	65·	149·	18	22·5	72·5	16	20·	4·
51	63·75	146·75	17	21·25	70·25	17	21·25	6·25
50	62·5	144·5	16	20·	68·	18	22·5	8·5
49	61·25	142·25	15	18·75	65·75	19	23·75	10·75
48	60·	140·	14	17·5	63·5	20	25.	13·
47	58.75	137·75	13	16·25	61·25			

instance, being sufficient, by increased expansion, to raise it 94 in the second.[1]

Expansion, or increase of bulk, is the most general effect of caloric, and, with very few exceptions, may be regarded as a general law of its operation.

When caloric flows into a body, it separates its integrant particles from each other, and hence augments its volume. This change is smallest in solids, more considerable in liquids, and most considerable in gaseous bodies; or the expansibility is greater in the inverse ratio of the force of aggregation. Thus, the expansion of air is 8 times greater than that of water; and the expansion of this 45 times greater than that of iron.

The expansion of solid bodies is, in general, so very inconsiderable as not to be easily ascertained by measurement; but, as far as it can be known, it is nearly equable. The degree of expansion, however, is not the same in all solids; thus, for example, the metals expand in the following order, commencing with the least expansible; platina, antimony, iron, bismuth, copper, tin, lead, zinc. Argil is an exception to the law of expansion in solids; for, as has been already remarked, the bulk of pure clay diminishes, when heated, in the ratio of the intensity of the heat to which it is exposed. The cause of this anomaly has not been discovered. The expansion of liquids is more evident than that of solids, but not at all uniform; the differences apparently depending on the fixity or volatility of the components of the liquids: those expanding the most the boiling point of which is lowest; and which, consequently, most readily assume the gaseous form. The degree of their expansion, also, increases, with the augmentation of their temperature; or, the nearer a liquid approaches to the boiling point, the greater is the expansion produced by a degree of caloric; and the further it is from this point, the more equable is the expansion. Liquids, in the same manner as solids, suffer a difference of expansion from a given change of temperature. The following Table, by

[1] For measuring *higher temperatures* than the thermometer can be subjected to, instruments named *pyrometers* have been employed; the best of which is that invented by Mr. Wedgewood. It depends on the degrees of contraction which pure argil suffers when exposed to high temperatures; and for this purpose small cylinders of pure clay are made in a mould, flattened on one side, and fitted exactly to the wider end of a gauge, consisting of two straight pieces of brass, 24 inches long, fixed on a brass plate so as to converge, and divided into inches and tenths. The length to which the pyrometrical pieces can be slid in the converging groove, indicates the heat to which they have been previously exposed; and as they do not expand again when cold, no fallacy can result from the action of heat on the gauge. Each degree of this scale is equal to 130° of Fahrenheit; and the 0, or commencement of it, corresponds with 1077½° of Fahrenheit's scale. The highest temperature that has been measured by it is 160° or 21·877° of Fahrenheit, which is 30° above the point at which cast iron melts. But, as much higher temperatures than this must exist, so also, there are temperatures much lower than can be measured by any thermometer.

Mr. Dalton, shows the expansion of the more common liquids, from 32° to 212° of Fahrenheit, the volume at 32° being denoted by 1.

Mercury.	Water.	Water saturated with salt.	Sulphuric acid.	Muriatic acid.	Oil of turpentine.	Ether.	Fixed Oils.	Alcohol.	Nitric acid.
·0200 = $\frac{1}{50}$	·0466 = $\frac{1}{21.5}$	·0500 = $\frac{1}{20}$	·0600 = $\frac{1}{17}$	·0600 = $\frac{1}{17}$	·0700 = $\frac{1}{14}$	·0700 = $\frac{1}{14}$	·0800 = $\frac{1}{12.5}$	·0110 = $\frac{1}{9}$	·0110 = $\frac{1}{9}$

To the general law of the expansion of liquids by heat, water furnishes an exception. Thus, from the lowest temperature at which water can remain liquid, to 40°, heat diminishes the bulk of water, instead of expanding it; but above 40° to 212° it expands it.

