X.—*Some Experiments illustrative of the Reciprocal Decomposition of Salts.*

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AMONG the conclusions arrived at by me in a paper published in the "Philosophical Transactions" of last year, were the following:—

"Where two or more binary compounds are mixed under such circumstances that all the resulting bodies are free to act and react, each electro-positive element arranges itself in combination with each electro-negative element in certain constant proportions."

"These proportions are not merely the resultant of the various strengths of affinity of the several substances for one another, but are dependent also on the mass of each of the substances in the mixture."

My impression is that these laws are of universal application; but this can be established only by the observation of a large number of varied instances in which they hold good, and by the investigation and explanation of every supposed exception.

The present paper contains the account of some reactions bearing upon the subject, which are of value, either from the experiments having been performed with elements hitherto untried, or from some novelty in the mode of observation. Every difficulty which,

to my knowledge, has been proposed by others, or which has occurred to my own mind, has been examined, and is here commented on.

Chromium Salts.—The soluble chromic salts have very remarkable optical properties. Their colour, by transmitted light, depends not only for its depth, but for its very character, upon the amount of salt which the ray has traversed in the solution. If the solution be weak, or if only a thin stratum be seen, it appears green; if a stronger solution or a thicker stratum, it appears red. As these two colours are complementary, or nearly so, the red on dilution passes into the green, not by a strictly speaking intermediate shade, but by a kind of brown or neutral tint. Now though, as far as I am aware, this description applies to all the soluble chromic salts, the amount of oxide requisite to give the red appearance depends greatly upon the acid with which it is combined. Thus, if equal portions of chromic oxide be dissolved in acetic and in sulphuric acids, it is very easy to arrange it so that, when viewed through glasses of equal capacity, the acetate appears red, and the sulphate green. If now to the red acetate a few drops of sulphuric acid be added, it passes through the neutral tint to the green colour; or if contrariwise, a little glacial acetic acid be added to the green sulphate, it assumes the reddish hue.

It is interesting to observe this change of colour by means of a prism. If a luminous object be viewed through any solution of a chromic salt, it exhibits two images, the one red, and the other green, fringed with blue. The relative intensity of colour of these two images differs with the amount of salt looked through, and with the character of the electro-negative element. On the addition of acetic acid, the red image becomes comparatively brighter and brighter, while the green image pales; and contrariwise, on the addition of hydrochloric or sulphuric acid, the green image becomes comparatively more and more distinct, while the red one fades. Again, if a solution of the acetate be seen through the sides of a wedge-shaped glass vessel, the stratum near the angle will appear green, that near the broad end red, while about a certain line neither colour will preponderate. On the addition of sulphuric acid this line advances towards the broad end, while acetic acid brings it again nearer the angle.

Ferrous Salts.—The mutual displacement of sulphuric and acetic acids may be also rendered visible by means of the protoxide of iron. If to a green solution of sulphate of iron a solution of acetate of potash be added, a brown colour is the result. If sulphuric acid

be added to this, the pale colour is more or less restored ; if an addition of acetate of potash be then made, the brown reappears. This may be repeated many times with the same solution.*

Cobalt Salts.—The sulphocyanide of cobalt in an anhydrous condition, like the chloride, is blue ; but, unlike that salt, it retains its blue colour when dissolved in a little water. As the solution is diluted, it gradually assumes the red tint which characterises solutions of the compounds of this metal. If very strong solutions, containing corresponding equivalents of chloride of cobalt and sulphocyanide of potassium, be mixed, a blue colour makes its appearance, showing the formation of sulphocyanide of cobalt. But that the double decomposition has not been complete, may be made evident by carefully diluting the blue mixture with water till it has become distinctly red, and dividing it into two parts. If to the one portion some of the very strong solution of sulphocyanide of potassium be added, the blue colour is restored ; on the addition of more water, it disappears ; and this may be repeated a number of times, until ten or twelve equivalents of sulphocyanide of potassium has been added to one of chloride of cobalt. If, inversely, to the other portion of the original mixture chloride of cobalt be added, that substance also produces a blue colour, which may be likewise caused to become red, or to reappear many times, by the successive addition of water or chloride of cobalt.

