Researches into the laws of chemical affinity / by C.L. Berthollet ; Translated from the French by M. Farrell.

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Berthollet, Claude-Louis, 1748-1822.
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Publication/Creation

London : Printed for John Murray; Edinburgh : Bell and Bradfute; Dublin : Gilbert and Hodges, 1804.

Persistent URL

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RESEARCHES
INTO THE
LAWS
OF
CHEMICAL AFFINITY.

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LONDON:
PRINTED FOR JOHN MURRAY, 32, FLEET-STREET; BELL
AND BRADFUTE, EDINBURGH; AND GILBERT AND
HODGES, DUBLIN.

1804.

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RESEARCHES,

&c.

ARTICLE I.

Object of this Treatise[*].

1. A THEORY of chemical affinities solidly established, and serving as a basis for the explanation of all chemical questions, ought to be a collection of, or contain, all the principles from which the causes of chemical phenomena can proceed, in every possible variety of circumstance; because observation has proved, that all these phenomena

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[*] The reading of this Treatise was commenced in the Institution of Cairo, June, 7th year.

are only the various effects of that affinity, to which all the various chemical powers of bodies may be attributed.

2. It cannot be expected that a work of this nature should have attained the utmost degree of perfection within the short space of time which has elapsed since chemistry has become regularly and philosophically progressive.

Bergman has treated this subject, and with more success than any other author. His work on elective affinity is useful and meritorious, not alone by the speculations which it contains on the nature of chemical affinities, on the opposition and concurrence of their various actions, and on the circumstances which can modify or disguise these actions; but still further, by the great number of chemical facts which it contains: and although observations have been made and multiplied since that great chemist wrote, and although some very learned treatises have been published on affinity since that time; yet his doctrine

trine is that generally adopted. I have been determined by that consideration, to make his work the basis of the principal part of the discussions which follow.

3. Let us suppose, says **Bergman**, the substance A completely saturated with the substance C, and that the combination be termed AC; if the addition of another substance, B, to this combination, removes C, there will result the combination AB, instead of AC. He prescribes then, for determining the elective affinity of two substances, to try if one of them can remove the other from its combination with a third, and *vice versa*. He takes it for granted, that that body which has removed another from its combination, cannot, in like manner, be expelled by that other, and that both experiments will concur to prove that the first has a greater elective affinity than the second. He adds at the same time, that it may be necessary to employ six times as much of the decomposing substance as would be ne-

cessary to saturate immediately the substance with which it tends to combine.

4. The doctrine of **Bergman** is founded entirely on the supposition that elective affinity is an invariable force, and of such a nature, that a body which expells another from its combination, cannot possibly be separated from the same by the body which it eliminated. Such was the certainty with which elective affinity has been considered as an uniform force, that celebrated chemists have endeavoured to represent by numbers, the comparative elective affinities of different substances, independently of any difference in the proportion of their quantities.

5. It is my purpose to prove in the following sheets, that elective affinity, in general, does not act as a determinate force, by which one body separates completely another from a combination; but that, in all the compositions and decompositions produced by elec-

tive affinity, there takes place a partition of the base, or subject of the combination, between the two bodies whose actions are opposed; and that the proportions of this partition are determined, not solely by the difference of energy in the affinities, but also by the difference of the quantities of the bodies; so that an excess of quantity of the body whose affinity is the weaker, compensates for the weakness of affinity.

If I can prove that a weaker degree of affinity can be compensated by an increase of quantity, it will follow, that the action of any body is proportionate to the quantity of it which is necessary to produce a certain degree of saturation. This quantity, which is the measure of the capacity of saturation of different bodies, I shall call *mass*.

Hence it follows, that in estimating the comparative affinities of bodies, their absolute weights are to be considered, and ought to be equal; but in comparing their actions, which depend

depend on their affinities and mutual proportions, the mass of each is to be considered.

6. I shall prove, therefore, in resuming the supposition of No. 3, that, in opposing the body A to the combination B C, the combination AC can never take place; but that the body C will be divided between the bodies A and B, proportionally to the affinity and quantity of each; that is, to their respective masses.

For the examples and proofs to be used in the following discussion, I shall refer principally to the action of acids and alkalis, comprising under the latter denomination, the earths which are endued with alkaline properties; because their great power and activity annihilates the influence of minute incidental causes, and because they frequently produce degrees of saturation which may be compared, and afford results that can be appreciated with facility. But the conclusions which I shall draw from their properties, will be applicable to all combinations in general. I shall adduce examples, to prove that the principle which I lay down, is applicable to the chemical action of all bodies.

After having proved by direct experiments, that the chemical action of bodies whose powers are opposite, does not depend on their affinity exclusively, but also on their quantity; I shall select observations on different kinds of combinations, which will confirm this principle, and prove its universality. I shall, in the next place, examine the circumstances by which this principle is modified, or those affections of bodies which favour, or impede, their chemical action, and which alter their proportions in the combinations which they are capable of forming: I shall apply the result of these considerations to compound affinities, and to those of compound bodies: I shall, finally, endeavour to point out, and fix the basis, on which ought to be established the general and particular theories of chemical phenomena.

ART. II.

Experiments which prove that in Elective Affinities, the Bodies whose Powers are opposed, divide between them the Body which is the subject of the Combination.

1. I HAVE kept an equal quantity of potash, and of sulphate of barytes, in a small quantity of boiling water. The potash had been prepared by alcohol, and contained no carbonic acid: the same served for the following experiments. The operation was performed in a retort, and consequently in communication with the air; and it was continued until the mixture was desiccated: the residue was washed with alcohol, which dissolved the potash, and after that with water, which also produced an alkaline solution, the alkali of which I saturated with acetic acid; after which, by evaporation, the solution yielded crystals, possessing all the characters and qualities of the

the sulphate of potash. Whence it appears, that the sulphate of barytes was partially decomposed by the potash, and that the sulphuric acid was divided between the two bases.

2. The sulphate of potash having been submitted to a similar experiment with an equal weight of lime, and the dried residue having been treated with alcohol, an alkaline solution was produced; and a part of the residue dissolved in water, and yielded a small quantity of sulphate of lime along with the sulphate of potash.

3. One part of the oxalate of lime, and two of potash, having been kept in ebullition in a small quantity of water until the water was totally evaporated, and washed afterwards with a sufficient quantity of alcohol, to dissolve the potash; the residue, treated with water, and evaporated, yielded crystals, bearing all the characters of the oxalate of potash.

4. One part of oxalate of lime was boiled to desic-

desiccation in two of nitric acid ; a part of the residue dissolved in alcohol, which solution was precipitated abundantly by oxalic acid ; a proof that nitrate of lime had been formed in the operation, and dissolved by the alcohol.

5. One part of phosphate of lime, and two of potash, were boiled together to desiccation in a small quantity of water. The alkaline parts were separated from the residue by alcohol, and the remaining part treated with water ; the evaporation of which, yielded crystals of phosphate of potash. The liquid which remained after this desiccation, contained still a great excess of alkali ; after the saturation of which by nitric acid, an abundant precipitate was produced, by a solution of lime and barytes ; a proof of its having still contained a considerable quantity of the phosphate of potash, to the decomposition of which, the formation of the phosphates of lime and of barytes was due.

6. Equal weights of potash, and of carbonate of lime, finely pulverized, were boiled in a small

quantity of water, which, after being filtered and rendered transparent, effervesced strongly with acids; and the residue, after evaporation, having been treated with alcohol, in order to dissolve the alkali, furnished a substance that had all the qualities and characters of the carbonate of potash.

7. Having boiled to desiccation equal quantities of soda, and of sulphate of potash, in a large quantity of water, and having treated the residue with alcohol, and afterwards with water, the alkali separated by the alcohol, was saturated with sulphuric acid, and the evaporation of the mixture produced sulphate of soda and of potash. The solution of the residue in water, gave, by evaporation, not only a sulphate of potash, but also a considerable quantity of crystallized sulphate of soda.

8. It is evident, from the preceding experiments, that the bases which are supposed to form the strongest combinations with the acids, may be separated from them by others,

whose affinities are supposed to be weaker, and that the acid divides itself between the two bases. It also appears, that acids may be partially separated from their bases by other acids, whose affinities were supposed to be weaker; in which case, the base is divided between the two acids.

If but a small quantity of the decomposing substance be employed, the effect will not be perceptible; but if, on the contrary, a large quantity be employed, as for instance: if I had treated the sulphate of barytes successively with additional quantities of potash, and removed, by repeated washing, the disengaged barytes, I should have ultimately decomposed the sulphate of barytes almost entirely. The greater then the relative quantity of the decomposing substance, the greater will be the effect produced.

Whence it appears, as remarked by BERGMAN, that if six times as much of the decomposing substance be employed as is necessary to saturate the base, a decomposition will be effected, which may be considered as total; because the antagonist substance retains so small a part of that with which it was combined, that it may escape the observer's notice, and be considered as an evanescent quantity. But if **Bergman** had carefully made the contrary experiment, as he recommends, he would have found that a similar decomposition could be produced by that means, as is evinced by the experiments just related.

In the experiment, No. 4, the nitric acid combined itself to a part of the lime of the oxalate of lime, and the oxalic acid retained the other; but after having separated the two combinations, another portion of oxalic acid, the energy of which was not diminished by any degree of saturation, was added to the nitrate of lime that had been formed, and a precipitation was effected, the lime sharing itself again between the two acids.

In the experiment, No. 5, the phosphoric acid divided itself between the lime and potash; and after the removal of the excess of potash, and the addition of the solutions of lime and barytes, the phosphoric acid was again divided between the three substances.

9. It results then from the preceding experiments, many circumstances of which I shall examine in the sequel, that when a substance acts on a combination, the subject of combination divides itself between the two others, not only in proportion to the energy of their respective affinities, but also in proportion to their quantities. The two substances which act on the combination ought to be considered as two antagonist forces, which act in opposition while they act on, and share between them the subject of the combination in proportion to the intensity of their action; which intensity depends on the quantity of the substance, and on the energy of the affinity: so that the effect increases or diminishes according as the quantity increases or diminishes. It has been already remarked, Art. I. No. 5, that the ab-

solute weight of any body, multiplied by the degree of its affinity, constitutes its mass.

10. It follows as a consequence of the preceding observations, that the action of a substance which tends to decompose a combination, diminishes in proportion as its saturation advances; for this substance may, in such case, be considered as composed of two parts, one of which is saturated, and the other free. The former may be considered as inert, and as unconnected with the latter, the quantity of which diminishes according as the saturation advances; whilst, on the contrary, the action of that which has been eliminated, increases in proportion to the augmentation of its quantity, until the equilibrium of the contending forces ends the operation, and limits the effect.

11. Another consequence is, that when a substance separates by precipitation, a part of the substance with which it was combined must also be precipitated along with it; be-

cause each particle of the precipitated body has yielded to the action of a particle of the precipitating, and the subject of combination must have been divided in the moment of the decomposition, in proportion to the respective masses which have acted.

ART. III.

Observations which prove that Chemical Action is proportional to the Mass.

1. I SHALL submit to the reader, observations on different kinds of combinations acted on by an elective affinity; in order to prove that the principle of chemical action proportional to the mass, applies strictly to their explanation.

Lime acting on the carbonate of potash, cannot completely decompose that combination, even by the addition of new quantities of lime, as is proved by the effervescence which the residue of the evaporated liquid produces with acids. In this operation, the action of the lime is checked by the influence of the potash, which remains present after its separation from the carbonic acid: the intensity of this influence increases according as the decomposition advances. See Art. II. No. 10.

When the operation has produced an equilibrium between the action of the lime and the resistance of the potash, the superfluous potash, or that part of it which is redundant to the constitution of the carbonate of potash, may be removed by a weak affinity, as, for instance, by alcohol; the liquor being previously filtered and evaporated; the alkaline alcohol gains the surface, and the carbonate of potash remains in solution in the under part. This latter might be acted on with an additional quantity of lime, and the carbonic acid reduced to an evanescent quantity.

It has been shewn (Art. II. No. 6), that the contrary effect may be obtained by the inverse operation; that is, the decomposition of the carbonate of lime by the action of potash, in sufficient additional quantities, and by the removal of the lime which has been eliminated from the combination. The only difference between the two operations, consists in the different quantities of the two substances which it is necessary to employ, in order to produce the opposite effects.

2. I have said that alcohol dissolves the potash which is superfluous or extraneous to the constitution of the carbonate of potash; but, in truth, the influence of the alcohol is counteracted before this effect is completely produced; for the carbonate of potash is not simply mixed with the superabundant potash, which prevents its crystallization, but forms with it a kind of combination, which might be called *alcalinulous*, from analogy with those termed *acidulous*. The potash is shared between the carbonate of potash and the alcohol, in proportion to the intensity of their action.

It appears, then, that alcohol can free the *alcalinulous* carbonate of potash of only a part of its superabundant potash. The carbonate acquires by this means, it is true, the property of crystallizing; but it becomes liquid again in a short time, by attracting the humidity of the atmosphere, whatever may have been the quantity of alcohol employed to neutralize it; so that, in order to bring it to the state of simple carbonate, it will be necessary to finish its saturation by adding carbonic acid.

Other neutral salts have a like property of retaining a part of the potash which exceeded the quantity necessary for their neutralization; a fact which explains a circumstance of the experiments cited, Art. II.; in which it was found that, after making use of alcohol to separate the superfluous potash, some was still found in the water with which the combination was washed. This property of salts ought to be attended to in analyzing; because, without that attention, one may fall into a double mistake on the quantity of alkali separated, and on the quantity of the substance from which the separation has taken place.

3. It has been supposed that sulphuric acid has a stronger affinity for lime than phosphoric acid; that the former can completely decompose the phosphate of lime; and that the phosphoric acid may be obtained by that means, combined only with a small portion of sulphate of lime, which it holds in solution. It has been proved, however, by the celebrated VAUQUELIN, that the phosphoric acid retains, in this operation, a portion of lime, and that it ought to be considered as an acidulous phosphate of lime*.

Sulphuric acid can deprive phosphoric acid of only a part of the lime with which it is combined in the state of phosphate; but as this part is not always in the same proportion, it would be a mistake to suppose that there were two degrees of saturation; that of the phosphate, properly so called, and that of the acidulous phosphate. The quantity separated is, therefore, always relative to that

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* Journal of the Polytechnic School. FOURCROY and VAUQUELIN have since published an interesting memoir on this subject.—*Mem. of the Nat. Inst.*

of the sulphuric acid, by the action of which the separation is effected; and the quantity of the sulphuric acid is limited by the necessary separation of the sulphate of lime, according as it is formed; for if too much of this acid was employed, the sulphate of lime would be dissolved as fast as formed; or, more accurately speaking, it would not be formed, and the lime would not be separated from the phosphoric acid, the crystallization of the sulphate of lime being impossible *.

4. The affinity of alumine may be looked on as one of the weakest of all the bases, and that base, therefore, which adheres with least force to its combinations; notwithstanding which, when the sulphate of alumine is decomposed by ammonia, as is usually done, and the precipitate treated with an additional quantity of ammonia, yet the alumine retains a considerable quantity of sulphuric acid, which becomes sensible by the following experiment:

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* The author supposes that salts do not exist ready formed in solutions, as they are obtained by crystallization, and that the solubility of salts is increased by mutual action.—*Translator.*

Let the precipitate be dissolved in muriatic acid, which forms, with alumine, a salt which does not crystallize: the liquid remains transparent. If a solution of the muriate of barytes be added to this liquid, there will be a precipitation of sulphate of barytes; or, if the liquid be condensed by evaporation, beautiful crystals of the sulphate of alumine will be formed, without the addition of any substance.

It appears, then, that the alumine, in precipitating, retains not only a portion of the sulphuric acid proportionate to its mass, compared with that of the contending substance, but also a portion of the alkali; by means of which, as is well known, the sulphate of alumine crystallizes. If the alumine has been precipitated, not from the sulphate of alumine, but from some other solution which contained no alkali, it must be a portion of that alkali which is employed to precipitate it, which it retains, since, after the precipitation, and the removal of the excess of alumine by an acid, the precipitate is in a state capable of forming a sulphate of alumine that crystallizes.

It results from the preceding facts, that, in the first place, in chemical analyses, an error is committed, in supposing the real weight of alumine contained in a combination, to be that which is precipitated by ammonia. To make a true estimate, it would be necessary to ascertain, by exact experiments, the quantity of acid, and of alkali, which remains in combination with the alumine.

Secondly, in the experiments in which alumine, precipitated from the sulphate of alumine, has been employed as pure, the result must have been erroneous and confused, on account of the sulphuric acid and alkali which remained in combination with the alumine. It is probable, for instance, that the uncommon solubility of alumine precipitated from an acid, in fixed alkalis, depends on a portion of that acid, of which it had not been deprived by the precipitation.

5. I recollect to have endeavoured to procure pure magnesia, by precipitating sulphate

of magnesia by potash, keeping this precipitate in digestion in a solution of potash, and by washing it afterwards. I submitted the magnesia thus obtained to a great heat, and was much surprized to find it acquire a very strong taste of sulphuret. I repeated the same operation with the greatest care, but with the same result. In this experiment, the magnesia had retained a portion of sulphuric acid, which being decomposed by the heat, its sulphur converted the magnesia into a sulphuret; though sulphur has but a weak affinity for magnesia.

It results equally from this experiment, that analyzers may be deceived, by supposing the real weight of magnesia contained in a combination, to be that of the precipitate obtained by elective affinity.

6. Atmospheric air dissolves carbonic acid, and as this latter resumes its elastic state by this change, an augmentation of volume takes place; whence it happens, that in leaving

atmospheric air in contact with water impregnated with carbonic acid, in a corked phial, an expansive effort is felt on drawing the cork: therefore atmospheric air, in contact with water impregnated with carbonic acid, will deprive the water of the acid, until an equilibrium be established between the action of the water and of the air.

By a similar reason, water, free from carbonic acid, or saturated proportionally less than the surrounding atmosphere, withdraws it from the latter, until an equilibrium be established. Lime-water produces the same effect in a much greater degree, but does not, however, totally free the air from this acid: the quantity remaining in combination with the air, is, in truth, small enough to be neglected, except in very particular circumstances; as, for instance, in the formation of water. If the oxygen gas employed in this operation, contain a small proportion of carbonic acid, whether communicated to that gas by the substance from which it was extracted, or whether formed in the operation, that portion cannot be totally separated; and the part of it which remains, is perceivable after the combustion by which the oxygen unites with hydrogen: besides, a certain quantity of carbonic acid may be formed by the carbon contained in the hydrogen.