All gaseous bodies suffer the same expansion by the same additions of caloric, supposing the circumstances to be equal. Their expansion is almost perfectly equable, or the same augmentation takes place by the same addition of caloric at every degree of temperature between the freezing and the boiling point of Fahrenheit's thermometer. By the experiments of Gay Lussac, 100 parts of atmospheric air, heated from 32° to 212° expand 137·5 parts, or $\frac{1}{480}$th for every degree of the thermometer: and the other gases, the steam of water, and the vapour of ether, undergo the same expansions by the same augmentations of temperature. The cause of the equable expansion of gaseous bodies, appears to be the absence of cohesion; so that, at a low temperature, there is no more resistance made to the expansive power of the caloric thrown into the gas, than at a high temperature.

But, besides the change in bulk produced by the introduction of caloric into substances in different quantities, they are changed in state, assuming the *fluid form*, and that of *vapour*; or, they are *ignited*.

Fluidity is an effect of caloric, arising from the repulsive force of the caloric which enters into any substance fitted to take on the fluid form, separating the particles from each other to such a distance as to render them easily moveable on one another in every direction. All solids, with a very few exceptions, are susceptible of the fluid form, when exposed to a suf-

ficient degree of heat; and all liquids, with the exception of alcohol, become solid when exposed to very low temperatures. The particular temperatures necessary for the production of these changes, however, are exceedingly various, but for the same bodies they are always the same.[1] In some cases, the change is sudden, or the body instantly passes from the solid to the liquid state; in other cases, it passes through several degrees of softness before it be perfectly liquefied: the conversion of ice to water is an example of the first; the melting of glass, of wax, and other unctuous matters, is an instance of the second. There are some bodies, nevertheless, which cannot be melted or *fused*, owing to their suffering chemical decomposition at a lower temperature than is required for their *fusion*:—a piece of wood, for instance, cannot be melted by any application of heat.

Although the melting point, in most cases, is always the same in the same bodies, yet circumstances may vary it; and the admixture of other substances may alter it very considerably. Thus, the melting point of ice, or, what is the same thing, the freezing point of water, is 32°; but, by exposing water slowly to the action of freezing mixtures, it may be cooled down to 22° before it freezes. The addition of salt renders this point still lower, as may be seen by the following Table.[2]

Names of salts.	Proportion by weight dissolved in 100 parts of water.	Freezing point.
Common salt.....	25·	4·
Sal ammoniac.....	20·	8·
Rochelle salt.....	50·	21·
Sulphate of magnesia	41·6	25·5
Nitre.....	12·5	26·
Sulphate of iron	41·6	28·
——— of zinc.....	33·3	28·6

When solids pass to the liquid state they receive an additional quantity of caloric, which combines with them, but does not sensibly elevate their temperature, and this *caloric of*

[1] Table, showing the degree of temperature, according to Fahrenheit's thermometer, at which several solid bodies melt.

Lead - -	594°	Copper - - -	4587°, *Fahr.*	27, *Wedg.*	Spermaceti	112°
Bismuth -	476	Silver - - -	4717	——	28	Phosphorus	100
Tin - - -	442	Iron - - - -	21637	——	158	Tallow - -	92
Zinc - -	700	Sulphur - - -	218			Oil of anise	50
Antimony -	809	Bees-wax - -	142			Camphor -	303
Mercury	—39	Lard - - - -	97			Ice - - -	32

[2] *Phil. Trans.* 1788, 27, quoted by Dr. Thomson—*Syst. Chemistry*, 4th edit. i. 520.

fluidity, or *latent heat*, as it has been named, is again given out in a sensible form, when the body returns to a solid state. If water, for example, be exposed to a great degree of cold, and kept free from agitation, it may be cooled several degrees below the freezing point, and yet remain fluid; but if it be then agitated, it instantly congeals, and at the moment its temperature rises to 32°. All fluids, therefore, are combinations of solids and certain doses of caloric. Thus, if snow at 32° be mixed with an equal weight of water at 172°, the snow instantly melts, but the temperature of the mixture is only 32°; so that 140° of caloric have disappeared or become latent: hence the quantity of caloric necessary to give fluidity to ice is 140°. These facts were first ascertained by Dr. Black in 1762; and fluidity in general has been proved to depend on a similar cause. Softness, plasticity, malleability, and ductility, probably depend also upon the repulsive force of the latent heat which combines with bodies.