Chromates.—During the past year the “*Journal de Pharmacie et Chimie*”† has published an extract, in which Margueritte proves that “chromic acid can displace hydrochloric, nitric, and even sulphuric acids, and take away from them a part of the base to which they are united, whether that base be strong or weak.” We all know that these acids are capable of displacing chromic acid ; indeed, the same investigator has shown that even boracic and carbonic acids will decompose bichromate of potash. By a method of observation almost identical with that adopted by myself, he found that the addition of such salts as chloride of potassium, or the nitrate or sulphate of potash or ammonia, to a solution of the red bichromate of potash, caused the production of yellow monochromate. Such experiments, he conceives, lend support to his view of “the partition of a base between the two acids, when any acid is added to any saline solution ;” which is identical with the

* This experiment was suggested by a remark in Professor Miller’s Chapter on “Some Circumstances which Modify the Operations of Chemical Affinity,” in his “Elements of Chemistry, Theoretical and Practical,” vol. ii.

† *J. Pharm.* [3] xxvii. 21.

law of Berthollet, or rather is included in the more general expression.

One objection, however, may be taken to this conclusion from Margueritte's experiments. It may be contended that the salt added merely displaces the one equivalent of chromic acid in the bichromate of potash, and that, in fact, the reaction is according to the formula :

Indeed, this idea seems to have been in the mind of Schweizer, in a paper published a few months ago on these reactions of chromic acid.* The point seemed to admit of easy determination, for if the decomposition really take place in that manner, the production of the yellow colour will be perfect when single equivalents of the two salts are mixed, and no subsequent addition of sulphate of potash will lighten the tint. On trying the experiment it was found to be otherwise. The addition of one equivalent of sulphate of potash to one of bichromate of potash caused certainly a diminution of the red tint; but successive additions of the sulphate to the previous mixture caused the yellow to become more and more decided. Hence it may be concluded, that the mixture of single equivalents contains both bichromate and monochromate of potash, besides sulphuric acid and sulphate of potash, and possibly free chromic acid.

Copper Salts.—M. Alvaro Reynoso has recently published some "facts relating to the double decomposition of salts."† By taking advantage of the power of glucose to reduce the acetate of copper, he finds that when acetates of the alkalies, earths, or metals, are mixed with the nitrate or sulphate of copper, the acetate of that metal is produced. This is, so far, in accordance with the law of Berthollet; but whether the decomposition be complete or not does not appear from his experiments, though the action of mass is very evident in some of them. One remark, however, presents some difficulty. He observed that acetate of copper, mixed with ferric nitrate or sulphate, loses the property of being reduced by glucose. This I have repeated quantitatively. Solutions of acetate of copper and nitrate of iron were prepared of known strength; they were mixed together in certain proportions, with the addition of glucose, and boiled.

* J. pr. Chem. lxx. 173.

† Compt. rend. xli. 278.

Salts mixed with glucose.					Result.
Acetate of copper					Immediate decomposition.
3 eq.	"	"	+ 1 eq.	ferric nitrate	Deposit after boiling.
3 eq.	"	"	+ 1.5 eq.	" "	Deposit after long boiling.
3 eq.	"	"	+ 2 eq.	" "	Deposit after very long boiling.

From this it may be concluded that $3(\text{CuO}, \text{AcO}_3) + \text{Fe}_2\text{O}_3, 3\text{NO}_5$ do not become wholly $3(\text{CuO}, \text{NO}_5) + \text{Fe}_2\text{O}_3, 3\text{AcO}_3$. This also was confirmed by the colour: for the mixture of two equivalents of the ferric nitrate with three of acetate of copper was deeper in tint than when the salts were mixed in the proportions merely necessary for the above double decomposition.

This reaction, then, instead of militating against the conclusion illustrated in this paper, serves to support it.

In the "Comptes rendus" for last year, there also appear papers by Tissier* and Bineau,† narrating experiments confirmatory of the views arrived at by myself and other investigators; but they call for no further remark.

EVIDENCE FROM CIRCULAR POLARISATION.