7. The observations which I have made on carbonic acid, are more manifestly applicable to other substances endued with a weaker degree of elasticity, but capable of combining with atmospheric air: hence the diffusion of odours. If ether be put in contact with atmospheric air, it will divide itself between the water, which it always contains, and air, in proportion to their respective quantities; and the portion which combines with, or dissolves in the air, assumes the gazeous state. If this combination of air and ether be again exposed to the influence of a sufficient quantity of water, this latter will take the greater part of the ether, and the augmentation of the volume of the air will disappear.

8. Although muriatic acid has a much stronger affinity for water than ether or carbonic acid, yet a considerable expansion is observed in a portion of air isolated by mercury, and exposed to the action of this acid in a concentrated state. This expansion or augmentation may be reduced to zero by exposing the air to pure water.

Odorous liquids become gradually inodorous by exposure to the air; because the action of the water increases in proportion as the state of the combination recedes from that of saturation; so that an equilibrium is at length established between it and the air; and though the water contains still some of the odoriferous matter, yet it produces no sensible effect, owing to the strength of the combination, and the smallness of the proportion of the odoriferous matter.

9. The observations cited in this Article, and which might easily be multiplied, confirm the conclusions drawn from the experiments

described in the foregoing Article. Both observations and experiments concur in proving, that the subject of every combination divides itself between the two substances which act, or are acted on by elective affinity, in proportion to the quantity and intensity of their respective actions.

A fact which merits particular attention, and which proves that chemical action depends on the affinity and quantity of substances, is the difference of result obtained by a difference of a quantity.

I have said, Art. II. No. 4, that nitric acid had deprived oxalic acid of a part of the lime with which it was combined. The two combinations being separated, and pure oxalic acid added to the acidulous nitrate of lime, a precipitation was produced; because the lime was again divided between the two acids. It has been shewn by No. 5 of the same Article, that phosphoric acid divides itself between potash and lime. The excess of potash having been removed from the phosphate of potash, an addition of lime produced another division of the phosphoric acid: so that a combination which was partially destroyed by the addition of one substance, was re-produced in part by an additional quantity of the opposing substance.

The observations of the Nos. 6, 7, and 8, of this Article, prove equally the opposite effects produced by a change of proportions.

The observations 4 and 5, prove the remark made No. 11, Art. II. on the nature of precipitates produced by elective affinity, and which must be considered as combinations due to the partition that takes place in the action of the opposing substances.

ART. IV.

Of the Modification of Chemical Action which depends on the Insolubility of Bodies.

1. I SHALL examine successively the affections of bodies which can disguise or modify the principle established in the foregoing articles.

In order that the substances which are in opposition may act with all their power, it will be necessary that all their parts concur, and, consequently, that they be in the liquid state; as then the parts become uniformly, though not simultaneously saturated; particularly if heat or agitation be employed. By these means, the liquid becomes quickly uniform, if no precipitate has been formed; but precipitations are frequently formed, and many of the substances which may be put into action are either not liquid, or are scarcely soluble.

It is necessary to determine what influence the insolubility of bodies can have in every variety of circumstance, on chemical action, independently of the cause of this insolubility, of which I shall treat in the following article.

2. If an insoluble substance be opposed to a combination, it is evident that only a very small quantity of it can act; for the points of contact alone can oppose their action to the resistance made by the liquid within the sphere of action; and whilst the solid parts exert successively this very feeble action, the resistance of the liquid increases according as the decomposition advances. (Art. II. No. 10).

3. When a body is in some degree soluble, its action is composed of that of the part dissolved, and of that of the part which has retained its solidity: it follows, that its action does not increase in proportion to the quantity employed: lime, for instance, acts by the part dissolved, and by that which remains solid; but it is probably the dissolved part which contributes

contributes principally to the effect produced. If the quantity of lime employed in an experiment be doubled, without any increase of the liquid, the quantity dissolved will be diminished rather than increased; because a part of the liquid is absorbed by the lime added.

4. If an insoluble combination can become soluble by being deprived of a part of its composition, the inconvenience of insolubility is easily removed. Thus it is, when the phosphate of lime is acted on by an acid; the part of it which is within the sphere of action is instantly converted into an acidulous phosphate, and the other parts successively, until both the opposed substances be reduced to a liquid state.

5. When an eliminated substance becomes insoluble, the precipitate which is formed retains a portion of the substance with which it was combined, in proportion to the isolated forces which acted in the moment of the precipita-

tion (Art. II. No. 11, Art. III. No. 9): this portion has no further influence on the operation; so that the quantity of the precipitating body adequate to the precipitation, is all that is necessary until the end of the operation: this is proved in the decomposition of the sulphate of alumine by ammonia, or by lime.

The case is different when the eliminated substance assumes the liquid state: then the resistance increases according to the progress of the decomposition; whence it follows, that if a substance nearly insoluble be opposed to a combination, and that its action be consequently only partial, whilst the substance eliminated remains liquid, that the decomposition must be quickly stopped, whatever may be the force of the affinities; because the decomposing action depends not merely on the affinities, but also on the relative quantities in action. Thus, when I decomposed the sulphate of potash by lime (Art. II. No. 2), the operation was necessarily stopped as soon as the sulphuric acid was entirely divided between the potash and lime, in proportion to their respective affinities, and to the quantity of each which had acted on the sulphuric acid; that is, in proportion to their respective masses.

In order to judge of the relative state of combinations which continue liquid when two substances exert opposing forces, it will, in general, be necessary to consider the quantity of each of these substances which is in a state of action, and the division of the substance on which they act relative to these quantities.

6. The difference of specific gravity between an insoluble substance and a liquid, affects their mutual action, even though it should be aided by agitation and heat; because it tends continually to separate the insoluble substance, and to withdraw it from the action of the other: there will be a difference in this respect between the sulphate of barytes and alumine.

The precipitate of alumine I have considered only in the moment of its formation; but, in reality, if an excess of ammonia be employed, all that part of it which is superfluous to the precipitation of the alumine continues to act, and that for a long time, if the suspension of the alumine, and the contact of the two substances be prolonged by agitation, so that an equilibrium may be nearly established between the contending forces. The sulphate of barytes, on the contrary, ceases to have any action from the moment of its formation.

7. It follows from what has been said (No. 5), that when a liquid substance acts on another which is solid, or when a precipitate has been formed during the operation, it is not the absolute weight of the liquid that determines the degree or quantity of its action, but the degree of concentration, or mass, within the sphere of action. The greatest possible concentration of the liquid marks the term at which the decomposition ceases; the action of the opposed substance

substance is then increased, and relatively strong enough to resist any further decomposition.

8. If the insolubility of a substance prevents the proportions which would otherwise take place, it retards even those which are possible, and may lead into error by fallacious appearances in the commencement of the operation. Thus, for instance, when concentrated sulphuric acid is added to a solution of sulphate of potash, or to that of any other salt which requires much water to dissolve it, the acid combines with the water, and the salt loses its liquidity; but by prolonging the operation, and multiplying the points of contact, the salt re-dissolves, and enters into combination with the liquid.

ART. V.

Of Cohesion and Crystallization.

1. THE cohesion of the moleculæ of a body is due to the reciprocal affinity of these moleculæ: this force of affinity is surmounted by any substance that unites with the parts of the body, or destroys their combination. It is well known that alumine, when its parts have contracted the utmost degree of cohesion by heat, is no longer susceptible of being acted on by an acid which could dissolve it in a different state.

It follows, that when a liquid acts on a substance, or combination which is solid and insoluble, its action is limited, not by the insolubility alone, but also by the force of cohesion by which the integral parts of this combination are held together; which force is very variable. The effect, therefore, does not de-

pend

pend on the forces exerted in the sphere of action by the liquid and solid parts, but on the proportion of these forces to the force of cohesion.

2. This reciprocal affinity it is, which causes the crystallization of saline bodies: its influence on chemical action merits particular attention.

If a crystallized salt be put in water, a smaller quantity of it will be dissolved than if the water had been saturated at a great heat, and reduced to the same temperature. If, in this latter case, crystals of the same salt be placed in the solution, a part of that which was dissolved precipitates, and attaches itself to these crystals. In the first case, the water being saturated to a certain point, its force cannot overcome that of the cohesion of the crystals. In the second, the affinity of the contiguous crystals deprives the water of a part of the substance which it held in solution, and which it could have dissolved only by the assistance of

heat:

heat: this effect shall, however, be overlooked in the following considerations.

3. The force of crystallization of a saline compound, limits the quantity of that salt which water is capable of dissolving; it does not follow, therefore, that the affinity of water for a salt is satiated when the dissolution ceases, as that term is anticipated by the resistance which the affinity of cohesion opposes to the action of the water. When water has taken all it can dissolve of one salt, it can still dissolve a considerable quantity of another. It has even been remarked, that the solution of the second salt is more abundant than if none of any other had been pre-dissolved; and that, after the solution of the second, an additional quantity of the first might be dissolved in the same liquid: this increase of solubility is owing to the mutual affinity of the dissolved substances which overcomes the affinity of cohesion.

4. A salt endued with the property of

crystal-

crystallizing, can form in the necessary proportions, and crystallize, even in the midst of a liquid which holds in solution an excess of one of its constituent parts: thus the force with which a saline substance tends to crystallize in certain proportions of its constituent parts, can overcome the influence of the acid or alkali which is redundant, and neutral crystals may be formed in a liquid holding an excess of acid or of alkali. This excess must not, however, be very great; for, at a certain degree, it would overcome the force of crystallization, to the process of which, consequently, a stop would be put, and an equilibrium established between the contending forces, until the excess of acidity, or *alkalinity*, should be removed: the force of crystallization varies much in different salts.

5. A substance considered as eliminated from a combination, continues to act by its mass, if not drawn from the sphere of action by precipitation; it continues, in reality, to constitute what may be still called a combination;

tion; and though this substance be termed *free, disengaged, eliminated,* yet these terms cannot be considered as rigorously exact: they indicate merely the part which exceeds a certain degree of saturation, and which can be separated by a feeble affinity.

6. All that has been said relatively to crystallization, is applicable to precipitation; and, in reality, the greater part of precipitates have a crystalline form; as may be seen by the aid of a microscope. The only difference is, that the cause which determines this sudden crystallization is more energetic than that which produces crystallization, commonly so called; and, consequently, the effects which accompany it are more marked. Every precipitation takes place, therefore, before the affinity of the substance with which it was combined be exhausted; and the moment of its taking place, and the proportions of the constituent parts of the precipitate, depend on the force of cohesion, relative to the opposing forces.

There is, however, this difference between saline crystallizations and precipitates, that the salts which crystallize regularly, assume the solid state only in certain proportions of their constituent parts; but the greater part of precipitates may be deprived of a greater or less quantity of acid, the force of cohesion being inversely as the quantity of acid.

7. The force of cohesion, which had been considered only as an obstacle to solution*, determines the quantities of substances which can act on one another in a liquid, and modifies by that means the conditions of chemical action: it is that, besides, which causes the separations, whether by crystallization or precipitation, and governs the proportions of the constituent parts of a combination which is formed in the moment of separation, when the insolubility depends on these proportions.

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* GUYTON was the first to give a clear insight of the influence of the force of cohesion, opposed to the action of solvents.—*Ann. de Chim.* vol. xxvi. p. 134.

This force, therefore, opposes the action of a substance in two different ways; first, by opposing its dissolving power; and, secondly, by tending to re-produce a separation. Thus, when sulphate of lime is to be dissolved in water, the force of cohesion is, in the first place, to be overcome; and when the action of the water is enfeebled to a certain degree, this same force produces a separation of the sulphate of lime. In like manner, nitric acid acting on the sulphate of barytes, has to combat the force of cohesion of this latter substance, which force tends to re-produce a precipitate formed of the barytes and of the sulphuric acid which had been separated. When I come to treat of the action of solvents, this matter shall be set in a clearer light. It is evident at present, that whenever a body has a strong tendency to assume the solid state, by combining with another in certain proportions, that tendency alone suffices to produce its separation in that state, independently of the force of elective affinity; and that the portion of this combination which continues in the

the liquid state, amounts only to as much as the liquid can dissolve; so that the quantity of the precipitate depends on these two forces.

ART. VI.

Of the Elasticity of Substances which exert a Chemical Action.

1. WHEN a substance assumes the state of gas, on separating from an intimate combination, it becomes elastic, and can oppose no further resistance to the decomposing action: whence it appears, that substances of this nature do not act by their mass. The decomposing substance can then effect a complete decomposition; and it will suffice to employ just as much of it, as would have been necessary to form the same combination immediately, or at least a very trifling excess.

Thus carbonic acid may be disengaged from its combination by another substance, whose affinity for the base of the carbonate might be less; because that other substance can act by its mass, and can therefore over-

come

come the affinity of the carbonic acid, by acting successively: but to expel the entire of the carbonic acid, the decomposing substance must be used in quantity somewhat greater than that necessary to produce saturation.

2. The insolubility of the carbonate does not produce the effects which have been examined (Art. IV.): it forms no obstacle to the combination which ought to take place, particularly if the combination remain in the liquid state. The initial resistance, therefore, is the only one that retards the combination, as the substance which, in other cases, produces an additional one, vanishes in this; and the operation is slower than if both substances were liquid, merely by the successive instants being more multiplied.

3. If concentrated sulphuric acid be poured on desiccated muriate of soda, the affinity of the muriatic acid is diminished; and that acid assumes the gaseous state in consequence, and acts no longer by its mass: but if an aqueous

solution of muriate of soda be employed, or a diluted acid, whether the sulphuric, or any other, then the muriatic acid may be retained in the water; in which case it can act by its mass. The effect of the elasticity is counteracted in some degree, even when concentrated sulphuric acid is employed; because, in proportion as the sulphuric acid combines, the remaining part of it becomes more aqueous, and consequently capable of retaining the muriatic acid.

4. What has been said of these two acids, is equally applicable to ammonia. When its combinations are acted on in the dry state by a base, a part of it is expelled from the combination, and becomes sensible by its smell, or by the vapour which it forms with an acid; but this effect is also limited by the quantity of water contained in the substances in action.

5. It is necessary, therefore, when a substance is in the gaseous state, to consider its elasticity as a force opposed to the affinity of liquid substances. When water is placed in

contact with carbonic acid, it does not become saturated with that acid, as its dissolving power is counteracted by the elasticity of the gaseous acid, and an equilibrium of force established before the dissolving force is exhausted. If the elasticity of the gas be diminished by compression, the water will attain a further degree of saturation.

Thus the force of elasticity opposed to the dissolving force of water, determines the degree of concentration to which substances endued with it can be brought; such as muriatic acid and ammonia.

6. If a substance tend to combine with another, which is in combination with a gas, as for instance, when sulphuric acid tends to combine with the water contained in a given volume of atmospheric air, the water is divided in proportion to the masses in action, so that the liquid and the air become uniform in this respect, because an equilibrium of saturation is established between them. But if

the acid be exposed to the open air, it continues to act until the stratum of air in contact with its surface, and within the sphere of action, offers a resistance equal to the action of the acid. As the humidity of the atmosphere varies, so will the degree of saturation of the acid. In some cases it yields water to the atmosphere; at other times the contrary effect takes place. On this principle depend all hygrometric phenomena.

7. If there be exposed to the air a mixture, in which a fixed acid, or base, is opposed to a volatile substance dissolved in water, the separation of that volatile substance is promoted by an additional force; that is, the affinity of atmospheric air, with which all volatile substances have the property of combining: an effect is produced in this case, analogous to that mentioned, Art. III. Nos. 6, 7, 8, and an equilibrium established between the action of the liquid and of the air.

8. It results from what precedes, that elas-

ticity produces effects analogous to those of the force of cohesion, by modifying in a contrary manner the effects of the particular affinity of each substance.

9. The inference made, Art. II. No. 10, cannot be rigorously applied to decompositions, in which one of the substances assumes the liquid state, whilst the others remain liquid, or become solid; for that substance which has no tendency to the elastic state, or which is deprived of that tendency by the saturation which it undergoes, is totally separated from that which becomes an elastic fluid. We shall see (Art. XIII.) that the force of cohesion produces the same effect, relatively to liquids, in certain circumstances.

ART. VII.

Of the Action of Caloric.

1. ALL bodies contain a certain quantity of caloric, which is determined by their particular constitution, and by the degree of their temperature. In every combination a change is made in the quantity of caloric; because a different proportion of it is required in every successive change of combination. But as every particular constitution has its due proportion, the superfluity being given off, or the deficiency supplied from the neighbouring bodies, the obstacle to chemical action, which could result from this circumstance, may be neglected, unless very great changes of temperature take place.

2. When caloric, whether produced by new combinations, or collected by artificial means, causes a great elevation of temperature, there

are two circumstances to be carefully distinguished; namely, much or little difference in the volatility of which the substances are susceptible by an elevation of temperature.

3. If the substances be equally fixed, or if they be not all in the liquid state, or if one of them be soluble only to a slight degree, heat will favour their mutual action, by diminishing the force of cohesion, which acts even between liquid parts.

4. When one of two substances expands much more by heat than the other, the elasticity which it acquires by this expansion, ought to be considered as a force counteracting the affinity by which the expanded body was combined with the other. Thus carbonic acid is entirely eliminated from the carbonate of lime exposed to a great heat, by the sole force of elasticity. It may however be remarked, that, even in that case, the base acts by its mass, and that the resistance increases in proportion as the quantity of carbonic acid di-

minishes;

minishes; for the decomposition commences at a much lower temperature than that which is necessary for completing it. If alumine saturated with water be exposed to a great heat, a part of the water will evaporate by a moderate heat; but to expel it entirely, will require the highest possible degree of temperature.

5. It is in virtue of this property of caloric, that fixed acids decompose, at an high temperature, the combinations of the volatile acids; and as they differ much in this respect, the same acids may be considered as fixed, with respect to one, and volatile, with respect to another. Thus sulphuric acid expels entirely the muriatic and nitric acids from their combinations, with the assistance of a sufficient degree of heat; and it is itself expelled from its combinations by phosphoric acid, independently of affinities, which can only render it necessary to employ a degree of heat which can annul their action.

6. Therefore when, by the aid of heat, one body has separated another from its combination, it must not be inferred that its affinity is greater at an ordinary temperature: the substance separated by a great heat is analogous, in this respect, to a body endued with great elasticity at the ordinary temperature.