Vapour, which is another effect of caloric, is that state into which all fluids and some solids pass when their temperature is raised to a certain point, or caloric is thrown into them in sufficient quantity to separate their integrant particles to distances beyond the sphere of the attraction of cohesion. The fluid passes to the aëriform state, becoming invisible and elastic, and possessing the other mechanical properties of air.

Evaporation, however, is also spontaneously produced, and besides being the conversion of a fluid to the state of vapour by the agency of caloric alone, seems to depend on the solvent power of atmospheric air, forming a solution of the body in the aërial fluid. By *spontaneous evaporation*, the fluid is gradually converted into the aëriform state at every temperature. Water, alcohol, ether, and volatile oils are susceptible of spontaneous evaporation, so that a portion of any of them exposed to the air in a flat vessel soon altogether disappears; "but sulphuric acid and the fixed oils never assume the form of vapour till they are raised to a certain temperature."

All fluids have a fixed point of temperature at which their vaporization commences, which is denominated their *boiling point*, and beyond this point fluids cannot be heated if freely exposed to the air, so as to allow the vapour to escape as it forms. Thus water at 212° boils, and is progressively converted into steam at the bottom of the vessel, which, rising in bubbles through the water, produces the ebullition that characterizes boiling; but although the fire be raised ever so much, yet the temperature of the water never exceeds 212°; the vapour carrying off every additional increment of heat in a latent form. The boiling point varies in different bodies;

and in the same body also, if it be placed under different circumstances, particularly with regard to pressure. Thus the boiling point of ether is 98°, of alcohol 176°, water 212°, mercury 660°, and so on. In a vacuum all liquids boil at a temperature 145° lower than in the open air; and in Papin's digester, in which water can be heated under a great pressure, the temperature may be raised to 300° without ebullition. Owing to this circumstance, highly volatile substances, as ammonia and ether, cannot be easily manufactured in elevated situations.

The elasticity of the vapour of liquids boiled in the open air is equal to that of the circumambient atmosphere; but under pressure, so that the temperature of the vapour may be much augmented, the elasticity increases with the temperature. At low temperatures, on the contrary, vapours lose their elasticity, are condensed, and return to their fluid state. The conversion, therefore, of liquids into elastic fluids depends on the same cause as the conversion of solids into fluids; namely, "to the combination of a certain dose of caloric with the liquid, without any increase of temperature."[1] The vapour carries off all the caloric which enters a body after it arrives at its boiling point; and retains it in a latent form: for the vapour is not hotter to the senses or the thermometer than the boiling liquid: thus, steam, the temperature of which is indicated by the thermometer to be 212°, is water combined with 940° of caloric, which remain latent as long as the temperature of the steam is maintained, but is again given out when a lower temperature changes that vapour to the state of a liquid.

Gases resemble vapours in their constitution, and differ from them only in the greater reduction of temperature which is required for their condensation, some of them not being reducible by ordinary pressure, or by any known reduced temperature, to the fluid or solid state. They are nevertheless very probably compounds of solid or liquid substances and caloric. Indeed several of the gases have been condensed into fluids, by the application of cold and pressure; oxymuriatic acid gas, for instance, becomes liquid at a little under 40°, and forms solid crystals at 32°; and ammoniacal gas condenses into a fluid at 45°.

Ignition is another effect of caloric, but differing altogether from expansion, fluidity, and evaporation, which may in some measure be regarded as different degrees of one general effect. It implies an emission of light from bodies which are much heated, or combined with a large portion of caloric, without

[1] The important discovery of the causes which produce the changes of bodies from the solid to the liquid and aëriform state was made by Dr. Black in 1760.

their suffering any change of composition. It is totally independent of the presence of air, and is a simple effect of caloric. Aëriform substances are not susceptible of ignition.