Camphorates.—It was an early idea of mine that the effect of chemical affinity among substances in solution might be tested by means of circular polarisation; yet the evident intricacies of the subject deterred me from making any experiments: nor, indeed, did I see a case suited to my purposes. M. Bouchardat,‡ however, has announced that camphoric acid dissolved in alcohol causes a right-handed rotation; and that when it is saturated with a base, the rotation is considerably diminished, but is restored again on the supersaturation of the base by another acid. Yet, if I understand his experiments rightly, it appears that in the latter case the original amount of rotation is not quite obtained. Thus he gives the numbers:—

Camphoric acid	12° R.
The same, saturated with soda	7° R.
The same, supersaturated with hydrochloric acid	11° R.
Camphoric acid	22° R.
The same, saturated with ammonia	12° R.
The same, supersaturated with hydrochloric acid	21° R.

* "On some Facts relating to Double Decomposition," p. 362.

† "On the Solubility of certain Metallic Oxides and Earthy Carbonates, and on some Reactions produced by their Solutions," p. 509.

‡ Compt. rend. xxviii. 319.

Are we wrong in deducing from these results that the hydrochloric acid did not completely decompose the alkaline camphorates first formed?

SALTS DISSOLVED IN ACIDS.

Sulphate of Baryta.—Within these last few months, no less than four papers have appeared, in which the solubility of sulphate of baryta in hydrochloric acid is discussed. Professor Rose,* Mr. Crace Calvert,† Dr. Noad,‡ and Messrs. Nicholson and D. Price,§ have shown by independent experiments, not only that sulphate of baryta is, to a certain extent, soluble in these acids, but that the amount dissolved is most materially diminished by the presence of an excess of baryta salt. Rose states that the solution of pure sulphate of baryta in either of the above-mentioned acids gives a small precipitate when treated with either chloride of barium or dilute sulphuric acid. He says, “It is a striking circumstance that the presence of the dissolved sulphate of baryta is indicated by both these reagents,” and he concludes that the salt in question “is less soluble in sulphuric acid and in chloride of barium than in hydrochloric acid and nitric acid.” Yet the great analytical chemist can scarcely offer this as a satisfactory explanation; for, in the experiment, the acid solvent still remains, capable, of course, of exerting its former power. Indeed, the next sentence shows the insufficiency of the reason; for Rose remarks that sulphate of baryta does not separate from the acid solution by means of water, although it is assuredly less soluble in water than in hydrochloric or nitric acids.

However, this “striking circumstance” is precisely what might be expected if the law of reciprocal decomposition, as quoted above, be true. If sulphate of baryta in excess be treated with an acid—say nitric—that portion which is brought into solution will suffer partial decomposition, and a solution will eventually result, containing as much sulphate of baryta as the free acid is capable of dissolving, and as much nitrate of baryta and sulphuric acid as is capable of counterbalancing the two other bodies. Such being the case, the addition of either sulphuric acid or baryta salt will disturb the equilibrium, with the production of fresh sulphate of baryta, which must precipitate, seeing that the acid solution was previously saturated.

Sulphate of Strontia.—Rose observed the same with sulphate of

* Pogg. Ann. xcv. 108.

‡ Chem. Soc. Qu. J. ix. 15.

† Proc. Roy. Soc. vii. 532.

§ Phil. Mag. 1856 [4], xi. 169.

strontia as he did with sulphate of baryta. Of course it is capable of the same explanation.

Sulphate of Lime.—On examining a solution of sulphate of lime in hydrochloric acid, Rose observed that a precipitate formed when it was treated with sulphuric acid, but not when it was treated with a solution of chloride of calcium. That this precipitation by sulphuric acid is incapable of the explanation offered by him in the case of sulphate of baryta, he shows by the observation that “a concentrated solution of sulphate of lime in water is *not* precipitated by sulphuric acid.” But the non-precipitation by chloride of calcium presented a difficulty to my explanation.

Two possible reasons suggested themselves to me, and, fortunately, each was capable of being put to the test of experiment. It might be that one equivalent of sulphate of lime is capable of being dissolved (or decomposed) by not more than one equivalent of hydrochloric acid. In that case, the formation of any amount of sulphate of lime from chloride of calcium would set free an equivalent amount of hydrochloric acid, which would keep it in solution. It was found, however, that one equivalent of sulphate of lime required three equivalents of hydrochloric acid (somewhat dilute) at the ordinary temperature to dissolve it.