7. The application of heat may therefore, in many cases, derange the effect intended to be produced, when the substances acted on differ in volatility, and may, from the same circumstance, deceive as to the force of affinities. When a mixture of nitric acid and sulphate of barytes is boiled, as is necessary, in order to procure a contact between the parts which the weight of the sulphate of barytes opposes, the influence of the heat diminishes considerably the action of the nitric acid, compared to that of the sulphuric. If the temperature be reduced to its ordinary state, the nitric acid cannot produce the effect which depends on its force, because the great weight of the sulphate of barytes with-

withdraws it from the influence of that force; but if the barytes be opposed by potash, as in the experiment, No. 1, Art. II. heat will be favourable to the action; because potash does not differ perceptibly from barytes, in the elasticity which it can receive from heat.

8. As an elevation of temperature diminishes the action of elastic substances on those which are fixed, so does a lowering of temperature favour that action. Thus water dissolves more carbonic acid at a low than at a high temperature; the acidulous carbonate of magnesia is more soluble in cold than in warm water; the volatile acids, as the nitric and muriatic, can be more strongly concentrated, in proportion to the coldness of the water. This circumstance merits particular attention, in the comparison of the action of volatile substances with that of such as are fixed; and a considerable difference ought to be observed in the action of muriatic acid, compared to that of the sulphuric; or in the action of ammonia, compared to that of potash, by the

the variation of twenty degrees of the thermometer.

9. Generally, heat diminishes the intrinsic action of bodies, as it augments the distance of their integral parts; but it diminishes the force of cohesion by the same reason, and multiplies the points of contact between liquid and solid parts: it aids the general result of reciprocal action, when the force of cohesion which it surmounts, more than compensates the dilatation which it produces; but when it acts on bodies which differ widely in expansibility, it ought to be considered as a force unfavourable to combination, or one analogous to elasticity, of which we have treated in the preceding Article.

10. It cannot be doubted, that the parts of elastic fluids are not endued with the force of cohesion, as the substances dissolved by them undergo an equal distribution, which could not happen but by the means of a reciprocal chemical attraction; that which constitutes the force of cohesion. It may hence be conceived,

conceived, how heat may facilitate the mutual combination of elastic substances, even in augmenting their elasticity.

11. Therefore, the effect of caloric, when it does not produce separations by a difference of expansibility, is to counteract the force of cohesion; as for instance, in the operation of glass-making, in which it produces a reciprocal action of bodies, which their natural solidity renders inert: in that operation it concurs with the reciprocal affinity of substances acted on; whence the liquefaction of those substances when mixed, which, singly, are not susceptible of fusion.

ART. VIII.

Of Efflorescence.

1. SOME saline substances, but particularly the carbonate of soda, have the property of rising to the surface of the mass in which they are mingled, if that mass be in a certain state of humidity: the carbonate of soda yields soon afterwards its crystallizing water to the atmosphere, and loses, consequently, its crystalline form; but the property which I would distinguish by the term *efflorescence*, is that by which a substance raises itself to the surface; withdrawing itself thereby from the sphere of chemical action.

It is necessary that the soda combine with the carbonic acid which it can draw from the atmosphere, previous to its rising by efflorescence; but the action of the carbonic acid, which

which being in the elastic state, and in very small quantity, cannot augment perceptibly the force by which the soda separates from its antecedent combination; it can only withdraw the separated part, and prevent it from acting on the combination. We shall therefore here consider efflorescence only as aided by carbonic acid, together with other causes which I shall not examine, because they are not as yet sufficiently known.

As the separated part which acted by its affinity, and by its mass, is withdrawn, we must apply to efflorescence what we have said of precipitation and elasticity (Art. VI.).

2. It appears to me, that SCHEELE was the first who observed the decomposition of the muriate of soda by lime, which GUYTON has applied to ordinary use. The operation of that decomposition is as follows: lime acts on salts with fixed alkaline bases, as has been proved by the experiments of Art. II. No. 2: it decomposes

poses, then, a small part of the muriate of soda with which it is in contact; and the soda eliminated by this means combines with the carbonic acid of the atmosphere. The carbonate of soda effloresces; so that the eliminated soda opposes no resistance to the action of the lime; the decomposition of the muriate of soda continues, therefore, until impeded and stopped by the quantity of muriate of lime formed; for as the muriatic acid must be divided between the two bases in proportion to their action, the two forces must be counterpoised at a certain term: in order, therefore, to procure a total decomposition, it would be necessary to remove the muriate of lime.

3. A similar decomposition, as has again been observed by Scheele, is effected by means of iron, of the muriate, sulphate, and nitrate of soda, but not with the salts of potash; and though this celebrated chemist was somewhat embarrassed how to reconcile these facts with the received doctrine of affinities; yet

yet has he very judiciously attributed them to efflorescence, which is a property of the carbonate of soda, and not of the carbonate of potash.

ART. IX.

Of the Action of Solvents.

1. THE general purpose for which solvents are employed, is to overcome the resistance arising from the cohesion of parts, the immediate contact of which is the object sought; or that arising from their elasticity: the points of contact are multiplied by their action.

Solvents act on bodies, which they dissolve by their affinity and quantity, like all substances which tend to combine; and whatever has been said of combination in general, is applicable to them. Let us take water as an example, it being the most ordinary solvent.

The action of water may be limited by the cohesion,

cohesion, or crystallization of the body on which it acts, as has been shewn (Art. V.), or by its elasticity (Art. VI.); it is sometimes favoured by heat, as has been shewn (Art. VII. No. 3), and at other times diminished (as Art. VII. Nos. 7 and 8); water itself yields to the force of cohesion at the freezing temperature: it loses its dissolving power by freezing, and allows the salts with which it was impregnated to precipitate.

The dissolving power diminishes in proportion as the point of saturation is approached to; so that if there be a great proportion of water, its action on the substance dissolved will be very considerable; and as all action is reciprocal, that of the dissolved substance will, in the supposed case, lose a great part of its energy, or of its tendency to combine with other substances. Consequently, when a liquid acts on a solid combination, its energy does not depend merely on the state of concentration, which determines the mass by which it acts (Art. IV. No. 7), but also on the absolute quantity of water which counteracts the action on the solid combination.

The action of a solvent must therefore be considered as an alien force, influencing the action of two or more substances: by surmounting the resistance of cohesion, or of elasticity, and by multiplying the points of contact, it favours the reciprocal action of bodies more than it diminishes it by its own immediate action; but it may very perceptibly change or modify the results. It is of importance, therefore, to examine in what circumstances it may have that effect.

2. When an action takes place between two substances equally liquid, from which no precipitation can take place, the influence of water may be considered null, as it acts equally on the two contending substances, and subtracts a nearly equal proportion from the force of each.

The action of water may again be considered as null when a crystallization takes

place;

place; for if the crystallization be produced by evaporation, the quantity of the water is diminished in proportion to that of the salt which crystallizes: if it be produced by cooling, the circumstances remain unaltered, the temperature alone excepted.

But if a precipitate be formed which retains but a small proportion of water, the remaining part of the water will then bear a greater proportion to the substances which remain in solution, and will diminish their force of cohesion, concurring thus with the action of the contending body to prevent the precipitation. To this circumstance is to be ascribed, in part, that, in the precipitations which do take place, the effect is not complete, especially when there is a great abundance of water, before a portion of the water be removed by evaporation.

From a similar cause, when a liquid tends to produce an insoluble compound, by acting on a soluble combination (Art. IV.), the effect is limited by the water; the proportion and force of which increases directly as the quantity of precipitate formed.

The foregoing reflections are but of small importance, as they may be said to be applicable to chemical phenomena in but a very general way.

3. Though the dissolving power of water impedes the formation of a precipitate, by its action on one of the parts that should go to the formation of that precipitate, yet does it produce a contrary effect when it acts on a weak combination, one of the constituent parts of which has a strong tendency to dissolve, the other being insoluble, or nearly so; in this case, the water acts distinctly on the two substances composing the combination, in proportion to its quantity; the soluble substance is divided between the water and that which is insoluble. But as the action of the soluble substance is only enfeebled by that of the water, it retains a part of the insoluble substance, so that two new combinations are formed;

formed; one with excess of the soluble substance, and the other with excess of the insoluble substance.

Sulphate of mercury, for instance, dissolves in a small quantity of water, without suffering any decomposition; but if the quantity of water be increased, a partial decomposition and separation will follow; a part of the sulphuric acid unites with the water, and retains a part of the oxyde of mercury; but the greater part of the oxyde is precipitated, and retains a small portion of sulphuric acid: a further augmentation of the quantity of water will produce a further precipitation of the oxyde of mercury, and the second precipitate will retain a still smaller proportion of sulphuric acid than the former. If water be added to the first precipitate, a part of its sulphuric acid will combine with the water, and retain a certain portion of the oxyde; so that two different combinations may be formed, which may be made to vary in their proportions by different proportions of water.

This effect of water is much augmented by heat; because the substances acted on being different in their expansibility, the action of the water on the sulphuric acid is much less diminished than that of the sulphuric acid on the oxyde of mercury.

4. Solvents are sometimes used as a means of producing a separation; but if attention be not paid to the effect which the separation may produce, or to the action of the solvent on the pre-existing combinations, error will be the consequence.

Thus, when in the experiment (Art. II. No. 1), I separated the free potash by means of alcohol, and treated the residue with water, the potash which acted against the barytes being removed, the latter resumed its superiority, and decomposed the sulphate of potash: but the effect was limited, first, by a part of the potash which had been retained by the sulphate of potash (Art. III. No. 2); secondly, by the little solubility of the barytes. It results, however, that I obtained only a part of the sulphate of potash which was really formed.

5. Bergman says, that having mixed arsenic acid with a solution of phosphate of potash, and added some alcohol to the mixture, he found next day, that all the phosphate of potash was precipitated by the alcohol, and that the arsenic acid had combined with the alcohol. He concluded from that experiment, that phosphoric acid has a stronger affinity for potash than arsenic acid.

It must appear evident, from the proofs adduced in this article, that the arsenic acid acted on the potash of the phosphate, which was thereby reduced to the acidulous state: but the result was still further modified by the action of the alcohol.

The alcohol, by dissolving the arsenic acid, decomposed the arseniate that was formed, and thus determined the re-combination of the disengaged potash with the phosphoric acid:

acid: the experiment proves merely, that arsenic acid dissolved in alcohol, cannot perceptibly decompose the phosphate of potash, which is insoluble with respect to alcohol.

6. I have boiled muriate of soda with an equal portion of lime, and after decanting the liquid, found it to have the odour of alkali, and other indications of alkalinity.

I precipitated the lime which it contained by oxalic acid, and found the quantity of precipitate much greater than that obtained from an equal quantity of lime-water. The excess of precipitate in the former case ought to be attributed to a muriate of lime formed in the operation: the quantity of this muriate was limited by the resistance of the soda, and by the feebleness of the action of the lime, which was proportionate to its mass in the sphere of action.

If the liquid be evaporated, and the residue treated with alcohol, the soda will not by that means be separated from the salt which has been formed,

formed, as it would from the sulphate of lime; but both the soda and the muriate of lime will be dissolved: then the free alkali will act on the muriate of lime which is not supported by an excess of lime, that having been separated by means of the alcohol, and will decompose it almost entirely; because, independently of its affinity, a given quantity of it requires for saturation a much greater proportion of muriatic acid than the same quantity of lime: there remains, then, only a small quantity of the muriate of lime, the existence of which may be ascertained by oxalic acid, or by the carbonated alkalis. What I have described as happening to the solution by alcohol, takes place during its action.

In the foregoing example, I have, strictly speaking, only one direct proof of the decomposition of the muriate; that is, the strongly characterized odour of the alkali: the other indications of alkalinity might be due to the lime. The solution of a greater quantity of lime might be attributed to the action of the muriate of soda, and not to that of the muriatic acid alone; but an examination of the circumstances proves that this uncertainty necessarily results from them; so that I am justified in considering it as an additional proof of the principle which I establish, and as an example of the differences which the action of solvents may occasion in the results of chemical action.

7. I have considered (No. 1) the effect produced on the solvent by the resistance made to its action by cohesion and elasticity: as chemical action is reciprocal, it follows, that the observations which we have made are applicable to the substance which resists its action by its cohesion or elasticity; and we shall find in this consideration, a means of uniting several phenomena which appear widely separated.

When lime is put into water, the first effect produced is the impregnation of the lime by the water, which cannot immediately overcome the force of cohesion of the lime; but as this latter becomes saturated with water, its force of cohesion diminishes: a term is at length attained, at which the dissolving power of the water can overcome the reduced resistance of the lime; but this dissolving power diminishes, in like manner, by saturation. The operation goes on until an equilibrium of forces is established, at which the lime may be considered as saturated with water, the fluidity of which is destroyed by the force of cohesion; and the water, as saturated with lime, the force of cohesion of which is destroyed; a term being thus produced, at which the two saturations oppose one another equally.

The case is the same with respect to a salt deprived of water: it imbibes water until its force of cohesion be so far diminished as that it may be vanquished by the dissolving power. In crystallizing again, it retains a certain portion of water; so that an equilibrium takes place between the dissolving power of the water, and a certain force of cohesion which the saline particles retain. But if the experiment be made with a salt furnished with its water of crystallization, the solution will be instantaneous.

A similar phenomenon is presented by two liquids which have but little reciprocal action; as for instance, by water and ether. Water can dissolve a certain proportion of ether, as it does of a salt: if the quantity of ether exceeds that proportion, the natural affinity of its parts will offer a resistance superior to the diminished action of the water. The ether also acts on the water, and in dissolving a part of it, continues distinct from its mass: this mutual action continues until the term be attained at which both forces are equipoised: the quantities dissolved depend on the respective proportions of the liquids.

To the same cause is to be ascribed the production of alloys in different proportions, which are obtained by exposing together to the action of heat, metals that respectively possess but a feeble affinity.

If a small proportion of zinc be melted with a large quantity of lead, or a small quantity of lead with a large quantity of zinc, an uniform alloy will be obtained; but other proportions give two separate alloys; one of which contains a small quantity of zinc and a great quantity of lead, and the other the inverse proportions. The zinc acts on the lead at first with all its force; but this action is gradually diminished, and counteracted by the force of cohesion of the parts of the lead, which is also saturated to a certain degree with zinc. The proportion of each metal which enters into each alloy, depends on the quantities which act on one another. The same takes place between iron and tin.

It has been shewn that water continues to dissolve carbonic acid, until its decreasing energy be counteracted by the force of elasticity of the acid: and the carbonic acid which is redundant to the saturation of the water, dissolves in its turn a certain portion of water, by the saturation with which, its action is considerably diminished.

8. A solvent may then be employed in any proportion with the substance to be dissolved, when that substance offers no resistance; but if it be endued with a resistance which may be equal to the diminished energy of the dissolving power, two combinations will be formed, and balance one another.

9. When a separation has taken place in consequence of this equilibrium of forces, a change of proportion of one of the substances will suffice for producing a difference in the result: thus, when water, which contains only a small quantity of salt in solution, becomes exposed to a temperature inferior to the freezing point, a separation takes place; one part of it freezes, and the other takes all the salt. If a salt be deprived of the water by which it is held in solution, and placed in contact with pounded ice, the salt and ice continue to dissolve one another

another mutually, until a term be attained at which the dissolving force of the salt is diminished by saturation, and the resistance of the ice increased by cooling, and an equation of force produced.

10. It appears, then, that solvents which have to overcome the force of cohesion, are submitted to the same equilibrium of action as substances which have to resist or counteract an affinity that opposes their entering into combination; and that all that has been said (Art. II. and III.) on the effects produced by a change of proportions, is applicable to them.

11. Caloric acts on bodies equally expanded by it, analogously to solvents, by combating the force of cohesion, and by reducing the parts to a condition which favours their reciprocal action. (Art. VII. No. 9.)

Its action concurs with that of solvents in opposing the force of cohesion: hence it is that the solution of a salt by water varies with the degree of temperature.

When caloric acts on bodies which it expands unequally, it determines separations and new combinations which are independent of the affinities of the substances; as solvents do when they act on bodies of unequal solubility.

ART. X.

Of the Limits of Elective Affinities.

1. TO ascertain the elective affinity of two substances for a third, according to our idea of that term, it will be necessary to determine in what proportion that third substance divides its action between the two former, and the degree of saturation which each of these two can attain when they act in competition; their respective affinities will be commensurate with the degree of their saturation, which degree of saturation must be still further influenced by the quantity of each which acts; so that if these quantities were equal, the degree of saturation would be the exact measure of the affinity.

2. When I speak of the saturation of a substance, I do not mean the ultimate degree of saturation at which all reciprocal action

ceases; but a certain degree of saturation, which is easily ascertained, and which is common to all combinations; that is, the term of neutralization, at which neither of the constituent parts predominates. The term at which salts crystallize, does not always coincide with that of their neutralization: the carbonated alkalis, for instance, which continue alkaline, and the acidulous tartrite of potash, which, on the contrary, retains an excess of acid, crystallize in these states. The latter combination may, however, be obtained in the neutral state, as it also retains then the property of crystallizing: if the experiment be made with an excess of base, the neutralized tartrite is that which is necessarily obtained; and when there is an excess of acid, the degree of saturation of the acidulous tartrite of potash may be determined by the quantity of potash necessary for the neutralization of the excess of acid.

3. It will be particularly necessary, in comparing affinities, to employ in all experiments, the same proportions of the substances which

are to be placed successively in opposition; for if the proportions vary, the result can no longer be the same; the affinity can no longer be represented by the same number. I shall endeavour to illustrate this observation by an example.

Suppose the number 100 represents a certain quantity of potash to be saturated with 100 parts of sulphuric acid; I oppose 100 parts of soda to the potash: suppose it is found, after the operation, that the potash has taken 60 parts of acid, and the soda 40; I shall conclude that the affinities of these two substances for the sulphuric acid are as 60:40: but there remain 40 parts of potash, which are not combined, but which continue really to act, and contribute to the effect produced; so that if this quantity varies, the result must vary also. If, instead of 100 of potash and 100 of soda, only 80 of each be taken, there will remain 20 parts of potash uncombined, with which the uncombined parts of the soda will not be in the same proportion as in the

the foregoing supposition: whence it follows, that the two saturations cannot be in the proportion of 40 : 60.