The degree of temperature at which all bodies capable of ignition begin to be ignited, or become red hot, is nearly the same,—about the 800th degree of Fahrenheit; and by raising the temperature the illumination increases, until a perfectly white light is produced, which is the highest point of ignition. Ignition is supposed to arise from the extrication of the light, which is regarded as a constituent of the ignited body, by the repulsive agency of the additional caloric; but this explanation of the phænomenon is liable to some objections, and the real cause remains still undetermined. As a pharmaceutical agent, *caloric* is of the first importance, in the majority of cases producing decomposition; but in others favouring combination. The decomposition most easily effected by it is the separation of the more volatile from the more fixed ingredients of compounds. Thus in the process of distillation (see *Operations*), when weak spirits are heated, the alcohol separates from the water, owing to its superior volatility, and by condensation is obtained as a distinct substance. Almost all compounds into which oxygen has entered without having occasioned combustion, as nitric acid, hyperoxymuriatic acid, and some metallic oxides, suffer likewise decomposition by caloric. All compound bodies containing combustibles are also decomposable by it; as are also compounds consisting of two or more combustible ingredients, in combination with oxygen, as almost all animal and vegetable matters. On the contrary, the compounds which are little or not at all affected by caloric, as far as regards the composition, are those which have been formed by combustion; such as water, phosphoric acid, and carbonic acid.[1] The proper application of caloric for the purpose of obtaining new combinations by lessening the force of aggregation, and thus favouring the attraction of affinity; or for producing decompositions by weakening or destroying altogether the force of these attractions, so as to obtain the principles of bodies in a distinct state, constitutes the most important feature of operative pharmacy. (See *Operations*.)

2. LIGHT.

Light is a substance consisting of very subtle particles which are constantly emanating in straight lines from luminous bodies. The size of these is too minute to be appreciated; but their velocity is estimated to be at the rate of 200,000 miles in a second. They appear to repel each other like those of caloric.

[1] *Thomson's Chemistry*, 4th edit. i. 546.

A ray of light falling upon a polished surface is *reflected* from it at an angle equal to the angle of its incidence.

When a ray of light moving in a straight line passes within a certain distance of a body parallel to its direction, it bends towards the body, or is *inflected*; but when the body parallel to its course is at a greater distance, the ray is bent from it, or *deflected*. When it passes obliquely from one medium to another of a different density, it is bent a little from the line of its former direction, and assumes a new one, or is *refracted*. In passing into a denser medium it is refracted towards the perpendicular; but from the perpendicular when passing into a rarer medium. The refraction is proportional to the density of the medium, but in that of a combustible the refraction is greater than the ratio of its density.

Every ray of light is resolvable into seven other distinct rays, each possessing a different degree of refrangibility; and consequently divisible from each other by the prism. The ultimate or component rays are distinguishable by the impression of colours they excite on the eye; and are arranged in the following order, *red*, *orange*, *yellow*, *green*, *blue*, *indigo*, *violet*. The red is the least refrangible, reflexible, and inflexible; the violet the most; and that of the others follows the order in which they are placed. The colour of bodies depends on their transmitting or reflecting those rays only which excite the impressions of their colour. The reflection of the whole prismatic rays constitutes white; the absorption or suffocation of all or the greater part of these occasions black, which is the total absence of light.

The illuminating power of the rays of light differs. Those towards the middle of the prismatic spectrum, as above arranged, possess the greatest illuminating power; but this diminishes as the rays approach towards the extremities.

Light enters into combination with bodies; and in some cases is again extricated without any change being produced, as in *pyrophori*, or substances which absorb light, and emit it again when carried into a dark place. In some cases, however, the absorption of light by bodies occasions very sensible changes in them: the colour of plants, for example, their taste and odour, and the quantity of combustible matter they contain, depend on light: for a plant reared in the dark is nearly colourless, insipid, inodorous, and contains a very small proportion of combustible matter.

The natural sources of light are the sun and fixed stars; but it is also artificially produced by combustion, chemical combination, heat, and percussion. The sun's rays, the greatest source of light, have been found to be composed of three dif-

ferent species of rays; 1. rays which produce light and colour; 2. rays of mere heat; and, 3. rays which produce neither light nor colour, nor affect the thermometer; but which have the power of deoxidizing: and, thus constituted, it produces very important chemical effects.