The other supposition was that chloride of calcium might itself exert a solvent action on sulphate of lime; but this was found not to be the case.

The only supposition, then, that seemed possible, if my view were correct, was that such a small amount of additional sulphate of lime was formed that it was soluble in the water which was added at the same time as the chloride of calcium. This, happily, was also capable of being put to the proof by employing a very concentrated solution of the chloride. On doing so, a cloudiness at once appeared, which soon became a decided precipitate of crystallised sulphate of lime.

These reactions are all explicable on the supposition that when sulphate of lime is dissolved in hydrochloric acid, nearly (but not quite) all is converted into chloride of calcium.

Though sulphate of lime is not rendered more soluble in water by the presence of chloride of calcium, it does dissolve more freely when *other* chlorides are present. A. Vogel* has shown this in reference to chloride of ammonium and common salt: I have tried the experiment with four metallic chlorides—those of zinc, copper, iron, and chromium, and have found it to be the case with each.

* J. pr. Chem. xi. 196.

Now this is precisely what might be expected, supposing the two salts to suffer reciprocal decomposition, with the conversion of more or less of the sulphate of lime into the very soluble chloride. Vogel observes that when the solution in chloride of ammonium is evaporated to dryness, and heated to redness, pure sulphate of lime remains; and this has been employed as an argument against Berthollet's views: yet when we reflect how very volatile is the ammoniacal chloride, while the sulphate is not volatilised without decomposition, we shall see that no other final result could be obtained.

Sulphate of Lead.—Wackenroder* states that sulphate of lead dissolved in nitric acid is precipitable by sulphuric acid. I find that such a solution gives a precipitate also when treated with nitrate of lead.

This case is mentioned, because a statement of Wackenroder has been employed as an argument against the Berthollian hypothesis. The German chemist says that sulphuric acid, in large quantity, precipitates the sulphate of lead *completely*, notwithstanding the presence of the nitric acid. Yet, farther on in his paper, he proves that the said precipitation is *not* absolutely complete, and it is evident that, by employing the word "*vollständig*," he merely meant to say that the action was sufficiently perfect for ordinary analytical purposes.

Sulphate of Mercury.—Wackenroder also shows that the insoluble sulphate of mercury dissolved in nitric acid is precipitable by sulphuric acid.

Oxalate of Lime.—In order to vary these observations by experiments on other salts than sulphates, a saturated solution of oxalate of lime in dilute hydrochloric acid was prepared. On the addition of oxalic acid, a white precipitate after a while made its appearance; and on the addition of chloride of calcium to another portion, a precisely similar result ensued.

Chloride of Lead.—Dilute nitric acid was saturated with chloride of lead, and divided into two portions. To the one, hydrochloric acid was added, which caused an instantaneous precipitate; to the other, nitrate of lead was added, and, after some time, long crystals of chloride of lead formed.

Phosphate of Iron.—Hitherto the fact, that when a salt insoluble, or slightly soluble, in water, has been dissolved in an aqueous solution of any acid, the base divides itself in certain proportions between the two acids, has been deduced merely from the reactions

* Ann. Ch. Pharm. xli. 316.

of which such a solution is capable. It seemed desirable to prove this, if possible, by direct ocular demonstration. Phosphate of iron appeared to offer an opportunity of doing so. It is white in the solid state, but dissolves in hydrochloric acid with an orange colour. Now, if this colour be due to ferric chloride, we have a means of judging whether the whole of the iron be in that condition. Accordingly, some dilute hydrochloric acid was saturated with ferric phosphate. A portion was found to contain the same amount of colour as an aqueous solution of 0.067 grm. of ferric chloride; but the acid liquid itself consisted of 0.585 grm. of ferric phosphate dissolved in 0.477 grm. of real hydrochloric acid. Evidently, therefore, the whole of the iron was not in the state of chloride; indeed, supposing the ferric phosphate to have been of the usual composition, $2(\text{Fe}_2\text{O}_3)\cdot 3\text{PbO}$, the amounts of iron in the two equi-tinted solutions were—

In the solution containing both phosphoric
and hydrochloric acids 0.164 grm. Fe.