4. In order to ascertain the degree of saturation at which each of these substances has arrived, it is necessary that a separation take place; and that can be effected only by crystallization, elasticity, precipitation, or the aid of a solvent: but we have already shewn, that these different means are to be considered as extraneous forces, which change the results, and occasion combinations, which are formed in such a manner as that the influence of these forces cannot be measured, nor their effects distinguished exactly from those of elective affinity: hence the separations which, in Art. I. II. III. were considered as solely due to elective affinity and proportion, were in reality the effects of several concurring causes; as is proved by the subsequent observations.

If it were necessary, for instance, to ascertain the quantity of sulphate of potash and of soda formed in the operation, the force of cohesion might be neglected, as differing little in these two sulphates, and therefore exerting but little influence on the quantity of each of these salts which should crystallize; but to obtain each crystallized, it would be necessary to separate the excess of alkali by means of alcohol, which, acting unequally on potash and soda, would therefore produce a difference in the result. To these considerations it may be added, that a change of proportions would produce a change in the force of the potash or soda (No. I.), and also in that of the alcohol, exclusively of the affinity of water, which serves as a solvent.

If barytes were compared with potash or soda, a much greater difference would be found; as then the great force of cohesion of the sulphate of barytes would leave to the alkali only a very small quantity of sulphuric acid, and this phenomenon would express the force of the solvent, relatively to the force of cohesion of the sulphate of barytes, rather than the affinity of the barytes, compared to that of the alkali.

The truth of this assertion is thus more obviously evinced: let us suppose that, in order to compare the affinities of acids, relatively to barytes, an excess of sulphuric acid be employed; the effect will be the total precipitation of the sulphate of barytes, unless the sulphuric acid be very much concentrated. It cannot be supposed that, in this case, the portion of sulphuric acid combined with the barytes, differs from that which has not combined, or that the one has a greater affinity for barytes than the other; yet this is affirmed, when we say that sulphuric acid has a stronger affinity for barytes than another acid has. An effect principally produced by the force of cohesion, is totally attributed to elective affinity.

It is manifest, then, that the elective affinity of two substances, with respect to a third, cannot be determined by a direct experiment, not even when it is made on two substances in the liquid state, and which can arrive at the neutral state, as extraneous forces must intervene, in order to enable us to ascertain the saturation.

5. We have shewn (Art. II. and III.) that the affinity of a substance may be compensated by its quantity.

It would appear from this consideration, that, in order to ascertain the relative affinity of acids and bases, it is sufficient to know their respective capacities of saturation, that is, the capacity of different acids for one base, or of different bases for one acid; for, considered under this point of view, the relative affinities ought to be inversely, as the quantities necessary to produce an equal degree of saturation.

An estimate determined by this inference, would be erroneous, if applied to elective affinities, because new forces are created on the

the moment that two substances are put to combine respectively with a third, which forces not only influence the results, but change even the constitution of the bodies.

Let the comparison of sulphuric and carbonic acids serve as an example: it is evident that the quantity of carbonic acid which neutralizes a certain quantity of potash, exerts a force exactly equal to that quantity of sulphuric acid which could neutralize an equal quantity of it; and yet if sulphuric acid be poured on the carbonate of potash, the carbonic acid will be totally expelled from it, and will assume the elastic state; and even though the carbonic acid should be retained in solution by a sufficient quantity of water, yet it will lose its former compression and constitution; so that it has lost its identity, relatively to chemical action. Finally, it is necessary to apply to substances unequally saturated, the observations made in the preceding Numbers.

It appears, then, that the comparison of capacities of saturation cannot serve to ascertain elective affinities, though it may lead to other important considerations.

ART. XI.

Of some Errors which arise from false Ideas of Elective Affinities.

1. I SHALL here enter on the discussion of certain opinions generally adopted on elective affinities; and shall prove their falsity, in opposing to them the principles established in the preceding Articles.

Beaume has observed, that, when sulphate of potash is dissolved in an equal weight of nitric acid, by means of heat, crystals of nitrate of potash will be obtained by cooling the liquid. He attributes the decomposition of the sulphate of potash to the influence of reciprocal affinities producing opposite effects, without, however, assigning the cause of this contrariety.

2. An erroneous explanation of this phenomenon

menon has been given by BERGMAN. He remarks, that there are some salts which have a tendency to retain an excess of acid; as for instance, the acidulous tartrite of potash. A salt of this nature, in the state of neutralization, he considers as having its base divided into two distinct parts, on one of which the whole action of the acid is directed, owing to the tendency of the salt to the acidulous state, the remaining part tending merely to combine with the excess of acid. The latter part of the base is, therefore, very feebly retained by the acid, and it may be taken up by an acid whose affinity is much weaker than that of the former: thus the acetous acid can take from the tartrite of potash, that part of the potash which exceeds what is necessary for the acidulous state, though the affinity of the acetous acid for potash be much weaker than that of the tartareous acid.

He further says, that the sulphate of potash is of the number of salts which tend to the acidulous state; that nearly two-thirds of its base enter into that state of combination, and receive alone the whole action of the sulphuric acid; and that the other third may be separated by an acid, whose affinity is much weaker than that of sulphuric acid, such as the nitric, muriatic, or tartareous acids. The decomposition having proceeded thus far, stops, whatever be the quantity of the other acid; and if that quantity be not too great, or if the excess be expelled by heat, an acidulous sulphate will be obtained by solution and evaporation, the crystals of which remain unchanged in the air.

3. The illustrious Bergman has, in this instance, widely deviated from the path which observation pointed out: even his own experiments prove that the excess of acid in the acidulous sulphate of potash, exerts its affinity; that it is in combination, and that it acts in proportion to its quantity: for he says, that the acidulous sulphate of potash dissolves in an additional quantity of sulphuric acid, by which it loses the property of crystallizing; that this excess of acid is with difficulty separated,

even by distillation, and that, in order to produce that effect, it is necessary to fuse the saline combination in a crucible, or to subject it to the reiterated action of the purest alcohol.

4. The limit which Bergman assigns to the action of acids on the acidulous sulphate, is therefore imaginary. This sulphate acts analogously to other salts which have the property of resisting, to a certain degree, the action of an excess of acid or of base (Art. V. No. 4), as also that of another acid or base. The only difference between the two sulphates, in this respect, depends on the force of cohesion, which may be more or less energetic in producing crystallization, and which belongs to certain proportions of acid and base; or probably it is a consequence of the form which the combining moleculæ assume.

5. It has been inferred, that an acid which has the property of forming a precipitate with a base previously united with another acid, possesses a stronger affinity for that base than the acid with which it was antecedently com-

bined,

bined, without so much as examining to what extent the new acid effected the decomposition, and without reflecting that the contrary decomposition takes place by a simple change of proportions, and that consequently an opposite inference could be made.

Thus the tartareous acid having the property of forming an acidulous and almost insoluble salt with potash, and consequently of precipitating potash from all its combinations that are not excessively diluted, it has been concluded that its affinity for potash is stronger than that of other acids. Bergman has excepted sulphuric acid, because he supposed that tartareous acid can act only on that portion of potash which constitutes a difference between the neutral and acidulous sulphates; a supposition which has been sufficiently refuted in the preceding Numbers. He has also excepted the nitric and muriatic acids, because he supposed that tartareous acid acted on the nitrate and muriate of potash as it does on the sulphate; but it appears that he did not ascertain the existence of an acidulous nitrate or muriate, analogous to the acidulous sulphate of potash.

He has inferred, from experiments made on salts, with soda for their base, without specifying them, that the tartareous ranks after the oxalic acid; with this single exception, tartareous acid decomposes, according to him, all the salts having a fixed alkali for their base.

A circumstance very embarrassing to BERGMAN is this, that tartareous acid does not produce a precipitate in solutions of salts having soda for their base: he attributes this apparent difference to the soda's not having the property of forming a nearly insoluble salt by taking an excess of acid; but then the proof of a decomposition having taken place does not exist, and the opinion must rest on the apparent probability that one fixed alkali has the same affinities as the other.

All his classification of affinities rests on the false supposition that one acid expels another by the sole force of affinity, considered as a constant and uniform power; which supposition must be followed by several others, to explain, as exceptions, facts which flow naturally from one general property.

6. I have examined the decomposition of the acidulous tartrite of potash by nitric acid, which, according to the opinion I then adopted, ought to decompose it entirely, by combining with its base. I poured nitric acid on the acidulous tartrite of potash, and placed the mixture to digest: by cooling, it yielded fine crystals of nitrate of potash. I reiterated the operation, by renewing the nitric acid until no more nitrate of potash could be procured; I then exposed the liquid to a heat sufficient to evaporate any nitric acid which might have remained in it, but not to produce any change in the tartareous acid. After this treatment, the liquid had the consistence of oil; was inodorous, and offered no indication of containing either nitric acid or potash; but, on exposing it to a strong heat, much nitrous gas was disengaged,

the tartareous acid was reduced to charcoal, and the residue yielded a considerable quantity of carbonate of potash.

7. In this operation a part of the nitrate of potash was separated by the force of crystallization, which force continued to operate until surmounted by the counteracting redundant acid. The acidulous tartrite was dissolved by the nitric acid, which deprived it at the same time of that part of its base necessary to its insolubility.

On the other hand, tartareous acid poured on nitrate of potash, deprives the nitrate of its base, to a certain degree, and forms an acidulous tartrite of potash, which precipitates; but as it has not the property of forming a nearly insoluble acidulous tartrite of soda, it produces no precipitate with the salts that have soda for their base.

In both cases, whatever cannot be separated by the force of cohesion, continues in the liquid state,

state, in which the substances act according to their mass.

Nothing, therefore, can be concluded respecting elective affinity from these separations produced by precipitation or crystallization, since, by a change of proportions, contrary effects may be produced.

8. The precipitation which, in comparing the affinities of bases, takes place, because an insoluble compound is formed, has given rise to a similar error; for, from this fact it has been inferred, that lime has a stronger affinity than alkali for fluoric, phosphoric, and arsenic acids, and in short, for all acids, with which it forms an insoluble combination; and consequently that it can entirely decompose the salts formed by the combination of any of these acids with an alkali. But the precipitation is not the result of an elective affinity, nor is it complete; the quantity of precipitate is determined by the dissolving force of the liquid, relatively to the force of cohesion of the precipitate.

pitate. Hence it is, that the precipitate is often re-dissolved by an additional quantity of the opposing substance.

9. Although BERGMAN has justly indicated the changes which heat may occasion in chemical action, when the substances are of a volatile nature; and though he has even recommended to avoid too great a heat in evaporation; yet the influence which heat has on the operations by which salts are separated, has been but incompletely estimated.

Had this particular been sufficiently attended to, it would not have been inferred that sulphuric acid has a stronger affinity for fixed alkalis than nitric or muriatic acids, on the sole ground of its expelling these acids from their combinations by the aid of a strong heat; but it has not been observed, that by the sole heat applied to produce or promote evaporation, and the crystallization of salts, the proportions of volatile acids may be very much changed with respect to the sulphuric acid which is opposed to them, and which may expel them completely, by means of its fixedness compared to their volatility (Art. VII. No. 5.)

10. Credit is due to BERGMAN, for some useful observations on the errors which may be occasioned by the solubility of a substance, the separation of which, though complete, escapes observation. He observes that potash or soda does not destroy the transparence of solutions of a salt having lime for its base, if the solution be diluted with fifty parts of water, because the separated lime dissolves in that proportion of water; but he forgets, that the natural solubility of lime is not such as to allow it to remain in solution in that proportion of water, seven hundred parts of water being necessary to dissolve one of lime: in this case, the solubility of the lime is augmented by the acid which continues in combination with it (Art. V. No. 5.), and of which the decomposition cannot deprive it (Art. III. No. 9.)

11. Notwithstanding his general observa-

tions,

tions, Bergman has, in many instances, mistaken the effects of solubility. Thus, he was of opinion that nitric and muriatic acids cannot act on phosphate of lime, though the sole difference, in this respect, between these two and sulphuric acid (the comparative force of their affinities being unknown), consists in the solubility of the salts formed by lime and the two former, compared to that of the salt formed by sulphuric acid and lime, which is easily obtained by crystallization.

12. It is the solubility of lime and barytes, augmented by the action of an acid, which prevents a precipitation from being produced in their solutions, by ammonia. The first portion of ammonia which is added to a solution of muriate of lime, ceases to be odorous; which clearly indicates its having entered into combination, and its action can be proved, as shall be immediately shewn.

I mixed ammonia with a solution of muriate of lime, and evaporated the liquid in a retort;

when evaporated to a certain degree, a considerable precipitate was formed. I continued the operation, and toward the end the quantity of precipitate was very much diminished, a pellicle was formed, and on cooling, a great number of long, needle-like crystals composed of a triple salt, from which the ammonia could be expelled by lime, was obtained; this salt re-dissolved, and the solution evaporated in the open air, gave no sign of ammonia when lime was added to it.

It appears, then, that the ammonia precipitated a part of the lime, when the muriate of lime was not too much diluted; although the lime had been rendered much more soluble than natural by the acid, and though the action of the ammonia was very much diminished by the heat, which diminished its affinity and quantity. According as the ammonia was diminished in quantity, the precipitate was re-dissolved; yet there remained some ammonia after a long evaporation; nor was it totally dissipated but by the action of the air. Doubtless the separation of the lime would be much more perceptible, if ammoniacal gas was received in a concentrated solution of lime.

The precipitation effected by ammonia in salts having alumine for their base, is owing to this earth being less soluble than lime, even when combined with that portion of acid which it retains in precipitating.

ART. XII.

Of Complex Affinities.

1. I SHALL examine, under the more general name of *complex affinity*, that which has been hitherto considered as produced by the action of four affinities, and which has been commonly denominated *double affinity*.

In order to give an idea of the action of four affinities, BERGMAN refers to the effects produced by the mixture of the solutions of the sulphate of potash, and muriate of lime: the effect is the same, he says, as if the same proportions of the acids and bases which exist in these salts were put together into water; the two bases act by their affinities on the two acids; and although the affinity of potash for sulphuric acid be greater than for the muriatic acid, yet the affinity of muriatic acid for potash, joined with that of sulphu-

sulphuric acid for lime, gives a sum of force which exceeds that of sulphuric acid for potash, and of muriatic acid for lime. This difference between the two concurring forces, determines an exchange of bases, so that instead of muriate of lime, and sulphate of potash, the combinations are sulphate of lime and muriate of potash. This explanation is also founded on the supposition that affinity is a constant and uniform force, independent of quantity, and of the state of saturation.

2. When two bases act in opposition on an acid, this acid divides itself, or rather, divides its action in proportion to their respective masses: if there be two acids instead of one, and if no separation result, either by precipitation or crystallization, both acids will act equally on both bases in proportion to their respective masses. If each of the acids be previously combined with a base, and the solutions of their salts be mixed, the sum of the reciprocal forces of the acids and alkalis will be the same as before: no muriate of potash, or

sulphate of lime will be formed; but there will be a combination of potash, of lime, of sulphuric and muriatic acid, which will have the same degree of saturation as before the mixture. Hence it is, that when two salts are mixed, the mutual decomposition of which would produce combinations of very different proportions, neither alkalinity nor acidity, which should necessarily result from such decomposition, can be observed: this has been very judiciously observed by GUYTON: a change of bases, therefore, does not take place.

3. An exchange of base was inferred from the result of crystallization or precipitation; but the effect was not ascribed to its real cause.

We have seen (Art. V.) that the force of cohesion causes the separation which takes place by precipitation or crystallization; a similar effect is produced by the same cause in complex affinities. If a solution of sulphate of potash be mixed with muriate of lime dissolved in a small quantity of water, the lime brought into contact with the sulphuric acid, will be more powerfully influenced by the force of cohesion, than the potash. It is therefore a force in addition to those which pre-existed, and determines the combination of the sulphuric acid with the lime, and the precipitation of the new compound.

4. If all the decompositions ascribed to complex affinities be investigated, it will be found that the prevailing affinity has been always ascribed to those substances which have the property of precipitating, or of forming a salt which can be separated by crystallization. For this reason it may be inferred, *a priori*, from a knowledge of the solubility of salts which may be formed in a liquid, that those substances which are least soluble, and most apt, therefore, to precipitate, will be found to be the same as those to which BERGMAN and other learned chemists have attributed the strongest affinity in their tables.

Lime, magnesia, strontites, and barytes, form insoluble salts with carbonic acid; all the soluble salts of these earths mixed with alkaline carbonates, produce an exchange, from which result the formation and precipitation of an earthy carbonate.

Barytes forms an insoluble salt with sulphuric acid; therefore, whenever a solution of a sulphate is mixed with that of a salt of barytes, there will be a precipitation of sulphate of barytes.

As the sulphate of lime is but little soluble, and consequently much disposed to precipitate, lime decomposes all the soluble sulphates to that term at which the precipitation is stopped by the solubility of the sulphate of lime. The sulphate of lime being much more soluble than the sulphate of barytes, the salts of barytes, which are more soluble than the sulphate of lime, decompose it.

The oxyde of silver forms an insoluble salt with

with muriatic acid: all the soluble salts of silver mixed with soluble muriates, produce a precipitate of muriate of silver: mercury, which is not highly oxydated, produces a similar effect.

As the muriate of lead is difficultly soluble, the soluble salts which the oxyde of lead forms with other acids, produce a precipitation in the soluble muriates. But the oxyde of lead forms an insoluble salt with sulphuric acid; and therefore the muriate of lead produces a precipitation in a soluble sulphate.

5. Therefore, when water in which different salts have been dissolved, is evaporated, the separation of these salts will be according to the order of their solubility; and it is by the same circumstance, that the interchanges of base which may take place can be foreseen.

But the solubility of salts is varied by temperature; it is therefore the solubility relative to temperature that ought to be considered.

Nitrate of potash, mixed with muriate of soda, will crystallize at a low temperature ; but the muriate of soda will separate during evaporation : there will be no change of base, because the nitrate of soda is somewhat more soluble, when cold, than nitrate of potash ; and because, on the contrary, muriate of potash is somewhat more soluble when hot, than muriate of soda.

6. I consider, at present, the result only as produced by a force of cohesion, strong enough to surmount the powers by which it is opposed ; but when no considerable force of this nature occurs in the combinations which may take place, the mutual action of the substances which continue in the liquid state, that of the solvent, the variety of proportions occasioned by the crystallization and separation of a salt, must produce different effects. The experiments which I have given will leave nothing undetermined on this subject.

