XLII. Researches respecting the laws of affinity

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The liquor furnished by the skins, &c. when subjected to the press is less coloured.

The southern wines, and, in general, those made from grapes collected in places well exposed to the south, are more coloured than the wines of the north.

Such are the practical axioms which have been sanctioned by long experience. Two fundamental truths thence result: the first is, that the colouring principle of wine exists in the skins of the grapes; the second is, that this principle does not detach itself, and is not completely dissolved in the vintage but when the alcohol is developed in it.

We shall treat in the proper place of this colouring principle, and shall show, that though it approaches resins in some of its properties, it is, however, essentially different.

Any one, after this short explanation, may account for all the processes usual for obtaining wines more or less coloured; and may readily conceive that it is in the power of the agriculturist to give to his wines whatever tint of colour he chooses.

[To be continued.]

XLII. *Researches respecting the Laws of Affinity.* By
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[Continued from p. 153.]

X. Of the Determination of Elective Affinities.

TO determine the elective affinity of two substances for a third, according to the idea which we ought to form of it, is to ascertain in what ratio this third substance ought to divide its action between the two former, and at what degree of saturation each of them ought to be when their forces are equally opposed. The respective affinities will be proportional to the degree of saturation which each has attained in proportion to the quantity which has acted; so that, if the quantities are equal, the comparative degree of saturation will give the measure of the respective affinities.

2d, When I speak of the saturation of a substance, I do
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not mean the absolute saturation at which all reciprocal action would cease; but a degree of saturation which it is easy to ascertain, and which is common to all combinations: it is that of neutralisation, when the properties of neither of the constituent parts predominate. The term of the crystallisation of salts does not always coincide with neutralisation: for example, in regard to alkaline carbonats, which still give signs of alkalinity, and in regard to the acidulous tartrate of potash, which, on the other hand, retains an excess of acid. The last combination, however, may be taken at the term at which it is neutral, because it still has the property of crystallisation: it is even this tartrate that is necessarily obtained when in the experiment there is present an excess of the base; but when there is an excess of acid, the degree of saturation of the acidulous tartrate of potash may be determined by the quantity of potash necessary to neutralise it.

3d, A consideration which seems to deserve some attention is, that in comparing affinities it would be necessary to employ in all the experiments the same proportions of all the substances successively subjected to operation; because, if the proportions vary, the result of the action not being the same, the affinity could no longer be represented by the same number. I shall render this observation more sensible by an example:

Let 100 represent the potash, which ought to be saturated by 100 parts of sulphuric acid, and let 100 parts of soda be opposed to it. Let us suppose that after the action it is found that the potash has taken up 60 parts of acid, and the soda 40. I should thence conclude that the affinities of these two bases for the sulphuric acid are in the ratio of 60 to 40: but there remain 40 parts of potash uncombined, which really continue to act, and which by their action contribute to divide the acid; so that, if this quantity be varied, the result cannot be the same; for if, instead of 100 parts of potash, and 100 parts of soda, we take 80 parts of each, we shall have for the uncombined portion 20 parts of potash and another quantity of soda; so that the forces exercised by these two parts are no longer in the former ratio: hence it results that the two saturations cannot be in the ratio of 60 to 40.

4th,

4th, But to ascertain the degree of saturation to which each of these substances can attain, a separation must be made, which can only be effected by the elasticity, crystallisation, precipitation, or action of a solvent: but we have seen that these different means ought to be considered as foreign forces, which alter the results, and which determine the combinations formed, without a possibility of our measuring their effect so as to disengage from it that of the elective affinity; so that the separations which in articles I, II, III. were considered only as an effect of elective affinity and of proportions, are really the effect of a concurrence of several forces, as is proved by the observations which followed these articles.

When it is necessary, for example, to ascertain the quantity of the sulphat of potash and of soda formed, as the force of cohesion of these two sulphats does not much differ, it is probable that it would not occasion much change in the proportions of the two salts which would crystallise, but it would be necessary to separate the excess of the alkali by means of alcohol in order to obtain the whole crystallisation; but alcohol not acting with equal force upon potash and soda, would produce a new change. To these considerations we may add, that a change of proportions would not only make the force of the soda and the potash (No. I.) to vary, but also that of the alcohol, not to mention the affinity of the water, which serves as the solvent.

If barytes were to be compared with either potash or soda, we should have changes still more considerable: in that case, the force of cohesion of the sulphat of barytes would be such that it would leave to the alkali but a very small quantity of sulphuric acid, which would be the expression of the ratio of the force of the cohesion of the sulphat of barytes to that of the solvent, rather than of the affinity of the barytes to that of the alkali.