In the solution of pure ferric chloride 0.023 „ „

Hence it would appear, that when ferric phosphate is dissolved in the smallest possible amount of hydrochloric acid, only one-seventh part is converted into the chloride.

It is here assumed that the ferric phosphate, which is white in its pure state, has no colour of its own when dissolved. In other ways, also, the above numbers may not be very exact; yet one thing is certainly proved,—that when phosphate of iron is dissolved in a minimum of hydrochloric acid, it is not wholly, or principally, converted into the chloride.

It may be expected that if a considerable amount of the iron still remain as phosphate, the addition of more hydrochloric acid will decompose more or less of this, and increase the colour. Such was found to be actually the case.

These experiments could not be advantageously performed by looking horizontally through the solution, for the golden tint of the ferric chloride is very little altered by dilution. A comparison, however, is easily made by looking perpendicularly through the solutions contained in glasses of uniform diameter.

The addition of phosphoric acid to the acid solution of ferric phosphate gave an immediate flocculent precipitate. I failed, however, to obtain a precipitate on the addition of ferric chloride. This is the first exception to the general inference that if a salt AB dissolve in an acid CD, the addition of either AD or CB will cause the production of more AB than the acid can keep in solu-

tion; yet when the peculiarity attending the saturating power of phosphoric acid is considered, it will probably present no great difficulty to the reception of that as a general law.

REPUTED EXCEPTIONS.

Beside the *primâ facie* difficulties already discussed, other reactions have been urged against the general conclusions adopted by me, and these claim a careful examination.

Cyanide of Mercury.—Reactions of an apparently anomalous character take place among mercury salts: thus, the cyanide affords two instances where an insoluble compound does not form, although, from the reciprocal decomposition of the compounds mixed together, it might be expected to make its appearance. When the cyanide of mercury is treated with potash in solution, the insoluble oxide does not precipitate; and when mixed with nitrate of silver it produces none of the insoluble cyanide of that metal.

The first of these apparent anomalies depends perhaps on the formation of the well-known oxycyanide of mercury, which is a ternary compound soluble in water. The annexed formula represents this decomposition:—

though such a mixture may contain, I apprehend, simultaneously all the four substances, besides the double cyanide of mercury and potassium.

As to the second anomaly, cyanide of mercury forms a soluble crystalline double salt with nitrate of silver, which has been analysed by Wöhler,* who assigns to it the composition $\text{AgO}, \text{NO}_5, 2\text{HgCy}, 4\text{HO}$. But were we to overlook this, the decomposition might be supposed to take place thus:—

all of which, beside the original salts, are soluble in water.

Boracic Acid.—The objections most frequently urged are founded on the behaviour of boracic acid. It is contended that this acid has no power to decompose sulphate of potash, and that borax is completely decomposed by an equivalent of sulphuric acid. I have already shown† that the non-alteration in colour of litmus does not prove this, but I have in vain sought for some property which would enable us to decide what actually does take place in the above-mentioned mixtures. Indications, however, have been ob-

* Pogg. Ann. i. 231.

† Phil. Trans. 1855, 220.

tained where boracic acid was mixed with another sulphate, and also where it was mixed with another potash salt; and in each of these cases it was found capable of effecting some decomposition.

The borate of quinine in solution, like the hydrochlorate, is non-fluorescent, or nearly so. If boracic acid be added to a neutral, and consequently non-fluorescent solution of sulphate of quinine, it immediately exhibits the beautiful surface blue, just as though a drop of hydrochloric acid had been added, and doubtless from the same cause—the formation of some bisulphate through the abstraction of some of the quinine by the other acid.* The addition of a very large quantity of boracic acid appeared to diminish the colour, and consequently to indicate the decomposition of the bisulphate; but I certainly never succeeded in destroying the fluorescence, as is easily done when the powerful hydracids are employed.

Three solutions were prepared—the first of boracic acid, the second of pure nitrate of potash, the third of a mixture of the two; and they were digested for some time with metallic copper, after which the solutions were tested with ammonia in excess. The first showed absolutely no blue, the second only a faint trace, while in the third the blue colour was very decided. From this it may be inferred that the boracic acid had displaced some of the nitric acid, which in its turn had attacked the copper. The quantity of copper dissolved must, however, have been exceedingly small.