7. Another circumstance which may change

the action of complex affinities, is the formation of a triple salt, which precipitates; but by knowing the solubility of this combination, the decomposition which shall take place may, in this case too, be foreseen; the same consideration is applicable to affinities termed *elective.*

8. A precipitate is sometimes formed by mixing two salts which have the same acid; as for instance, by mixing muriate of magnesia with muriate of lime: it is probable that two combinations are formed in this case, one with excess of acid and a small portion of both bases; the other, with a large portion of the bases, and a small one of acid.

This effect is analogous to that which we have observed (Art. IX. No. 3.); but in this case, it is the mutual affinity of the two bases which causes the precipitation.

9. We have seen (Art. VII.) that heat, by augmenting the volatility of a substance, en-

feebles its combination; and this cause is not less efficient in complex than in elective affinities: it is a force added to those already in action, and which determines the union and separation of the substances which are most disposed to form a volatile compound.

If, therefore, 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. Many examples of this nature are furnished by ammonia, and the oxyde of mercury, among the bases; by carbonic and muriatic acids among the acids.

10. Efflorescence should be considered as another force which, in complex affinities, might determine a combination that is endued with that property; and to it is to be

ascribed the formation of *natron*, in the valley of the Lakes of Natron, and in other places where the same circumstances concur.

The observations which I have presented to the Institution (of Egypt), and which ought to be considered as the continuation of the interesting description of the valley of the Lakes of Natron, for which we are indebted to General Andreossy, prove that the circumstances necessary to the formation of natron are, 1st, a sand containing a great quantity of carbonate of lime; 2d, humidity; 3d, muriate of soda. I have also remarked that reeds contribute much to its formation.

I have bound myself to explain the formation of the carbonate of soda by the influence of these circumstances; I shall now proceed to the discharge of that duty.

The calcareous sand impregnated with humidity, may be considered as a solution of muriate of soda, which acts incessantly on the

the carbonate of lime; but it follows from what has been proved (Art. IV.) that though the insolubility of a solid substance acted on by a liquid, diminished much their reciprocal action, yet it did not destroy it entirely. This action is opposed to the insolubility of the carbonate of lime, which insolubility is not absolute: a small portion of the carbonate of lime will therefore be dissolved; and consequently (No. 1 and 2) the constituent parts of this carbonate and of the muriate of soda which are in solution, will act on one another reciprocally, otherwise the presence of carbonate of lime would not be a condition necessary to the formation of the carbonate of soda *.

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* The solution of the carbonate of lime by the muriate of potash and sulphate of potash, which undoubtedly act in the same way as the muriate of soda, is proved by a direct experiment made by GUYTON (Memoirs of SCHEELE, Part II. Note, page 18): " the solution of sulphate and muriate of potash, &c. poured into lime-water disturbed by a solution of carbonic acid in water, caused the precipitate to dis-

appear;

The humidity of the calcareous sand must therefore be considered as a solution of muriate of soda, and of a small portion of carbonate of lime, in which, consequently, carbonic acid and soda are, at the same time present, and the formation of carbonate of soda rendered thereby possible; the disposition to which formation is further aided by efflorescence, which is a property of the carbonate of soda, and which removes that combination from any ulterior action. The fact is, that

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appear instantaneously; nor was there any earthy precipitate produced by adding water impregnated with carbonic acid, to a solution of lime and the fore-mentioned salts; the liquid retained always some free alkali." **Guyton** combats the opinion of **Scheele**, who had not observed any decomposition of the muriate or sulphate of potash, but merely of the salts that had soda for their base.

The difference of opinion between these two celebrated chemists, proceeds from the one having merely stated the decomposition produced by efflorescence, which is peculiar to salts of soda (Art. VII.); the other, that produced in a liquid: but in the latter case it is much more limited.

when reeds, which favour efflorescence, are found to grow in a soil impregnated with muriate of soda, not only an accumulation of carbonate of soda takes place about their stalks, but their presence is sometimes absolutely necessary to its formation; as for instance, when the argillaceous nature of the soil, or other circumstances, are unfavourable to its production, hence muriate of soda is found at but a little distance from the carbonate of soda, formed as described.

I have endeavoured to bring this theory to the test of experiment: I placed for this purpose a large vessel in one of the gardens of the Institution, and put into it some carbonate of lime, mixed with siliceous sand, both being previously well washed; and I added afterwards some muriate of soda: a hollow was now made in the middle of this mixture, into which water was occasionally poured. An incrustation of muriate of soda formed on the surface, which already changed the colour of paper tinged with fernambucca; but a considerable efflorescence can be expected only after a much greater lapse of time than that allotted to my experiment.

11. The preceding considerations shew, that the only difference between complex affinities and those called elective, consists in this, namely, that in the former case, substances already saturated to nearly an equal degree are put into action, and in the latter, substances, one of which (or many) is not saturated. In the former a certain degree of saturation is attained by these combinations only, which have a tendency to separate; but in the latter, the unsaturated substances assume a degree of saturation that is in an equilibrium with those that were already saturated. From these different circumstances, the forces of cohesion and affinity act with more effect in complex than in elective affinities.

ART. XIII.

Of the Precipitation of Metals from their Solutions by other Metals.

1. WHEN metals are precipitated by a substance which does not deprive them of their oxygen, the precipitates retain a part of the acid, and sometimes of the precipitating body.

A striking example of the division which takes place in these cases, is had from the precipitate obtained from oxygenated muriate of mercury, by a fixed alkali, ammonia or lime. More or less of this precipitate is reduced by exposure to a sufficient heat; another sublimes and forms a muriate, not because the muriatic acid is combined with only a part of the oxyde of mercury, as I formerly thought *(Memoirs of the Academy)*, but because the expensive power of heat, and the tendency of the muriatic acid to enter into combination, act on the oxyde of mercury, and make a new division of it. If the precipitate by ammonia be examined, it will be found to retain a portion of the ammonia: the precipitate obtained from the muriate of iron by potash, retains a portion of potash. Similar facts might be multiplied at pleasure.

There can be no doubt, therefore, but that the observations which have been made on the precipitation of substances that lose their solubility, ought to be applied to metallic precipitates, which vary according to the circumstances that modify the forces which act on the moment of precipitation.

But when metals precipitate one another from their solutions, their affinity for oxygen has a considerable share in the action that takes place; and in some cases the precipitate is entirely reduced to the metallic state. If the affinity of the precipitating metal for the oxygen of the precipitated, was not aided by some other force, it ought to follow from the principles established in this Memoir, that the oxygen should be divided between the two metals, in proportion to their respective actions: it is necessary, therefore, to examine what force it is which determines the precipitation of metals in their metallic state.

2. Mercury, gold, and silver, have but a very feeble affinity for oxygen. The mutual affinity of the parts of these metals, when in the state of fusion, as mercury is at the ordinary temperature of the atmosphere, is sufficient to prevent their combination with oxygen in the state of gas; but the expansion given to the parts of mercury by heat, diminishes the force of cohesion of its particles so much as to admit of their combining with oxygen: a greater degree of heat, by the unequal expansion which it occasions in mercury and oxygen, produces the separation of these two substances. The influence of heat concurs with affinity in the commencement of the operation, by overcoming the force of cohe-

sion, but it opposes it in the latter part, by occasioning a difference of expansion ; and the continuance of its action renders the difference of expansion so great as to totally prevent combination, or destroy it when formed.

As the force of cohesion of mercury suffices to prevent its oxydation, so this same force may concur to its reduction when in the state of oxyde, and when placed in contact with another metal which acts directly on its oxygen. This force is analogous to that which produces crystallization and precipitation (Art. V.)

3. The homogeneous particles of a metallic body, have an affinity not only for one another, but also for other metallic particles ; hence the formation of alloys and amalgamas. To effect a combination of mercury and copper, it suffices merely to place these two metals in contact. When, therefore, a metal acts on a metallic solution, one part of it may act on the oxygen and acid, whilst another part tends

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to combine with some of the metal itself. Let us investigate these two causes, namely, the reciprocal affinity of homogeneous particles, and that of one metal for another, in the precipitations of mercury, gold, silver, and copper, in the metallic state.

4. When a piece of copper is immersed in a solution of mercury in nitric or muriatic acids, the copper becomes instantly white, the mercury is reduced, and combines at the same time with the copper.

If, instead of copper, a piece of iron, perfectly clean and pure, be plunged into the same solution, several hours will elapse before the liquid becomes turbid, or a precipitation can be perceived: a precipitation, however, takes place at length, particularly from the solution in muriatic acid; but this precipitate is partly in the state of an oxyde, and retains probably a portion of acid.

If the affinity of one metal for oxygen was the sole cause which produced the precipitation of another, iron ought to act with much more energy than copper, as its affinity for oxygen is much stronger; and yet its action is slow, difficult, and incomplete, whilst that of copper is instantaneous. The indecomposable acids are retained, with nearly equal force, by the oxydes of copper and of iron, as is proved by the exposure of their combinations to heat. There can be no doubt, then, but that the affinity of copper for mercury, which, in fact, combine, contributes powerfully to the precipitation of the latter in the metallic state ; but in the experiment with iron, the mutual affinity alone of the parts of mercury, produced, though with difficulty, a precipitation in the metallic state ; thus, a part of the mercury was precipitated in the state of oxyde, and retained, probably, a portion of acid, as all the precipitate would have done if the affinity of iron for oxygen had been the sole acting cause, and if the part precipitated in the metallic state had not combined with the iron.

5. When silver is precipitated from its solution by copper, the precipitate which assumes the metallic state is not pure silver, but a combination of silver with a small portion of copper. This portion of copper could not have been furnished immediately by the piece of copper which was immersed in the liquid: it must have been previously in solution, and must have been precipitated along with the silver from the solution itself; the mutual affinity of the two substances effecting their reduction. By means of this force, two combinations were effected in the same manner as in several other circumstances: one of oxyde of copper and acid, the other of silver and part of the copper. An equilibrium is established between the action of the acid on the oxyde of copper, and that of the silver on the copper.

6. In like manner, when a solution of gold is precipitated by copper, the colour of the gold precipitated indicates a mixture of copper, and all the copper lost by the piece put into the

the solution of gold is not found in solution after the precipitation of the gold; consequently a part of it must have united with the gold.

If a blade of iron be placed in the same solution, the gold which precipitates probably brings with it, in like manner, a part of the iron; this at least is certain, that the precipitation of the gold is determined by the affinity of the iron, to the surface of which it attaches itself: for gilding is only a combination of two metals at the surfaces by which they are in contact; when the first stratum of precipitate is formed, the precipitation may be continued by the mere force of cohesion of the gold.

7. What I have just advanced, is verified by the precipitation of copper by iron: when a solution of copper is decomposed by a piece of iron, if the stratum of copper which is formed on the surface of the iron be taken off, it will be perceived by the colour of the inside, that it is not pure, but that it contains some

iron: after the formation of the first stratum, the copper continues to precipitate in uniting with it, and afterwards with the strata successively formed; thus the affinity between iron and copper commenced the decomposition, which is continued by the mutual affinity of the parts of the copper.

8. Phosphorus precipitates several metals from their solutions, as has been proved by Sage and Bullion*. Although phosphorus has a very strong affinity for oxygen, yet what has been said on precipitation effected by metals may be applied to its action.

Pelletier has proved, that phosporus has the property of combining with metals; for which reason, while one part of it combines with the oxygen of a metallic oxyde, the other part may combine with the metal itself.

There are some metallic solutions on which

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* Journal de Physique, 1781.

phosphorus has no effect; there are others, from which it precipitates the metal in the state of oxyde, which precipitate retains, doubtless, a part of the acid in which it was dissolved, or of the phosphoric acid which is formed in the operation: there is still a third species of metallic solution, from which the metal is precipitated by phosphorus in the reduced or metallic state. The solutions of gold, copper, silver, and mercury, are those from which the metal is precipitated in its reduced state.

From the foregoing remarks it appears, that copper and silver are precipitated by phosphorus, and that they combine with the phosphorus in the proportion of about one of the latter to six of the former; thus, three grains of phosphorus were consumed in precipitating twelve grains of silver: something short of three grains of phosphoric acid were obtained in a thick, gelatinous state, for the formation of which less than one grain of phosphorus sufficed; more than two grains, therefore, combined with the precipitate.

A part only of the precipitate of mercury by phosphorus resumes the metallic state; the other part retains its oxygen, and combines with the phosphoric acid that is formed. In this instance the force of cohesion is weak, and no combination is formed between the phosphorus and mercury: the effect is, therefore, only partial, and similar to that produced by the action of iron. (No. 4).

Although the affinity of gold for oxygen is very feeble, and far inferior to that of copper, yet the precipitation of gold by phosphorus is less prompt, and a part of the precipitate is in the state of oxyde. This difference must originate from the little disposition in gold to combine with phosphorus, compared to that of copper: it is, therefore, the strong tendency of copper to combine with phosphorus that determines its precipitation in the metallic state.

Some of the foregoing observations require, for their more perfect and total explanation, a further elucidation from experiment; but it appears to me to be proved beyond all shadow of doubt, that the force of cohesion which tends to unite the particles of an homogeneous metal, and the reciprocal affinity of some metals, are the causes which produce precipitation in the metallic state; for which reason, this effect is more or less prompt, or complete, according to the energy with which these causes act*.

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* FABRONI has just published some very interesting observations on the reciprocal action of metals (Journal de Physique, October, year 8.

ARTICLE

ART. XIV.

Of resulting Affinity.

1. BY *resulting affinity,* I mean the action produced by different affinities existing in one substance; for instance, nitric acid is composed of oxygen and azote, and in combining with potash, acts by an affinity which results from those of oxygen and azote: the reciprocal action of potash is also composed of its different actions on the oxygen and azote, which constitute nitric acid.

2. All substances have an affinity for one another. Though the universality of this principle should be denied, yet it must be admitted that there are but few exceptions to it; I may therefore reason on this hypothesis, and apply to all substances the result of our observations on affinities and their modifications. If this reasoning be admissible, and

if it account for properties which cannot be proved by direct experiment, the considerations contained in this Article will throw some light on several phenomena arising from a chemical action not yet understood.

3. In my definition of resulting affinity, I have taken for granted, that the affinity of a compound substance is derived from those of the substances of which it is composed. It is necessary to examine the circumstances which modify the elementary affinities, and ascertain the change produced in that which results from them.

4. The chemical action of substances diminishes in proportion to their saturation (Art. II. No. 10.)

From this principle it follows, that resulting affinities must be less strong than elementary affinities considered abstractedly, as the former are in a certain degree of saturation: other circumstances may augment the action of resulting

sulting affinity, or may concur with saturation to diminish it still further.

5. If one of the substances which combine, change from the solid to the liquid state, it acquires thereby the advantages derived from solution; and its affinity, which was disguised by the solid state, becomes more active, for which reason resulting affinity may appear to be much more considerable than the elementary affinities appeared to have been.

Thus, when sulphur is dissolved by potash, and the sulphuret rendered liquid by water added to it, or by its attracting the humidity of the air, it acts with increased energy on oxygen gas; because it has lost its cohesion by the change it has undergone, as if it had been liquefied by heat; and because the potash too acts on the oxygen, though much more feebly than the sulphur, as is evident from the insufficiency of its action, when unaided, to surmount the elasticity of that gas. The action of the sulphur is, in fact, diminished by by the quantity of force which it exerts on the potash, and water in which the sulphuret is dissolved; but it gains more by the liquid state than it loses by that saturation. Strictly speaking, all substances changed from a solid to a liquid state by a dissolving power, act by a resulting force.

6. Contrary circumstances produce contrary effects; thus when substances, by combining become more solid, or acquire an additional tendency to crystallize, this circumstance adds to the loss of force produced by saturation.

For instance, potash and nitric acid are separately soluble in alcohol, which does not, however, dissolve the nitrate of potash; the reason of which may be found in the force of cohesion of the nitrate. That this is the case is proved by this circumstance, that salts which cannot crystallize in water, on account of their feeble force of cohesion, are soluble in alcohol, and crystallize in it; because their force of cohesion, though weak, suffices,

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however, to surmount the still weaker action of alcohol.

The solubility of nitrate of potash in water is accounted for, by the greater solubility of its constituent parts in water than in alcohol.

7. The action of substances is in proportion to their quantity within the sphere of action (Art. IV.)

It follows manifestly from this principle, that the action of a compound may surpass by much that of its constituent parts, when both or one of them, by entering into combination, pass from the state of elastic fluid to that of a liquid: in that case, the great quantity brought into the sphere of action more than compensates for the diminution of force occasioned by saturation.

Thus the action of potash on azote or oxygen gas, is not sufficient to counteract the elasticity of these gases; but when they are combined and reduced to the liquid state, in the form of nitric acid, their action on potash is considerably increased; and the result of that action, though the oxygen and azote have lost some energy by combining to form nitric acid, is greater, on account of the quantity within the sphere of action than if the oxygen and azote were used separately.

8. The affinity of a substance which combines with a compound, concurs with the elementary affinities of the latter, according to the degree of saturation which it produces, to the maintenance of its composition, in opposition to other forces acting on it. Thus iron deprives azote of the oxygen combined with it in nitric acid, or, rather, causes a partition of it, one part uniting with the iron, the other remaining combined with the azote; but when nitric acid is combined with potash, iron cannot separate the oxygen from the azote at a moderate temperature: at an elevated temperature, however, the difference of expansion counteracts the affinity of the pot-

ash,

ash, so far as to favour the decomposition of the nitric acid by iron.

The oxygen of oxygenated muriatic acid which is only slightly saturated, and, consequently, weakly combined, is easily separated from the muriatic acid; but though the proportion of oxygen, in oxygenated muriate of potash, is much more considerable than that in oxygenated muriatic acid, yet it is much more difficultly separated.

The phosphate of lime is not decomposed by charcoal, even at a very high temperature; but if it be in the acidulous state, a part of the acid, which may be considered as redundant, is decomposed by charcoal, because it is not supported by a sufficient quantity of base: this is the only part of the acidulous phosphate from which phosphorous is obtained by charcoal.

9. The contrary effect is produced, when,

instead of a saturating substance supporting the resulting affinity, a substance is added which tends to form a combination with one of the constituent parts of the pre-existing combination. When, for instance, sulphuric acid is added to a mixture of iron and water, the decomposition of the latter is accelerated by the acid tending to combine with the iron and a portion of oxygen; the concurring action of the acid and iron surmounts the mutual affinity of hydrogen and oxygen.