This is so certain, that if, with the view of comparing the affinity of the acids for barytes, we should begin by treating the barytes with an excess of sulphuric acid, it would be almost entirely precipitated, unless the acid were highly concentrated; it would even be impossible to distinguish the
combined

combined portion from that which is not, and to say that the barytes has more affinity for the former than for the latter. This, however, is what is really said when it is affirmed that the sulphuric acid has more affinity for the barytes than any other acid has, because a sulphat of barytes is formed by precipitation; and thus an effect, which depends in particular on the force of cohesion peculiar to the sulphat of barytes, is ascribed to elective affinity.

It is manifest, therefore, that the elective affinity of two substances in regard to a third, cannot be determined by a direct experiment even when trial is made on two substances which are in a liquid, and which may become neutralised by saturation; since, in order to ascertain the saturation, it is necessary to employ the intervention of foreign forces.

5th, We have shown in articles II. and III. that the affinity of a substance may be compensated by its quantity.

From this consideration it would appear that it is sufficient to ascertain the capacities of saturation of different bases for an acid, or of different acids for a base, in order to establish the ratio of their affinity; for it ought to be in the inverse ratio of the quantities necessary to produce the same degree of saturation.

This consequence, however, is erroneous when we are desirous of applying it to the elective affinities; because, as soon as the two substances are put in circumstances to combine with a third, new forces are established, which not only determine other results, but even change the constitution of these substances. Thus, if we compare the sulphuric acid with carbonic acid, it is certain, that if a quantity of potash be brought to the term of neutralisation by carbonic acid, it exercises a force as great as the quantity of sulphuric acid which would be necessary to produce the same effect: and yet if sulphuric acid be poured on the combination thus formed, all the carbonic acid is disengaged; because, not being retained by an equal force, it resumes the elastic state: and even if it be retained by a sufficient quantity of water, it will no longer be in the same state of compression; it will no more have the same constitution; it will no longer be the same substance in regard to chemical action. In a word,

we must apply to the action of substances unequally saturated the observations made in the preceding articles.

A comparison, then, of the capacities of saturation, though it may conduce to important considerations, cannot be applied to the determination of elective affinities.

XI. Of some Errors which arise from a false Idea of Elective Affinity.

1st, I shall here discuss some opinions adopted respecting elective affinities: I shall show how little foundation they have, and shall oppose to them the application of principles established in the preceding articles.

Beaumé observed that when the sulphat of potash was dissolved, by means of heat, in an equal weight of nitric acid, crystals of nitrat of potash were obtained by cooling. He ascribes this decomposition of the sulphat of potash to reciprocal affinities, which produce opposite combinations without determining the cause of this contrary effect.

2d, The explanation of this remarkable fact has been contradicted by Bergman. He observes that there are salts which tend to have an excess of acid; such as the acidulous tartrate of potash. He is of opinion that, when these salts are in a state of neutralisation, we must consider their base as divided into two parts; one upon which the whole action of the acid is particularly exercised to form an acidulous salt, while the other part only tends to satisfy the excess of acidity in the acidulous salt. This part of the base is retained then only by a weak acidity, and it may be taken away by an acid very inferior to that which enters into the first combination. Thus the acetic acid may take away part of the potash, which in the tartrate of potash is superfluous, to the combination that constitutes the acidulous tartrate of potash, though this acid has a much weaker affinity than the tartareous acid.

But the sulphat of potash is among the number of those salts which tend to form an acidulous salt; nearly two-thirds of its base enter into this combination, and it is only this portion which is subject to all the affinity of the sulphuric acid; the other third may be separated by an acid of an affinity inferior to that of the sulphuric acid, such as the nitric, muriatic,

muriatic, or tartareous acid. When the decomposition is carried to its boundary, it stops, whatever may be the quantity of the acid opposed; and if the quantity is not too great to prevent crystallisation, or if the excess be expelled by heat, an acidulous sulphat, which forms crystals permanent in the air, will be obtained by solution and evaporation.

3d, How could the illustrious Bergman deviate from the route traced out to him by observation? His own experiments, even, prove that the acid, which is superabundant in the acidulous sulphat of potash, exercises its affinity; that it is in combination; and that it acts in the ratio of its quantity: for he says, that if sulphuric acid be added to the acidulous sulphat of potash, this salt dissolves, and loses its property of crystallising; that this excess of acid can with difficulty be expelled even by distillation in a retort; and that, to produce this effect, the saline combination must be fused in a crucible, or be exposed several times to the action of very pure alcohol.