Light partially deoxidizes metallic oxides and salts. Thus it blackens muriate of silver; and as this takes place when the salt is placed beyond the violet ray, or out of the prismatic spectrum, the effect is apparently to be attributed to the action of the third species of rays. It also reduces the nitro-muriatic solution of gold, when it is placed in contact with charcoal, or any other vegetable, or any animal matter; and the red oxides of mercury and of lead become much lighter when exposed to the sun; the rays that produce these effects are the least refrangible. Dr. Wollaston, however, has pointed out one exception to this effect of these rays, in guiaicum, which becomes green or oxidized in the least refrangible rays; and is again changed to yellow, or deoxidized in the most refrangible.

Light has a powerful tendency to decompose liquid oxy-muriatic acid; and also nitric acid, which it renders red and fuming, even when it is contained in vessels accurately closed. Almost all the vegetable and animal colouring matters have their brilliancy and colour much impaired by long exposure to the sun's rays: they affect also the colour and the properties of vegetable powders kept in clear glass bottles. Light even seems to have a strong influence on the process of crystallization; for, if light be only partially admitted to a crystallizing solution, the crystals will be larger and more numerous on the enlightened side; and often the whole mass will radiate towards this point. Chaptal[1] found that by using a solution of a metallic salt, and shading the greater part of the vessel, capillary crystals shoot up the uncovered side, and the extent of the exposed part is distinctly marked by the limit of the crystallization.

Such are some of the properties of light, the chemical effects of the operation of which seem to be perfectly independent of its heating power; and there is even reason to believe that the greatest chemical changes are produced by the invisible rays: for Ritter[2] affirms that, by transmitting the coloured rays through different prisms, he has separated them from the invisible or chemical rays, and obtained a coloured spectrum devoid of any chemical power.

3. ELECTRICITY *and* GALVANISM.

THE phænomena of electrity depend on a very subtile fluid, which is a powerful chemical agent, capable of producing im-

[1] *Journal de Physique*, xxxiii. 297. [2] *Nicholson's Journ.* viii. 216.

mediate decompositions and new combinations. Galvanism appears to be essentially the same as electricity, differing however, in some degree in its effects and the mode of its production. Both are to be regarded as repulsive powers.

a. Electricity may be communicated to all substances: by some it is transmitted without any perceivable obstruction, but by others with much difficulty: hence bodies in their relation to electricity are distinguished into two classes, *conductors* and *non-conductors:* and as it can be accumulated in the latter by friction and other means, these are also denominated *electrics;* while the former are named *non-electrics*, to indicate their incapability of being excited.

Metals, water, and charcoal are conductors: all other substances are non-conductors; although many of these, when made very hot, become conductors. All electrics or non-conductors when rubbed, as, for instance, a glass rod with a piece of woollen cloth, attract light substances; and, when a conductor is approached to them, exhibit an appearance of light, attended with a peculiar sound and smell. Some electrics can be excited by simple heating or cooling. It is necessary, however, for obtaining any considerable excitation, that the rubber have some communication with the earth; from which it appears that the great source of electricity is in the earth, and that excitation consists in the mere transferring of the electrical fluid from one substance to another. By rubbing electrics on each other, the distribution of the electric fluid they contain is altered; and on separating them, more than the natural quantity remains with the one, and less with the other: the one is then said to be electrified *plus*, and the other *minus*, or *positively* and *negatively*. When two bodies are both electrified positively, or both negatively, they repel each other; but if one of them be electrified positively, and the other negatively, they attract each other. Instead of this distribution of the same fluid, the existence of two fluids has been assumed, each of which repels its own particles, but attracts those of the other; and this assumption is more favourable for the explanation of the chemical agency of this fluid.