10. From what precedes, it may be concluded that the properties of the resulting affinity of compound substances may be referred, 1st, to the advantages of liquidity, in which point of view, what has been said on the theory of solvents may be applied to it, (Art. IX.); 2dly, to a disposition to solidity, which produces contrary effects, and which are explained by the theory of the force of cohesion (Art. V.); 3dly, and finally, to the concentration of elastic substances: this latter circum-

circumstance requires particular attention; it may, however, be associated with one of the two former.

The observations made, No. 7 and 8, prove that affinities which may be considered as new, result from combinations by which elastic fluids are brought to a liquid state: an additional force is acquired by this change of constitution; and the inverse of what has been said on the effects of elasticity, may be applied to the present case (Art. VI.)

That which really distinguishes complex affinities, which I have treated of (Art. XII.), from those under consideration at present, and which result from the combination of substances, is, that in the former very little change is produced in the constitution of the component parts of the compound; so that as long as the force of cohesion or affinity does not interfere, they may be considered as they have been (Art. XII. No. 1); whilst a new force is developed by the combining together

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of elastic substances which experience a condensation; which force may be considered as analogous to that of the cohesion which supervenes by the mixture of different substances, and which determines the combinations that take place, unless the tendency to unite be surmounted by opposing forces.

11. Caloric, by augmenting the elasticity of substances, destroys their resulting affinity, if their parts be unequally expansible. This observation is conformable to what has been said (Art. VII.)

12. Experience teaches us still further, that when resulting affinity is not active enough to prevent decomposition, it can, however, retard and impede that effect. To a similar slowness of action, to progressive changes of constitution, and to the different degrees of saturation which result from them, are to be attributed the greater part of the phenomena observed in vegetation, fermentation, and the animal economy; and, in general, in the ac-

tion of all substances which contain elastic fluids in a state of condensation*. This subject requires very ample discussion, and admits of great development.

13. Resulting affinity should be considered as a single and integral force, as long as the substances from which it is derived continue combined; but the elementary parts of the compound must be considered separately, when a separation takes place; and what has been said on the division of substances, relatively to the forces which act on them, may be applied to this separation.

14. It happens sometimes, that a body acts partly by a resulting affinity, and partly by its elementary affinities. When a metal is dis-

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* I have frequently applied the effect of a change of constitution to the explanation of chemical phenomena; but I particularly mentioned it in the lectures I delivered in the Normal School, in which I called *collective,* the affinity which we term here *resulting.*

solved by nitric acid, one part of the acid acts by its resulting affinity, whilst the other part acts by its elementary affinities: so that the oxygen of this latter part is divided between the metal and azote, and the oxyde itself is dissolved by the undecomposed nitric acid.

15. It appears from what has been said on resulting affinity, that a false notion may be conceived of the properties of bodies, if the attention be confined, as it too often has been, to the mere consideration of their constituent parts, without adverting to other conditions of their constitution, or to the changes which some of their constituent parts may have undergone. The same portion of oxygen gas does not exert the same degree of action in the gaseous state, as it does when in combination with azote, hydrogen, carbon, sulphur or a metal, in which cases it acts by a resulting affinity.

Thus the oxygen of sulphuric acid differs in its action, and in its resulting affinity, from the oxygen of sulphureous acid: it is much more strongly combined in sulphuric than in sulphureous acid; though it is combined in the former with a quantity of sulphur much smaller than that of the latter; in the former, too, its action is much stronger, owing to its greater condensation*. Oxygen dissolved in water must not be confounded with that which, in combination with hydrogen, constitutes that liquid; the difference in their state of condensation renders them different substances relatively to chemical action.

It is necessary, then, to consider all the conditions of the constitution of a body, in order to be able to explain its chemical properties; and, in like manner, to attend to all the circumstances of chemical action, in order to be able to explain its results.

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[*] I have illustrated the effects of condensation in a memoir on sulphuric acid.—*Annales de Chimie, année* 1796.

ART. XV.

Recapitulation.

1. IT has been repeatedly observed, that the action of a substance decreases in energy in proportion to the degree of its saturation; and this diminution of force has been frequently adduced in the explanation of chemical phenomena. It was commonly understood, that a metal could deprive nitric acid of only a part of its oxygen, because the proportion of this latter being diminished, the remaining part was more strongly retained by the azote; hydrogen was supposed to have the property of depriving certain metallic oxydes of only a part of their oxygen; and the property of a substance to attract humidity from the atmosphere was known to extend only to a certain degree; there being a term of equilibrium, on either side of which the more saturated substance gave out humidity to the other; it was also

also well known, that the last particles of a substance in combination with another, were disengaged, whether by affinity or heat, with much more difficulty than those that were disengaged in the commencement of the decomposition, and that in some cases, the difficulty was such as not to be overcome; thus it has been proved by experiment, that the oxyde of manganese cannot be completely deprived of its oxygen by heat.

The combinations which result from opposing forces do not therefore depend on mere affinity, but also on the proportions of the substances in action; I have therefore applied to chemical phenomena in general, only what observation has compelled me to admit in a great number of cases, and I have deduced from this some immediate consequences.

2. These consequences are, that substances act in the compound proportion of the quantity in the sphere of action, and of the affinity with which they are endued; that the latter

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may be compensated by the former, and that the chemical action of each is proportional to the degree of saturation which it produces. I have distinguished by the term *chemical mass*, or *mass*, the quantities as determined by an equal degree of saturation, which quantities are consequently relative to their capacity of saturation: when two substances tend to combine with a third, their respective saturations will therefore be proportional to the mass of each. The subject of combination is also affected by the same law of action which is proportionate to the masses, any change in which will produce a change in the results.

3. I have considered all the forces which can, by their concurrence with, or opposition to, the reciprocal affinity of substances acting according to the preceding principle, exert any influence on chemical combinations and phenomena. They are reducible to the following: the action of solvents, or the affinity which they exert in proportion to their quantity; the force of cohesion, which is the effect

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of the mutual affinity of the parts of a simple or compound substance; elasticity, whether natural or produced by caloric, which ought to be considered as an effect of the affinity of caloric; efflorescence, which may be attributed to an affinity not yet determined, acts only in very rare circumstances; gravitation too exerts some influence, particularly when it produces the compression of elastic fluids; but no inconvenience can result from its being confounded with the force of cohesion.

4. I have endeavoured to find if it were possible to ascertain the relative affinity of two substances by means of a third; and I have observed that, in order to do so, it would be necessary to ascertain in what proportion that third substance would combine with a given quantity of the two former, or rather in what degree they should participate of its action. I have pointed out the insurmountable obstacles which preclude us from ascertaining and determining this participation of action, and the changes of constitution which may follow.

5. As all tables of affinity have been formed on the supposition, that substances are endued with different degrees of affinity, from which originate all the combinations and decompositions that take place, independently of proportion and other circumstances which influence the results, they must give an erroneous idea of the degrees of the chemical action of substances.

6. The very term, *elective affinity*, must lead into error, as it supposes the union of the whole of one substance with another, in preference to a third; whereas there is only a partition of action, which is itself subordinate to other chemical circumstances.

7. The action of two, three, or more substances, is subject to the same law, and the result depends on their affinity, proportion, degree of saturation, and the concurrence or opposition of the forces which they bring into action.

A reciprocal saturation takes place in every case of liquidity, from which results an individual combination, in which all the forces are balanced by one another, provided there be no precipitate formed, nor elastic substance disengaged; but as there is a partition of action in every case of opposition of force, and difference of saturation, some of the substances will be retained in the new combination with less energy than they were before being mixed, and may consequently yield to the force of cohesion, elasticity or affinities, which could not, in their former state, effect their separation.

8. Force of cohesion, which had been considered only as an obstacle to solution, not only limits the quantities of substances which may be brought to act in a liquid, by which circumstance it modifies the conditions of the saturation that takes place; but further, it produces the precipitations and crystallizations which result, and determines the proportions of the combinations that separate from the

liquid;

liquid; it is it also that sometimes produces the precipitation of a substance without its having combined with any other, as we have already remarked in the instance of some metallic precipitates. I have distinguished insolubility from the force of cohesion, because one is relative only to the action of solvents, whilst the other, considered absolutely, is the effect of the mutual affinity of the parts of a simple or compound substance.

Elasticity acts in producing effects contrary to those of the force of cohesion, either by effecting the removal of some substances from the action of others, or by diminishing their proportion within the sphere of action; but if all the substances in action be in the elastic state, this effect will not be produced, because they all exist in the same condition.

Therefore, tables which would represent the tendency to insolubility or elasticity of various substances, would enable us to foresee a great number of the combinations which would re-

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sult from the mixture of different substances, and from the influence of heat.

9. Caloric acts on bodies like other solvents, when it is not in the radiant state, because, in the latter case, it does not act until it enters into combination with bodies.

It surmounts the greater part of the force of cohesion of a body in liquefying it; but affinities may concur with it in producing this effect, in the same manner as caloric itself co-operates with the action of other solvents.

It does not distribute itself among bodies in proportion to their absolute weight or volume, to produce in them equal degrees of thermometric heat: in this respect it is similar to an acid which does not require an equal quantity of different alkalis to produce the same degree of saturation; and tables of specific caloric would correspond to those of specific acidity and alkalinity which might be formed: the former would give the capacity of bodies for caloric, the latter would determine that of saturation *.

A difference would, however, exist between these tables, as those of acidity and alkalinity would represent the saturation from zero to some certain degree, because pure acids and alkalis might be employed for that purpose: but specific caloric can be determined only from a degree of saturation which is unknown to another; because, every body on which the experiment can be made, is already partially saturated with caloric. The results obtained between two different degrees of the thermo-

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* Several chemists have endeavoured to ascertain the constituent parts of chemical compounds; but none more extensively, nor with more success, than the celebrated KIRWAN; his method may, however, be somewhat objected to.

This chemist proceeded on the principle that affinity is proportional to the quantity which produces saturation; but he considers that force as independent of quantity and other circumstances which modify it.

metric scale have no known relation with the total quantities. An attempt to infer the latter from the former, would be as vague as an attempt to determine the comparative solubility in water of muriate of soda and of nitrate of potash by two experiments only; one at the boiling, and the other at the freezing point. In the first case, three parts of water would be necessary for the solution of one of muriate of soda, whilst the nitrate of potash would dissolve in one half its weight of water; but in the second experiment, much less water would be necessary for the solution of the muriate of soda, than for that of the nitrate of potash *.

The force of cohesion of a body, in producing the solid state, expels a part of the caloric

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* The sole consideration, that specific caloric bears no ascertained ratio to the combined caloric of a body, shews that the experiments, by which Rumford has of late endeavoured to prove that caloric is not a constituent part of bodies, do not establish his conclusion.

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of that body; as a salt which crystallizes, relinquishes a part of its solvent, or even of the acid or alkali with which it was combined.

10. Affinities might be considered as really represented by tables of capacity, as the latter would give the measure of the action of each substance on another, a common term of saturation being found, as neutralization for acids and alkalis, and thermometric temperature for caloric; but nothing of what relates to chemical action, at a different temperature, should be inferred from these tables, nor of what relates to another term of saturation, a change of constitution, and all those circumstances which may favour the forces of elasticity or cohesion.

11. After having examined all the affinities which can contribute to chemical action, I have endeavoured to shew that the affinities of compound substances result from that of their constituent parts; and I have done so, in order to reduce to one general property of

simple bodies, all the various forces by which chemical phenomena are produced.

From the view we have taken of this subject, it would appear, that what particularly distinguishes compound substances whose action is considered as simple, is the condensation of their constituent parts, from which a new affinity arises, widely different from that which the same parts possess in the elastic state: the elementary affinities are modified by the state of saturation, the force of cohesion, or the variations of elasticity; the resulting affinity may acquire a new degree of saturation, by the body which possesses it entering into another combination, and the compound thus formed may be difficultly decomposable, or a disposition may exist between its constituent parts, to form new combinations with one another, or with other substances.

12. All the observations that I have advanced on the modifications of chemical action,

tion, admit that the chemical action which a body exerts in a given case, whether by its constitution, proportion, or even the concurrence of other affinities, may be expressed or designated by the word *affinity:* but care must be taken not to consider this affinity as an uniform force which produces compositions and decompositions; for that would be to conclude from what it is in one circumstance, what it would be in others very different, and under conditions which give it a very different degree of force: such a conclusion would lead us to neglect all the modifications which it undergoes from the commencement of action to the term of equilibrium.

13. I have pointed out in this Essay, the constant and uniform cause of chemical action; I have considered all the forces which contribute to the production of combinations, and chemical phenomena arising from them; and have endeavoured to ascertain the influence of each force in different circumstances. Should it be regretted that this Essay excludes the

hope of being able to class the chemical power of bodies, independently of the conditions which modify it; yet it must be acknowledged, that tables of affinity were mere memorandums of barren facts, and that they precluded the advantages resulting from the consideration of the most productive properties, by attending to which, a great number of the results of chemical action may be foreseen, and that action understood and directed, without having occasion to recur to suppositions, and particular principles.

Of the Influence of Proportions in complex Affinities.

I HAVE established, in this Essay, the principal results presented by complex affinity, when the force of cohesion, or that of elasticity, is sufficient to produce the exchange of base which has been attributed to a superiority in the divellent forces, or inferiority in the quiescent; but I deferred entering into details necessary for ascertaining the changes which may result from different proportions of the substances in action, when the force of cohesion is not sufficient to render imperceptible the effects of this difference. I have mentioned (Art. XII. No. 6) my intention to resume the consideration of this subject, and I shall now endeavour to throw some light on it.

According to the theory which I have laid down (Art. V. No. 5), all substances in the liquid

liquid state exert a reciprocal action ; so that in a solution of sulphate of potash and muriate of soda, for instance, these two salts are not distinct, nor do they become so until some extraneous cause produces their separation ; sulphuric and muriatic acids, potash and soda, are contained in the liquid. I shall, however, use the ordinary terms, as this remark will be sufficient to prevent any error.

2. I shall, in the first place, treat of mixtures, in which combinations are produced by the force of crystallization.

Experiment A.—A mixture was made of equal parts of nitrate of lime and sulphate of potash : after the separation of the sulphate of lime formed in the commencement, and of which no further mention shall be made in the following experiments, the liquid was evaporated, and nitrate of potash and sulphate of lime were alone obtained by successive operations. Yet, after the last evaporation, some crystals of sulphate of potash were obtained : there

there was but a small residue of incrystallizable liquid, in which carbonate of soda and nitrate of barytes produced precipitations; whence it appears that it consisted of a small quantity of sulphuric acid and lime, and very probably of a larger portion of nitrate of potash.

The quantity of sulphate of lime which precipitated during this evaporation, was much greater than what could be dissolved in an equal quantity of water; whence it appears that its solubility was augmented by the action of the other substances.

Experiment B.—Two parts of sulphate of potash, and one of nitrate of lime, yielded, by the first evaporation, sulphate of potash and sulphate of lime; and, by the following, nitrate of potash with the two sulphates, the proportions of which continued to diminish until the salts ceased to crystallize: only a few drops of incrystallizable liquid remained, in which no precipitate was formed on adding to it some carbonate of soda, but this effect was produced by the nitrate of barytes; whence it appears probable that the liquid consisted of sulphate of potash, and a small proportion of nitrate of potash.

Experiment C.—Two parts of nitrate of lime, and one of sulphate of potash, yielded by the first evaporation a small quantity of sulphate of lime, and on cooling, some nitrate of potash; by the succeeding evaporations nothing but nitrate of potash was obtained. After the last, however, some crystals of sulphate of lime were perceivable on the surface of the liquid. Though the residue, which was abundant, was repeatedly put to evaporate and cool, no crystallization was effected. This incrystallizable residue, treated with alcohol, yielded an abundant precipitate, in the solution of which in water no precipitate could be produced by nitrate of barytes; whence it appears that it contained no sulphuric acid, and that it was composed of pure nitrate of potash. What had been dissolved in the alcohol

hol was nitrate of lime, with a small proportion of nitrate of potash: the incrystallizable residue consisted, therefore, of nitrate of potash and nitrate of lime.

It appears that the sulphate of lime was rendered much less soluble in this than in the preceding experiments; and that the action of the nitrate of lime prevented a considerable quantity of the nitrate of potash from crystallizing.

3. Sulphate of lime was necessarily formed in these three experiments, because its component parts were in contact; and the insolubility of the compound formed by them, occasioned its precipitation to a certain extent.

In the experiments A and B, the sulphate of lime was rendered much more soluble than it naturally is, by the action of the substances in solution; but in experiment C, its solubility was not perceptibly increased, for this reason probably, that the nitrate of lime and nitrate

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of potash, which existed in the uncrystallizable liquid, had mutually saturated each other so much as to diminish their action on the sulphate of lime.

4. I shall deduce from these considerations the theory of uncrystallizable residues: the succeeding observations will tend to confirm it.

Saline substances exert a mutual action, which augments their solubility; as has been proved by the experiments published by my learned colleague Vauquelin (Annales de Chimie, vol. xiii.) This reciprocal action varies in different salts; it was once supposed that the solubility of nitrate of potash was not augmented by the action of earthy salts; and yet it is augmented more by them than by any others.

There must be, doubtless, in this respect, some difference arising from the nature of the salts, in the effect which they produce, but this difference is, in general, very trifling, com-

compared to that resulting from the force of crystallization.

Experiment D.—A mixture of equal parts of nitrate and sulphate of potash, yielded by evaporation, and successively, according to their solubility, sulphate of potash and nitrate of potash, without leaving any uncrystallizable residue; but having made a similar experiment with a mixture of nitrate and sulphate of soda, each of which has but a feeble tendency to crystallize, and nearly an equal degree of solubility, there was separated by crystallization but a small portion of the sulphate of soda, the other parts of the mixture continuing in the liquid state, incapable of being crystallized by any means. Muriate of soda and sulphate of alumine submitted to the same treatment, were perceived to become more soluble; but they were totally separated in the end by alternate evaporation and cooling.

It appears, then, that substances which are endued with an active tendency to crystallize, though

though rendered more soluble than they naturally are, separate however in the order of their insolubility, without leaving any, or but very little, uncrystallizable residue.

But when a mixture consists of salts which have but a weak tendency to crystallize, their mutual action counteracts that tendency, so that a large portion of uncrystallizable liquid remains: this effect is still more complete when the mixture contains a substance naturally uncrystallizable, as in the Experiment C, in which there was an excess of nitrate of lime, the action of which excess on the nitrate of potash rendered a great portion of it uncrystallizable.