4th, The limit, then, which Bergman gives to the action of acids on the acidulous sulphat is ideal. This sulphat exhibits the same phænomena as all the salts which are capable of resisting, to a certain degree, the action of an excess of acid or base (Art. V. No. 4.), as well as the action of another acid or a foreign base. The only difference there is between them in this respect depends on the force of cohesion which may act more or less to produce crystallisation, and which is proper to certain proportions of acid and base; probably a consequence of the figure assumed by the molecule of their combination.

5th, When an acid has the property of forming a precipitate by combining with a base, it is concluded that it has more affinity for that base than for the acid with which it was first united, without examining how far the new acid may have operated the decomposition, and without reflecting that an opposite decomposition takes place by a simple change of proportions, and might consequently conduct to an opposite conclusion.

Thus, as the tartareous acid has the property of forming, with potash, an acidulous salt very little soluble, and consequently forms a precipitate with all salts having a base of

potash, and not diluted with too large a quantity of water, it has been concluded that it has more affinity for potash than the other acids. Bergman has excepted the sulphuric acid, because he supposed that the tartareous acid could act only on the potash redundant to the combination of the acidulous sulphat of potash; a supposition which, I think, I have already destroyed in the preceding articles. He has excepted also the nitric and muriatic acids, because he supposed that the tartareous acid showed the same phænomena in regard to the nitrat and muriat of potash as in regard to the sulphat; though he has not ascertained the existence of an acidulous nitrat and muriat of potash analogous to the acidulous sulphat of potash.

He also concludes, from experiments made on salts having a base of soda, but without making the experiments known, that the tartareous acid ought to be placed after the oxalic acid: but, not to dwell on these exceptions, the tartareous acid, according to him, decomposes completely all the other salts with a base of fixed alkali.

What embarrasses Bergman is, that the tartareous acid produces no precipitate with salts that have a base of soda. In his opinion, this apparent difference depends on the soda not having the property of forming a salt but little soluble, by taking up an excess of acid; but in that case there is no evidence of a decomposition, and we are to be satisfied with the probability that the affinities of the one fixed alkali follow the same order as those of the other.

All this classification of affinities is founded on the false supposition, that one acid expels another from its combinations by its affinity alone considered as a constant force; and this supposition renders others necessary in order to explain, as exceptions, those facts necessarily arising from a general property.

6th, I have examined the decomposition of acidulous tartrite of potash by the nitric acid, which, according to the received ideas, which I then adopted, ought to decompose it by seizing entirely on its base. I digested acidulous tartrite of potash and nitric acid, and obtained, by cooling, beautiful crystals of nitrat of potash. I repeated the operation several times,

times, adding nitric acid until no more nitrat of potash was separated. I then exposed the liquor to a heat sufficient to cause the nitric acid which might be free, to evaporate without altering the tartareous acid. After this the liquor had an oily consistence; it was destitute of smell, and announced neither the existence of nitric acid nor that of potash; but when exposed to a strong heat there was disengaged a great deal of nitrous gas, the tartareous acid was reduced to charcoal, and its ashes gave a considerable quantity of carbonat of potash.

7th, In this operation there is separated a part of the nitrat of potash, effected by the crystallising force of that salt, and carried by it just to the degree when that force is exceeded by the superabundant acid. The acidulous tartar is rendered soluble by the action of the nitric acid, which takes from it at the same time, by crystallisation, a part of the base necessary for its insolubility.

On the other hand, tartareous acid added to a solution of nitrat of potash, takes up, to a certain term, the potash from the nitric acid, and forms an acidulous tartrate, which is precipitated; but, as it has not the property of forming an acidulous tartrate of soda little soluble, it does not produce a precipitate with salts having a base of soda.

In both these cases, every thing that cannot be separated by the force of cohesion forms a liquid, in which the substances exercise an action proportioned to their present masses.

Nothing, then, can be concluded in regard to the respective affinity from these separations, which are effected by precipitation or crystallisation; since, by the change of the proportions alone, opposite decompositions may be often obtained.

8th, The precipitation observed to take place, when, in comparing the affinities of two bases, one of them was found to have formed an insoluble combination, gave rise to an error of the same kind; and it is on this foundation alone that it has been asserted that lime has more affinity than alkali for the fluoric, phosphoric, and arsenic acids: in a word, for all those which form with it an insoluble combination; and, consequently, that it has the property of decomposing entirely the salts formed by an alkali and these acids.

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This precipitation is not the result of elective affinity, and it is not complete, but its quantity is determined by the ratio of the action of the liquid to the cohesive force of the precipitate: hence it happens that the precipitate is often re-dissolved on augmenting the quantity of the substance opposed to it.