It has also been objected that boracic acid occasions no precipitate in a solution of nitrate of lime, although borate of lime is an insoluble salt. Now there are said to be compounds of boracic acid and lime, which are not insoluble in water: and, moreover, the production of borate of lime from the nitrate must liberate an equivalent amount of nitric acid, which of course will exert its own solvent power. But while the non-precipitation of a borate is evidently inconclusive as to what really happens in the mixture, it appeared to me that metallic copper would also in this case furnish an indication. The experiment was accordingly tried as with the potash salt, and it was found that the neutral nitrate of lime had no action on copper, while the mixture of nitrate of lime and boracic acid produced a solution which was rendered blue by ammonia, and during the digestion a gelatinous substance formed in small quantity about the shreds of copper.

* See Stokes's paper, *Phil. Trans.* 1852, 542; also, 1855, 210.

It thus appears that boracic acid is able to displace other acids from their combinations, though but to a slight extent, in the cases just examined.

REGULAR PROGRESSIVE CHARACTER OF THE INFLUENCE OF MASS.

From the experiments detailed in the paper already referred to, I was led to the conclusion, that—"An alteration in the mass of any of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regular progressive ratio; sudden transitions only occurring where a substance is present, which is capable of combining with another in more than one proportion." Yet there is one experiment recorded which appears to offer an exception, and to indicate changes of ratio somewhat similar to those observed by Bunsen and by Debus, in cases where the resulting compounds were not capable of reacting. This experiment is where a solution of oxalate of lime in hydrochloric acid was precipitated by the addition of acetate of potash or soda. The table drawn out, and the curves projected from the experiments, show considerable irregularities; but as each experiment consists of six or eight separate observations, it was thought desirable to repeat the experiment, taking every precaution to ensure the observations being all made under the same circumstances.

Into each of ten glasses were poured 400 grain measures of a solution of oxalate of lime in hydrochloric acid. Different amounts of a solution of acetate of potash were mixed thoroughly with these, and the solutions were made up to the same bulk by the addition of water. After standing twenty-four hours, the resulting precipitates were washed the same number of times by suffusion and decantation; they were then boiled with pure water, and collected.

Oxalate of lime in hydrochloric acid.	Acetate of potash added.	Oxalate of lime precipitated.
400 gr. meas.	50 gr. meas.	0·015 grm.
400 "	100 "	0·049 "
400 "	150 "	0·102 "
400 "	200 "	0·136 "
400 "	250 "	0·193 "
400 "	300 "	0·278 "
400 "	350 "	0·336 "
400 "	400 "	0·350 "
400 "	500 "	0·354 "
400 "	600 "	0·354 "

On the addition of potash to the filtrate from the last experiment of this series, a slight turbidity was produced, from the separation of oxalate of lime, showing that the whole of the hydrochloric acid had not even in that case been converted into chloride of potassium.

From the table it will be seen that a larger addition of acetate of potash caused a larger deposit of oxalate of lime, and that in a ratio which, though somewhat remarkable, was tolerably regular in its character. As it may be interesting to know the proportionate equivalents of the substances in each experiment, they are given in the annexed table. The initial 400 grain measures of acid solution contained 0.375 grm. of oxalate of lime, dissolved in 2.26 grms. of hydrochloric acid, nearly the proportion of 1 equiv. to 12; and each 100 grain measures of the acetate of potash solution contained 1.80 grm. of the anhydrous salt.

Oxalate of lime. 1 equiv.	Hydrochloric acid. 12 equiv.	Acetate of potash. 1.75 equiv.	Oxalate of lime deposited. 0.04 equiv.
1 „	12 „	3.5 „	0.12 „
1 „	12 „	5.25 „	0.27 „
1 „	12 „	7. „	0.36 „
1 „	12 „	8.75 „	0.51 „
1 „	12 „	10.5 „	0.74 „
1 „	12 „	12.25 „	0.90 „
1 „	12 „	14. „	0.93 „
1 „	12 „	17.5 „	0.95 „
1 „	12 „	21. „	0.95 „

The examination of these new substances, and of those reactions which appeared to be exceptional, tends therefore only to confirm the former conclusions. I propose to investigate, as they arise, any further objections founded on experiment.