How has it happened then, that the most intelligent chemists, LAVOISIER, FOURCROY, VAUQUELIN, GUYTON, and the Commissaries of the Academy of Sciences, one of which I was, were induced to believe, from experiments made on saltpetre, that nitrate of lime exerts no action on nitrate of potash, and that, consequently,

sequently, it does not increase its solubility (Annales de Chim. v. xi. xiii. xv. xxiii.)? This mistake arose from a circumstance of the experiment; that is, the use of desiccated sulphate of lime with the solution of nitrate of potash: the former deprived the nitrate of potash of a part of its solvent, its desiccation having given it a great tendency to combine with water, and it would have precipitated a considerable part of the nitrate, if its own dissolving power did not compensate for the diminution of the quantity and action of the water: but if the solution had been evaporated, it would have been found that the whole of the nitrate of potash contained in the liquid would not have crystallized, and that an uncrystallizable residue would have remained, as in Experiment C: the experiment on saltpetre, though conclusive with respect to the object in view, must however have given an erroneous notion of the chemical phenomenon.

It follows, therefore, that there may be obtained from the solution used by the manufacturers of saltpetre a greater quantity of nitre than that obtained by the ordinary mode of crystallization; for a considerable portion of it is rendered uncrystallizable by the action of the earthy salts with which it is mixed.

5. *Experiment* E.—Equal parts of crystallized sulphate of soda and desiccated nitrate of lime, dissolved, and put to evaporate, yielded only a small portion of nitrate of soda: the uncrystallizable residue, which was abundant, yielded a precipitate by the addition of oxalic acid, but not by that of muriate of barytes.

Experiment F.—Two parts of sulphate of soda and one of nitrate of lime, yielded by evaporation a larger proportion of nitrate of soda than was obtained in the preceding experiment; and a precipitate was produced in the uncrystallizable residue by muriate of barytes, but not by oxalic acid. In order to judge of the results by comparing the two last experiments with those of A, B, and C, it is necessary to recollect, that crystallized sulphate of soda contains more than half its weight of water of crystallization.

No sulphate of soda was formed in Experiment F, though sulphate of potash was formed in Experiments A and B; because sulphate of potash possesses a stronger crystallizing force then sulphate of soda.

The residue of the Experiment E, did not contain a quantity of sulphuric acid sufficient to become perceptible by muriate of barytes: it consisted of nitrate of soda and nitrate of lime, the dissolving power of each of which was probably so much exhausted by their action on one another, that the separation of the sulphate of lime was not opposed by them (No. 3).

In Experiment E, a precipitate was produced in the residue by muriate of barytes, but not by oxalic acid; whence it appears that it consisted of sulphate of soda, and of a greater proportion of nitrate of soda, the mutual action of which prevented their crystallization, as in Experiment D.

Experiment G.—Equal parts of nitrate of potash and sulphate of soda gave, by successive crystallizations, 1st, sulphate of potash, and a few small crystals of nitrate of potash; 2d, a small quantity of sulphate of potash, and much nitrate of potash; 3d, some small crystals of nitrate of potash, and a large quantity of nitrate of soda. Though every endeavour was made to obtain all the salts the solution contained, yet an uncrystallizable residue remained; this residue consisted of nitrates and sulphates; for a precipitate was produced in it by nitrate of barytes, and after being desiccated, it entered into fusion on burning charcoal; probably it was analogous to that of Experiment F.

Experiment H.—One part of nitrate of potash and two of sulphate of soda gave, 1st, sulphate of potash; 2d, sulphate of potash, and some needle-like crystals of nitrate of potash; 3d, sulphate of potash in small prisms suspended from a pellicle formed by nitrate of soda, fine crystals of nitrate of potash, and some nitrate of soda; the residue contained nitrates and sulphates.

In these two experiments, the least soluble salt of the two which could form, namely, sulphate of potash, is that which first crystallized. When the proportions were changed by this crystallization, the action of the nitric acid on the potash became predominant, and nitrate of potash was formed, though there was still some sulphuric acid in the liquid.

In the second Experiment, the greater quantity of sulphuric acid occasioned the formation of a greater proportion of sulphate of potash; yet, after the first crystallization, some nitrate of potash was formed, although there had been a sufficient quantity of sulphuric acid for effecting a complete exchange of base, if that exchange could take place in the manner supposed

posed by elective affinity; even in the Experiment G, the residue consisted of sulphate and nitrate of soda, and probably of a salt of potash.

7. *Experiment* I.—Equal weights of nitrate of potash and muriate of lime were mixed together; by evaporation there were obtained, 1st, nitrate of potash; 2d, muriate of potash containing a small portion of nitrate of potash: an abundant precipitate of sulphate of lime was produced in the residue, and vapours of nitric and muriatic acids disengaged by the addition of sulphuric acid.

Experiment K.—An experiment having been made with two parts of muriate of lime, and one of nitrate of potash, a great quantity of muriate of potash, without any appearance of nitrate of potash, was obtained by crystallization; the residue, treated as that of the foregoing Experiment, gave similar results.

Experiment L.—A mixture, the proportions of which were the inverse of the preceding, was made,

made, that is, equal parts of muriate of potash and nitrate of lime were mixed ; from which were obtained, 1st, nitrate of potash mixed with a little muriate of potash ; 2d, muriate of potash mixed with a little nitrate of potash : the uncrystallizable residue was dissolved in alcohol, and the solution yielded some nitrate of potash which was fusible by heat, but which contained a small portion of muriate of potash, as was proved by a solution of silver. The part dissolved by the alcohol consisted of lime, nitric, and muriatic acids, as was proved by the addition of sulphuric acid.

It is manifest from the foregoing experiments, made with substances possessing nearly an equal force of crystallization, that the formation of salts obtained by crystallization depends on the proportions of the substances put to act on one another : thus, in the Experiment I, from which might have resulted nitrate or muriate of potash, the solubility of both being nearly the same, the former was the first obtained by crystallization, because its solubility is somewhat less than that of the muriate of potash; but in the Experiment K, as the muriatic acid was in greater proportion than the nitric, muriate of potash alone was obtained by crystallization. A part of the potash and muriatic acid, the nitric acid and lime, remained in the residue. The proportions used in Experiment L, do not differ much from those of Experiment I, and the results were nearly the same.

Combinations may then be obtained, which vary from the proportions of the substances employed, or the stage of the operation; that is, from the proportions which continue in action, when the combinations which might take place are not endued with a force of cohesion sufficient to withdraw them from the sphere of action. How different are the results of experiment from the opinion generally adopted by chemists, who consider the first crystallization as a proof of a total exchange of base?

If, for instance, nitrate of potash be first obtained

obtained from a mixture of nitrate of lime and muriate of potash, it is concluded that the nitric and muriatic acids have exchanged bases; if different proportions had been employed, as in Experiment K, muriate of potash alone would have been obtained, and a contrary conclusion would have been equally warrantable. The error did not stop here; for having concluded that an exchange of base took place between the nitric and muriatic acids, or rather having observed a fact, which was not examined in its full extent, it was inferred that no exchange of base could take place between the salts thus formed when they were again mixed together.

8. I have examined the changes induced in the results of combination by substances endued with the property of forming triple salts: magnesia is one of this kind.

Experiment M.—Equal parts of sulphate of potash, and muriate of magnesia, gave, 1st, sulphate of potash; 2d, sulphate of potash, a small portion of muriate of potash, and a triple salt composed of sulphuric acid, potash, and magnesia; this latter salt formed in rhomboid crystals, which retained their transparence in the air; its solubility was nearly the same as that of sulphate of potash; 3d, muriate of potash, and sulphate of magnesia. The residue contained sulphuric and muriatic acids, potash, and magnesia.

Experiment N.—Two parts of muriate of magnesia, and one of sulphate of potash, gave 1st, sulphate of potash; 2d, muriate of potash, and a triple salt, the same as that obtained in the preceding Experiment; 3d, muriate of potash, and sulphate of magnesia: the residue was analogous to that of the preceding Experiment.

In the Experiment M, sulphate of potash was obtained in two crystallizations; but in the experiment in which the muriatic acid was in greater proportion, sulphate of potash was obtained only by the first crystallization: the triple salt, which has nearly the same solubility as sulphate of potash, crystallized by the second evaporation. When the proportion of sulphuric acid was sufficiently diminished by these successive crystallizations, the separation of the muriate of potash succeeded conformably to the order of solubility, and finally the magnesia, which was still abundant, crystallized with some of the sulphuric acid.

It is manifest that different, or contrary conclusions, might be inferred from these Experiments, according to the period of them, to which the attention is directed; and it is equally manifest, that the received opinion of chemists respecting a complete exchange of base between muriate of magnesia and sulphate of potash, is erroneous.

In Experiment M, where the proportion of sulphuric acid is greater, sulphate of potash was obtained in the two first crystallizations; but in Experiment N, where the muriatic acid predominated, sulphate of potash was obtained only

only in the first crystallization; the greater part of the magnesia remained in the uncrystallizable residue, having no crystallizing force with muriatic acid, and but a weak one with sulphuric acid: the other salts, which could crystallize in other circumstances, remain dissolved in this residue, their tendency to crystallize being counteracted by mutual action.

The difference between the results of these two Experiments, and those of A, B, C, in which a calcareous deliquescent salt was put in action with sulphate of potash, corresponds exactly with the difference of solubility between sulphate of lime and sulphate of magnesia.

9. After having considered saline substances in the foregoing Experiments, as if they could exist distinctly and separately formed in a liquid, I shall proceed to consider some effects, which in reality all salts have on one another, when they are mixed in the liquid state.

Experiment O.—A solution of acetate of lead was poured gradually into a solution of muriate of soda, until no further precipitate could be produced: the liquid in which the precipitate was formed reddened the blue vegetable infusions, which the solution of acetate of lead could not do. No precipitate was produced in this liquid by the acetate of lead or muriate of soda; but it assumed a deep colour on the addition of an hydro-sulphure, and an abundant precipitate was produced in it by sulphuric and muriatic acids: a precipitate of muriate of lead was formed by evaporating it, and with it a crust which had no crystalline form, and of which mention shall be made presently; in the last place, fine crystals, consisting of acetate of soda and oxyde of lead, were obtained. In dissolving the saline crust, a deposit of muriate of lead with excess of oxyde was formed, analogous to that which has been described by VAUQUELIN (Annales de Chimie, v. xxxi.) The solution and crystallization were frequently repeated before the deposit ceased to take place; then the saline crust was found divided into two substances, namely, muriate of soda, and muriate of lead.

If muriatic acid and acetous acid be superabundant in the liquid, the excess of both, which is but feebly retained, can be expelled by heat, because both are volatile. This is proved by experiment: having distilled a mixture similar to the preceding, from which was separated the precipitate formed in the commencement, I found the liquid which passed into the receiver to contain acetic and muriatic acids: this fact merits particular attention, as it serves to explain several phenomena.

10. Prieur has observed, that when lead was used for purifying the solution of silver mixed with muriatic acid, a part of the latter acid passed off by distillation; the cause of which is found in the solubility of the muriate of lead, which solubility is considerably increased by nitric acid: the liquid was composed, then, of oxyde of lead, of nitric and muriatic acids; the oxyde of lead was divided

between the two acids, and both one and the other were subjected to the expanding power of heat.

If it were an object to fix sulphuric acid, or prevent it from being volatilized, it might be easily done by means of lead; 1st, because sulphate of lead is much less soluble than the muriate; 2d, because sulphuric acid is less volatile than muriatic acid.

Muriate of silver being much less soluble than muriate of lead, silver is therefore much better than lead for retaining the muriatic acid mixed with nitric acid; yet WELTER and BONJOUR have observed, that some muriatic acid always passed by distillation, if the precautions indicated by these learned chemists were not attended to. To obtain nitric acid pure in a direct manner, it is necessary that the acid to be distilled be diluted, so that it may not have strength sufficient to dissolve muriate of silver, and that the muriate of silver which is precipitated, be separated before the liquid be submitted to the action of heat; or, still better, the muriatic acid of nitrate of potash may be precipitated by a solution of silver; and by decomposing afterwards the nitrate of potash, nitric acid will be obtained quite pure, and free from muriatic acid.

Even when there is some muriate of silver in solution in nitric acid, a pure acid may be obtained by distillation, if the parts first distilled be separated until it appear by trial that no more muriatic acid passes over; because, as observed by the chemists just quoted, the muriatic acid becomes oxygenated, and passes off in that state in the commencement of the operation.

Experiment P.—Sulphate of potash having been treated with acetate of lead, in the same manner as the muriate of potash, sulphate of lead was formed and precipitated; the liquid retained only a small quantity of the oxyde of lead: crystals of sulphate of potash were obtained

tained by evaporation, although no precipitate was produced by acetate of lead before the evaporation was commenced; and, lastly, some acetate of potash mixed with oxyde of lead was obtained. The decomposition of the sulphate of potash was much more complete in this case than that of the muriate of soda in the other.

It appears, then, by the preceding Experiments, that decompositions, or exchange of bases, follow the order of solubility of the combinations that can take place; and that the sole difference observable between the results of the latter and of most of the preceding Experiments, arises from the oxyde of lead having the property of combining with other substances to form a triple salt, which triple combinations separate in like manner, according to the difference of their solubility, as in the instances of the muriates of soda and lead, Experiment O.

11. The following Experiment will prove, that the effect of the force of cohesion is considerably varied by the properties of the solvent.

Experiment Q.—I mixed a solution of *plombate* of soda with a solution of sulphate of soda, the precipitate resulting from which was very trifling, but was rendered abundant by the addition of sulphuric or muriatic acid: the Experiment being repeated with muriate of soda, the precipitate was much more abundant than with the sulphate of soda.

These effects might appear, on a first view, to be contrary to the principles which I have established; for the sulphate of lead is much less soluble than the muriate, for which reason, a more abundant precipitate might be expected in the Experiment with sulphate of soda than in that with the muriate. This apparent contradiction is owing to the sulphate of lead being more soluble in soda than the muriate of lead with excess of oxyde; and of this kind was the precipitate in the foregoing Experiment. The precipitation in this case is not the direct effect of the force of cohesion, but of the relation between the force of cohesion and that of the solvent.

12. The observations which I have presented in this part of the Memoir, may be reduced to the following: force of cohesion, when considerable, and very unequal in the combinations which may take place, determines the exchange of bases, so that the most insoluble combination is formed and precipitated, independently of proportions which are influenced only by the substances that continue in solution. It is easy, therefore, to foresee what effect will be produced by the mixture of different saline substances, from the sole consideration of their solubility.

The theory of quiescent and divellent affinities does not lead to error in this case, as to the principal result, that is, as to the formation of an insoluble salt; but not being deduced from any leading principle, its application is limited,

and

and an experiment is required for the explanation of each particular case; it presents nothing that can lead to a previous knowledge of the effects of the action of substances; and, finally, it has the disadvantage of diverting the attention from the consideration of the properties of the substances which remain liquid, and which are developed by evaporation, or the addition of another substance.

The foregoing Experiments may appear to be involved in some degree of obscurity, owing to a certain relation or analogy in the results; but when the combinations that may take place differ but little in point of solubility, that source of uncertainty cannot exist, as the formation of the different salts is then determined by the proportions of the substances in action: the first crystallization is not alone produced by this cause, but also the successive ones, by means of which the proportions change, so that each varying tendency to crystallize influences the successive formation of salts. The theory of quiescent and divellent affinities might lead into error in cases of this kind, as, according to it, we should infer the first effect of the operation to be the sole result; whereas, on the contrary, a succession of different combinations takes place, according to the forces which predominate at the moment on which the separation commences.

The combined influence of the difference of solubility and proportions, can alone guide us in explaining the successive formation of salts whose solubility is nearly equal: the mutual action of the substances may, however, occasion some difference in the results.

All substances in solution exert a mutual action, by which their solubility is increased; hence the difficulty of obtaining from a mixture, a salt in a state of purity by a first crystallization, unless it differ widely from the others by its force of crystallization: the same mutual action is the cause of uncrystallizable residues, in which several salts possessing but a weak tendency to crystallize, remain in solution;

lution ; but in this case also, the consideration of the proportions and solubility of the salts enables us to foresee the existence, quantity, and composition of the uncrystallizable residue.

The reciprocal action which substances exert when in solution, facilitates the expulsion of an acid from a combination ; though this effect, according to the received opinion, is attributed to its tendency to take the place of a weaker acid.

Solubility must not be considered as an absolute quality, but as relative to that of the solvent ; thus a compound insoluble in water, may be soluble in an alkaline solution.

In all the Experiments I have described, and in many others which I think it useless to mention here, I have observed no change of saturation, neither after the mixture of neutral salts, nor after the separation of the precipitates or crystallized salts that took place, except in the Experiments P, Q, made with a

metallic

metallic substance. This permanent state of neutralization, which continues after the exchange of bases has been effected, seems to indicate a uniform relation of quantity between the acids, in their different neutral combinations, whether with earthy or alkaline bases; so that if sulphuric acid, for instance, be in greater proportion in sulphate of potash than in sulphate of lime, the muriatic acid with which it exchanges base, will exist in the same relative quantity in muriate of lime and muriate of potash: this conclusion does not agree with the proportions of the constituent parts of salts as settled by chemists.

Guyton has already made some very just and important reflections on this subject, and he quotes some observations from a work of Richter's, with which I am not as yet acquainted.

Of

Of Metallic Solutions and Precipitates.

1. In the two preceding parts of this Treatise, I have principally considered simple substances, and compounds which are subject to no variation in their composition; but metallic substances are well known to have different properties, according to their degree of oxydation, which difference must necessarily affect their chemical action.

I shall now endeavour to discover what influence a different degree of oxydation of metals may have on their chemical action; and to compare, independently of those properties already treated of (Art. XIII.), the action of metals in that state, to that of other substances.

Mercurial solutions and precipitates appear to me to particularly merit our attention, as they

they have been repeatedly observed by chemists, and as their conditions are easily ascertained.

2. Fourcroy described in the Memoirs of the Academy for the year 1790, a sulphate of mercury, which he has proved to be analogous to *mercurius dulcis*, that is, that the mercury in both cases is combined with only a small portion of oxygen: he has shewn that the sulphate of mercury divides itself, by the action of heat and water, into two sulphates, one of which may be termed mild and the other oxygenated: this effect more certainly takes place if the degree of heat be so moderate as not to produce the perfect desiccation of the sulphuric acid and mercury. The mild sulphate of mercury may be obtained by simply diluting with an equal quantity of water the sulphuric acid, before it is added to the mercury. During the ebullition of this mixture, very little sulphureous acid is disengaged, and instead of an oxygenated sulphate of mercury,

that which Fourcroy has so well described is formed.