9th, Though Bergman has explained very clearly the changes which heat may produce on chemical action when the substances have a disposition to volatilisation; and though he even recommends to avoid too strong heat in evaporation, the extent of the influence which it may have in the operations by which salts are separated, in order to form a judgment of their affinities, has not yet been fully discovered.

It ought not to have been concluded that the sulphuric acid has more affinity for fixed alkalies than the nitric or muriatic acids, merely because that by a strong heat it expels these acids from their combinations. Chemists should have observed that, even by the heat employed to produce evaporation, and to cause salts to crystallise, the proportions of the volatile acids may be considerably changed in regard to the sulphuric acid which remains opposed to them, and that the latter may at length entirely expel them, by means of the difference which exists between its fixity and that of these acids. (Art. VII. No. 5.)

10th, We are indebted to Bergman for useful observations on the errors which may arise from the solubility of one substance, which is eliminated, and of which the separation is not observed. He remarks that potash and soda do not disturb the transparency of the solution of a salt with a base of lime, if this solution be diluted with fifty times as much water, because the lime separated, being soluble, remains in the water; but he did not reflect that, if the lime, in that case, had no more than its natural solubility, it would be a very weak obstacle to its precipitation, for it requires nearly seven hundred parts of water to dissolve it: what adds greatly to its natural solubility is, that it continues to be in combination with the acid (Art. V. No. 5.), and that it cannot be separated but by retaining a part (Art. III. No. 9.), which increases its solubility.

11th,

11th, Notwithstanding his general observations, Bergman mistook the effects of solubility in several cases: thus, he did not think that the nitric and muriatic acids had an action on the combination of the phosphat of lime, though the only difference that can be established in this respect between these two acids and the sulphuric acid, the comparative force of their affinities not being known, is, that the two former form only soluble combinations, while that produced by the sulphuric acid may be withdrawn, in a great measure, by the force of crystallisation.

12th, It is the solubility of the lime as well as of the barytes, increased by the action of the acid on these earths, which causes ammonia not to produce any precipitate in the solution of the salts of which they are the base. The first portion of the ammonia, however, mixed, for example, with the muriat of lime, scarcely suffers any odour to be exhaled; which indicates that it has entered into combination, and that its action may be rendered sensible, as shall be here shown.

I mixed ammonia with a solution of the muriat of lime, and I caused the liquor to evaporate in a retort: when it was reduced to a certain point, there was formed a pretty considerable precipitate. I continued the operation, at the end of which the quantity of the precipitate was very much diminished; there was formed a pellicle; and, by cooling, a large quantity of crystals in pretty long needles. It was a triple salt, from which the ammonia could be disengaged by lime. This salt, when redissolved, and evaporated in the open air, gave no more indications of ammonia in the proof by lime.

It is seen, then, that, when the water has not been too abundant, the ammonia precipitated a part of the lime, though it was rendered much more soluble by the acid, and though the action of the ammonia was considerably weakened by the heat, which diminished its affinity and its quantity. In proportion as the latter was reduced, the precipitate was re-dissolved: there however still remained ammonia after a long evaporation, and it was only by the help of the action of the air that it was entirely dissipated. The separation of
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the lime would, no doubt, become much more sensible if the ammoniacal gas were received in a strong solution of the muriat of lime.

If the ammonia produces a precipitate with salts having a base of alumine, it is because this earth has less solubility than lime, even when it is combined with the portion of the acid which it retains while it is precipitated.

[To be continued.]

XLIII. Experiments and Remarks on Galvanism. A Letter from a Correspondent to the Editor.

SIR,

HAVING read, with much pleasure, in your very valuable monthly publication, the several opinions and experiments respecting the influence excited in the pile of Volta, I take the liberty of submitting to you some observations on the same subject.

It has been said by some very ingenious experimentalists that the oxydation of one side of the plates, or the difference of oxydation in the two metals, or between one metal and different fluids, is the cause of the production of the galvanic influence. I find that the acids increase the power of my pile, and I also find, when the papers or cards are moistened with the pure alkalies, and particularly with a solution of pure ammonia, that the effect is much greater than by any other substance. This fact is, I believe, sufficient to prove that the oxydation of the metals is not the cause of the phænomenon.

It is very convenient to use the alkalies in this manner, as it does not require so much trouble to clean the metals, or to keep the pile in order.

I took ten saucers, and placed in each a plate of silver and a plate of zinc; I connected these metals in the several saucers together, by means of slips of tin-foil, and completed the circuit by means of wires in water. I first filled these saucers with salt and water, and found that the wires in the water produced a trifling effect: some few air-bubbles escaped, which proved that the influence was excited. I then re-
moved