The chemical effects of electricity seem to depend chiefly on its power of producing a sudden high temperature; and this appears to be proportioned to the resistance opposed to its transmission. It often favours chemical combinations, as that of oxygen with the metals, and promotes the instantaneous chemical union of gaseous bodies. It also effects chemical decompositions, as those of water, ammonia, alcohol, and metallic oxides. But for neither purpose is it employed as a pharmaceutical agent.

b. Galvanism may be regarded as a modification of electricity, in which the fluid is evolved during certain chemical actions. It is transmitted through those substances which are conductors of common electricity, and with the same degrees of facility and rapidity. The metals, charcoal to a certain extent, plumbago, water, the mineral acids, and saline solutions, are perfect conductors; water, alcohol, ether, sulphur, oils, resins, and metallic oxides, are imperfect conductors: but glass, dried and baked woods, the dry animal cuticle, and dry gases, are non-conductors of the galvanic fluid.

Galvanism is generally excited by arranging two different metals, as, for instance, copper and zinc, and a fluid, as nitric acid, diluted with twenty or thirty parts of water, in such a manner that the metals touch each other in one part, and have the fluid interposed between them in another.[1] The metals soldered together in pairs are placed transversely in the grooves of a well seasoned wooden, or an earthenware trough, and fixed in with a cement of resin and wax, to prevent any liquid from passing through; after which, the diluted acid is poured between the pairs, so that it touches the zinc of one pair, and the copper of another, alternately, the copper side of each double plate looking towards the same extremity of the trough throughout the arrangement, and the zinc side to the other extremity. This apparatus is named the galvanic battery; and the distances between the pairs of soldered plates should be from one-fourth to three-fourths of an inch each, according to the width of the trough. The intensity of action of this apparatus, as far as the production of heat is concerned, seems to depend on the size of the plates, or extent of surface; but, for producing chemical decomposition, on the number of plates, the more improved apparatus now used, is a trough of earthen-ware, divided in its length by numerous partitions of the same material. Into each of the cells thus formed, and filled with the diluted acid, a plate of zinc and of copper are placed, but not so as to touch each other; and a communication is made by a metallic arc between the zinc in one cell, and the copper in the next.

As a chemical agent, galvanism is the most powerful of all the repulsive forces, and is capable of producing decompositions which could not otherwise be effected. By its means the chemical constitution of the alkalies and the earths has been established, and their bases discovered to be substances hitherto unknown, which have been added to the list of metals.

[1] The pile of Volta, which is not now employed, consists of plates of zinc and silver, and pieces of moistened woollen cloth, piled in the order of zinc, silver, cloth; zinc, silver, cloth, for twenty or more repetitions.

By placing a compound, one, for instance, of oxygen and an inflammable body, in connexion with the metallic wires proceeding from each end of a galvanic battery, the oxygen is attracted by the wire that is in the positive state, and repelled by that which is negative; while, at the same time, the inflammable is attracted by the negative wire, and repelled by the other. Hence the components are separated, and obtained in an insulated state. In the decompositions thus effected, substances can be conveyed to a distance, and even through interposed ponderable matter, by the galvanic influence; a result which, however singular, is well ascertained.

Galvanism, like electricity, acts as a stimulus to the living system. Its effects on the animal body are a sensation of light when applied to the eye; a sensation of acidity on the tongue; and the excitement of strong muscular action.

It would be entering too much into hypothetical discussion to attempt an explanation of the phænomena of galvanism; particularly as philosophers are not yet agreed upon the subject. Galvanism has not yet been employed as a pharmaceutical agent.

On the forces of attraction and of repulsion every chemical, and consequently every pharmaceutical effect, more or less depends. A knowledge, therefore, of the laws which regulate these powers is of the greatest importance, and forms the basis of all chemical science.

SECTION II.[1]

EVERY substance, whether it be regarded generally as forming a part of the mass of this globe, or particularly as an object of science, may be arranged in one or other of the three following classes; *Solids*, *Fluids*, and *Gaseous Bodies*. We shall now examine each of these classes separately, and endeavour to describe the constitutions and combinations of the substances composing them, inasmuch as they are objects of pharmacy.

I. SOLIDS.

SOLID bodies are masses of homogeneous particles combined and held together by the attraction of aggregation or cohesion. The arrangement of the particles with regard to each other is

[1] In drawing up this section, I have borrowed very freely from the third book of Thomson's System of Chemistry, 4th edition.