In the estimate which Fourcroy has given of the constituent parts of the mild sulphate of mercury, he fixes the proportion of oxygen at 0.05; but in making his estimate, he supposes that the precipitate resulting from the decomposition of this salt by potash is a pure oxyde; by which supposition he overlooked that portion of acid which we have proved to be always retained by metallic precipitates: I would conclude, therefore, from his own experiment, that the proportion of oxygen somewhat exceeds his statement. It is to be remarked, that modern chemists, from not attending to this circumstance relating to precipitates, have made many similar conclusions, which are, consequently, inaccurate to a certain degree.

The mild sulphate of mercury is a permanent combination, and is not decomposed by water, though the oxygenated sulphate is. I shall make some further observations on these sulphates.

If FOURCROY's process be followed, that is, if concentrated sulphuric acid be boiled with mercury, without carrying the ebullition to perfect desiccation, a white mass will be obtained, composed of mild sulphate of mercury and oxygenated sulphate: by washing this mass carefully as he prescribes, the excess of acid, which has some influence on the mild sulphate, but a still greater on the oxygenated sulphate, may be separated.

When the operation is pushed further, or when the sulphate is exposed to a sufficient degree of heat, a considerable quantity of sulphureous acid is disengaged; the mercury becomes too much oxygenated to form a mild sulphate, and the whole will be changed to the state of oxygenated sulphate, the properties of which vary according to the quantity of acid which it retains: let us examine the state of the sulphate when the operation has been carried on until a dry mass was obtained, which consequently may be considered as free from excess of acid.

Water effects a change in the sulphate when in this state; the mass which had been previously white is rendered yellow by it; the liquid becomes acid, and retains a part of the sulphate in solution: a salt with excess of acid, and one with a less portion of acid, as they are usually termed, are formed; but the proportions of these two salts are varied; 1st, by the quantity of acid which the first combination had retained; 2d, by the quantity of water employed; 3d, by the degree of temperature, for the action of heat concurs with that of water.

If, instead of simple water, an alkaline solution be employed, the action of which on the acid is greater than that of water, two different combinations will take place; one will consist almost exclusively of oxyde, and the other will contain almost all the acid: the precipitate formed

formed in this case differs from that produced by pure water, by its containing a smaller proportion of acid, according to the strength of the alkaline solution which acts on it.

When the oxygenated sulphate of mercury retains a very considerable excess of acid, the action of the acid may be so far enfeebled by water, that no separation will take place.

3. I have hitherto supposed, that there were only two sulphates of mercury, in one of which the mercury was united with the smallest possible portion, and in the other, with the largest possible portion of oxygen; but it is manifest that these two terms are only the extremes, between which may exist intermediate degrees of oxydation: the salts formed by the mercury in these intermediate degrees of oxydation differ in their properties, but in such a manner, as that the particular properties of each cannot be determined, unless the degree of oxydation, and quantity of acid, be previously known.

What has been remarked here of the intermediate degrees of oxydation, is equally applicable to other metallic salts; as to the sulphate of iron, for instance, which exists in two fixed states, in one of which the metal is oxydated *ad maximum*, and in the other *ad minimum*; but it may exist in intermediate states, which are, however, very transitory.

4. **Bergman** had already perceived that the solution of mercury by cold nitric acid, differed in its properties from that produced with the assistance of heat; and remarks, in his excellent Treatise on the Analysis of Waters, that the former does not occasion a precipitate so easily as the latter in solutions containing sulphuric acid, and that in the first case the precipitate is white, and in the second, yellow: the reason of which is, that a mild sulphate of mercury is formed when the solution in cold nitric acid is used, which is more soluble in water than the oxygenated sulphate, the combination resulting from sulphuric acid and

the mercury oxydated *ad maximum* by the nitric acid and assistance of heat.

When nitrate of mercury is prepared by the assistance of heat, nitrous gas escapes in the commencement of the operation; but at a certain succeeding period of the operation, the mercury dissolves, and no more nitrous gas is disengaged. I am indebted for this observation to GAY, a young chemist of the Polytechnic School, possessing great zeal and sagacity. It appears, then, that an oxygenated nitrate is formed by means of heat, which, if the operation be not stopt, unites afterwards with more mercury, as, in another operation, the oxygenated muriate of mercury unites with an additional quantity of that metal*; but

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* FOURCROY has observed, that the oxygenated sulphate of mercury acts on an additional quantity of mercury, if made to boil with it in water; by which means the oxygenated sulphate passes to the state of a mild sulphate. Corrosive sublimate dissolved in water, does not act on mercury,

but in the fluid nitrate of mercury, it appears that there are no determined proportions between the salts in which the mercury is oxydated *ad maximum*, and those in which it is oxydated *ad minimum*. It appears that nitrates, similarly to what I have already observed with respect to sulphates, may exist in intermediate degrees of oxygenation.

When muriate of soda is added to a solution of nitrate of mercury, mercurial muriates are obtained, which differ according to the degree of oxydation of the metal. When a nitrate, in which the mercury is in a low degree of oxydation, is used, a white precipitate is obtained, which retains a part of the nitric acid, and is not soluble in muriatic acid, nor concentrated nitric acid, without occasioning a copious disengagement of nitrous gas. From the nitrate prepared by the assistance of heat, a yellow precipitate is obtained,

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mercury, but triturated with it, and without water, it yields a part of its oxygen to it, and combines with it in a certain proportion: the combination becomes uniform by sublimation.

obtained, which is insoluble in muriatic acid, but which dissolves with facility in nitric acid, without occasioning the disengagement of much nitrous gas; the liquid residue yields a small quantity of corrosive sublimate by evaporation.

If the experiment be made with a nitrate prepared so as that the mercury may have attained the *maximum* of oxydation, and if the solution be diluted with a sufficient quantity of water, no precipitate will be formed; but the entire mercury is in the state adapted to the formation of corrosive sublimate: however, very little or no corrosive sublimate is obtained, because it has the property of forming a quadruple salt with nitrate of soda.

This salt is obtained in rhomboidal crystals of a considerable size, and grooved on their surface: it fuses on ignited charcoal, and by exposure to a sufficient heat in a retort, all the mercury is separated from it in the state of corrosive sublimate: the residue is a nitrate of soda, which retains a portion of muriatic acid; so that the separation proceeds from a difference of volatility in the substances, and from a difference of affinity between the nitric and muriatic acids, relatively to the oxyde of mercury.

After this salt ceases to crystallize another is obtained, in the form of small needles: it appears to be a complex salt, in which the oxyde of mercury predominates.

Nothing determinate can be established as to the effects arising from the mixture of nitrate of mercury highly oxydated, and muriate of soda, because these effects vary according to the proportions of the substances which act.

I mixed one part of corrosive sublimate with four of muriate of soda, and I obtained a triple salt, more soluble than corrosive sublimate.

The preceding observations prove, that mercury may exist in solution in nitric acid from the lowest to the highest degree of oxydation; that it may exist in it, in the state necessary for the formation of corrosive sublimate, and in all the intermediate degrees between that and the *minimum*; and that the properties of the solution are relative to the degree of oxydation.

5. FOURCROY lays it down as a principle, that all metallic oxydes give their colour to the acids in which they are dissolved; and from this he concludes, that if a white mercurial salt yields a precipitate of a different colour, the change of colour must originate from some change in the degree of oxydation of the metal: I do not think this opinion well founded.

I took a red oxyde of mercury and dissolved it in muriatic acid; the solution was effected with facility, and without the formation of oxygenated muriatic acid, or disengagement of oxygen: fine crystals of corrosive sublimate formed by letting the solution remain at rest. I may observe here, that this appears to me to be the cheapest and simplest mode of preparing corrosive sublimate.

This salt contained the red oxyde, with all its oxygen ; it had, however, no colour ; and it would have given a white precipitate with ammonia, or an orange-coloured one with lime or the alkalis.

The red oxyde of mercury dissolves easily in nitric acid, without the disengagement of oxygen, and a white salt is formed from the solution by crystallization ; but if the solution contain a large quantity of acid, it will give a white precipitate with simple water ; a yellow with a larger quantity of recently distilled water, and one of a much deeper yellow, with lime and the alkalis.

White salts may, therefore, be formed from oxydes of a different colour ; which oxydes may acquire another colour by precipitation, without any change of oxydation.

6. Many

6. Many chemists have observed, that muriatic acid has a greater tendency to combine with very highly oxydated metals, than nitric or sulphuric acid. FOURCROY has applied this observation to the explanation of several chemical phenomena. He reasons thus (Mem. of the Acad. 1790, p. 381): "Every acid requires, for its union with a metal, that the metal itself should be united with a certain proportion of oxygen; muriatic acid combines, in general, only with highly oxydated metals; for which reason, it appears that mercury contains more oxygen in the state of corrosive sublimate, than in that of nitrate." I shall take the liberty of making some observations on the principle laid down by my learned colleague.

The assertion, that acids cannot combine with metals, unless the latter be in a state of oxydation suited to them, appears to me incorrect; nitric, sulphuric, and muriatic acids, combine with mercury at every degree of oxydation, from the lowest to the highest;

and all the variety of mercurial preparations, from corrosive sublimate to the *panacea mercurialis*, differ only in the degrees of oxydation: but there is this difference, that the combinations of nitric and sulphuric acids with mercury oxydated *ad maximum*, are much weaker, being decomposable even by water, than that with muriatic acid, which is, on the contrary, very permanent.

The same relative action of these acids, is observed with respect to metals whose oxydes contain a great proportion of oxygen, such as those of iron, tin, and antimony: the action of the nitric and sulphuric acids on these diminishes in proportion as the degree of oxydation of the metals increases; so that in some cases this action absolutely ceases when the metals are oxydated *ad maximum*. Muriatic acid, on the contrary, dissolves them, and holds them in solution in such a manner as that no change in its action is perceivable, either from a higher or lower degree of oxydation.

An explanation of the difference of action of these acids may be attempted; sulphur and azote, the bases of sulphuric and nitric acids, are saturated with oxygen, so that their resulting affinity must be very weak for substances equally saturated with that substance; but muriatic acid, which appears to have only a very small proportion of oxygen in its composition, should, on the same principle, have a stronger tendency to combine with oxygenated substances.

7. In the preceding observations, I have supposed that the action of the acid of a metallic solution is divided between the alkali and the oxyde which precipitates: I do not mean to include ammonia, which is decomposed, in some circumstances, and thus alters the constitution of the precipitate, as has been particularly pointed out by FOURCROY; but this property of metallic precipitates is subject to modifications which require particular attention.

The experiments of BAYEN have proved beyond all doubt, that the precipitates formed from mercurial nitrates and muriates retain a part of the acid, so that, on exposing to a strong heat the precipitate obtained from the mercurial nitrate, nitrous acid was disengaged; and by submitting the precipitate obtained from the mercurial muriate to a similar process, a greater or less quantity of an insoluble mercurial muriate was sublimed. I shall here add some observations to what I have already said on this subject (Art. XIII. No. 1.)

When oxygenated muriate of mercury is decomposed by the quantity of carbonate of soda precisely necessary to precipitate all the mercury, the precipitate consists of muriatic and carbonic acids, and oxyde of mercury in excess: by exposing this precipitate to heat, the carbonic acid and oxygen will be expelled in the gaseous state; the half of the mercury will be reduced, and the other half will sublime with all the muriatic acid that had continued united with the oxyde: the sublime substance is the muriate of mercury observed by **Bayen**.

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The liquid in which the precipitation took place, gives, first, carbonate of soda by evaporation, and afterwards a triple salt, in which soda predominates. Different phenomena are observed when the carbonate of potash is used; a very small quantity of it occasions a precipitation in the solution of the corrosive muriate of mercury, and the precipitate obtained does not exceed half what the same quantity of oxygenated muriate of mercury would give if precipitated with the carbonate of soda. This precipitate, by exposure to heat, gives out carbonic acid, and then sublimes almost entirely in the state of muriate of mercury with a small portion of acid: the small portion that does not sublime, assumes the metallic state. The liquid residue does not effervesce with acids; so that all the carbonic acid combined with the precipitate, which was composed of the oxyde, carbonic acid, and a portion of muriatic acid, double as great as that in the precipitate by the carbonate of soda. It gives, by evaporation, a triple salt, much more soluble than the oxygenated muriate of mercury: this salt crystallizes in needles.

Carbonate of ammonia occasions an effervescence in decomposing corrosive muriate of mercury, and no vestige of carbonic acid can be found in the precipitate or in the liquid: the weight of the precipitate amounts to about five-sixths of the decomposed muriate: the ammonia may be expelled from the precipitate by the addition of lime; but if the precipitate be exposed to heat, the ammonia is decomposed, and azote alone is disengaged, and no part of the oxyde is reduced; it sublimes entirely: but it is evident that the mercury of this sublimate cannot be as highly oxydated as in the case of precipitates produced by fixed alkalis or lime, as the decomposition of the ammonia deprives it of a part of its oxygen. The liquid residue contained a combination of oxyde of mercury, muriatic acid, and ammonia.

The precipitation by ammonia produced, the effervescence excepted, the same results as that produced by the other alkalis.

8. The other metallic solutions and precipitates will be found to be affected analogously to those of mercury, with the exception of such modifications as depend on the particular properties of each species of oxyde: I think, therefore, I have established the following principles.

1st, Acids act on metallic oxydes as on other substances, not merely in proportion to their affinity, but in proportion to their mass; for when a metal becomes insoluble, or nearly so, it may be dissolved by an excess of acid, or may form, by means of that excess, a more permanent combination.

2d, When a metallic salt is decomposed, the alkali, or alkaline earth, by which the decomposition is effected, takes a part of the acid proportionate to the energy of its action. If the metal and acid be but feebly united, water alone will destroy their combination; in which case, two combinations, one with a greater portion of acid, the other with a less, will take place. In this respect also, the phenomena presented by metallic oxydes accord exactly with those observed in other substances; but it happens sometimes, that the acid is not divided between the alkaline base and oxyde, but that, on the contrary, the precipitating base is divided between the metallic oxyde and the acid, as when fulminating gold, or the orate of ammonia, is formed: in some cases, too, the precipitant, the acid, and the metallic oxyde, form two complex combinations, of which one is insoluble, and the other soluble, as we have seen in the decomposition of the corrosive muriate of mercury by ammonia, and in the experiments which I have given in other parts of this Memoir.

In general, but particularly in the case of metallic solutions, the consideration of the precipitant should not be separated from that of the liquid in which the precipitation is effected; all the substances which are within the sphere of action, and which are capable of forming new combinations, ought to be equally the objects of our attention.

3d, Coloured oxydes may form colourless salts; but by losing a part of the acid with which they were combined, they resume their original colour, in proportion to the quantity of acid which they lose; so that colour indicates the existing constitution of the substance, provided no change be induced in the state of oxydation by any extraneous cause.

4th, Metallic oxydes cannot be compared with one another, unless taken in a determinate state of oxydation; all the combinations which they are capable of forming are varied, not only by the influence of this cause, but also by the proportion of acid which they retain: with respect to oxydation, there are only the two extremes, the *minimum* and *maximum*, which can be considered as constant.

It ſollows then, that a nomenclature can give

give only a vague indication of the proportions of the constituent parts and states of metallic salts, in most of which the degree of oxydation, and proportion of acid, are not determined.

5th, The affinities of acids for oxydes are not progressive, with respect to the degree of oxydation. The affinity of some diminish in proportion to the increase of the degree of oxydation; as for instance, that of nitric and sulphuric acids; while, on the contrary, it augments, in direct proportion to the degree of oxydation, with respect to muriatic acid. From these considerations, and those already presented, it must appear that all attempts to class the affinities of metals for acids, must have been fruitless, inasmuch as the affinities were considered as constant and uniform forces.

6th, The results of complex affinities of metallic solutions mixed with other neutral salts, are liable to still further variations from the proportions of these salts, *conformably to what has been established on the influence of proportions in complex affinities*; so that the degree of oxydation, the proportion of oxyde in solution, and that of the salt with which it is mixed, influence and determine the new combinations that take place.

The chemical action of metallic solutions must be acknowledged, then, to accord exactly with the principles or laws which we have established relatively to other combinations; with this difference, however, that the degree of oxydation changes the affinity of the metal for acids, or other substances, and multiplies (if the term be allowed) the property which metals have of forming combinations: this latter circumstance varies, and complicates the results in such a manner, as that they cannot be foreseen, from the sole consideration of the known properties of metals; but they may be distinguished and ascertained

by

by a close observation of the circumstances from which they originate.

9. The state in which oxygen is combined with metals, influences the comparative properties of oxydes and metallic precipitates. Bayen has observed, that several mercurial precipitates, and also the red oxyde, fulminate strongly, though unequally, by exposure to heat, after being mixed with sulphur; and that others of these precipitates do not possess that property: he has not assigned the reason of the fact or exception.

It appears to me that this property of the oxyde of mercury, and precipitates in which it predominates, depends on the oxygen of these containing a greater quantity of caloric than it does in union with sulphur or in sulphuric acid. The effect, then, is of the same nature as that produced by nitrate, or oxygenated muriate of potash, differing only in its being weaker; but in the precipitates obtained from the

the corrosive muriate of mercury, that part only can produce a detonation, which may be considered as free from the action of muriatic acid, and which may be reduced by the action of heat. Such of these precipitates, then, as retain a large proportion of muriatic acid, and which consequently are reducible to the metallic state in but a very small proportion, cannot explode: of this kind are the precipitates by ammonia, by carbonate of ammonia, and carbonate of potash.

The property discovered by BAYEN must be, then, analogous to the fulminating property of the orate and argentate of ammonia. As this property is not found in other metallic oxydes and precipitates, we may safely conclude that their oxygen is more destitute of caloric than that of the fulminating oxydes.

The properties which depend on oxydation, vary, then, in each metal, according to the proportion of oxygen ; and those which depend on the degree of condensation of the oxygen, are the primitive source of the phenomena presented by elastic substances in their changes of combination. (Art. XIV. Nos. 12, 15.)

THE END.

Printed by B. M'Millan,
Bow-Street, Covent-Garden.

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