

XLI.—*Additional Notes on Reciprocal Decomposition among Salts in Solution.*

By J. H. GLADSTONE, Ph.D., F.R.S.

SINCE the publication of my paper on "Circumstances modifying the action of Chemical Affinity,"* and of "Some experiments illustrative of the reciprocal Decomposition of Salts,"† I have from time to time thought and experimented further upon the subject. The present communication is simply a gathering together of such observations as appear to me capable of throwing additional light on these laws of combination.

I reserve to some future occasion the experiments I have made on the time required to bring about a perfect state of equilibrium among various salts in solution, as the results are not yet sufficiently matured for publication, and the subject is a very distinct one.

The ultimate disposition of the various elements in solution is independent of the manner in which they were originally combined.

Suppose there be two basic elements M and M', and two salt-radicles R and R'; the question is, whether if MR' be added to

* Phil. Trans., 1855, 179.

† Chem. Soc., Qu. J. ix, 144.

M'R in solution, the same distribution of elements will take place as if MR were added to M'R'. From the law of reciprocal decomposition it follows, as something like a corollary, that it must be so, and in my first paper I was content with one quantitative experiment; yet, as the opposite has been contended for, I thought it well to test the law in other instances.

The former experiment was this:—Two solutions were prepared, the one containing equivalent proportions of sulphocyanide of potassium, sulphate of potassium, and ferric nitrate; the other, equivalent proportions of sulphocyanide of potassium, nitrate of potassium, and ferric sulphate. These two mixtures, each containing the same absolute quantity of salts, were made up to the same volume with water; and the resulting colour was found to be identical, leading to the inference that the ultimate distribution of the four salts in each solution was the same.

The law was tested with a mixture of single equivalents of acetate of copper and nitrate of lead, and a mixture of single equivalents of acetate of lead and nitrate of copper. The colour was identical. A similar result was also obtained with sulphate of copper and nitrate of potassium, as compared with nitrate of copper and sulphate of potassium.

But it would rarely happen that a result perceptible to the eye could be obtained in this manner. The majority of metals that give colour to their compounds produce (unlike iron and copper) the same or nearly the same tint with whatever radicle they may be combined; and the same holds good with the colour-producing acids; whilst the great multitude of salts are colourless, and therefore invisible in solution. It occurred to me, however, that perceptible reactions might be obtained with these also, if mixtures were made of two colourless salts and then added to some coloured salt, such as ferric sulphocyanide, which is capable of reduction in colour by a redistribution of its components. The amount of alteration in this third salt would, of course, depend on the proportion of all the four salts ready to act upon it; indeed, the question would just be enlarged so as to include six elements instead of four—M, M', and M'' with R, R', and R''.

The experiment was tried in this manner:—Equivalent quantities of the sulphate and nitrate of potassium, and the sulphate and nitrate of magnesium, were dissolved in equal volumes of water; a mixture was made of equal quantities of the solutions of sulphate of potassium and nitrate of magnesium, and another mixture of equal

quantities of the solutions of sulphate of magnesium and nitrate of potassium: these were added to two equal portions of a solution of sulphocyanide of iron in the isoscope; and the diminution of the colour effected by them was observed. Now, the sulphate of potassium is known to have a much greater power of reducing the sulphocyanide than the nitrate has, but it was found that the two mixtures produced exactly the same tint.

In like manner, acetate of potassium with nitrate of lead produced the same diminution of colour (within the limits of probable errors of experiment) as acetate of lead and nitrate of potassium. The same two mixtures were tried also on ferric meconate, and gave a similar result:

The same experiment on the red sulphocyanide was also made with mixtures respectively of sulphate of copper with nitrate of magnesium, and sulphate of magnesium with nitrate of copper. The same shade was produced by each.

A similar result was obtained with chloride of sodium mixed with sulphate of magnesium, and sulphate of sodium mixed with chloride of magnesium. These two mixtures were also tried on the deep scarlet bromide of gold, and they were found to produce an equal reduction of the colour. The two had the same effect likewise on a solution of the double iodide of platinum and potassium.

Two solutions were prepared, the one of the double sulphate of copper and potassium, the other of an equivalent of sulphate of potassium mixed with an equivalent of sulphate of copper. They produced the same effect on a solution of ferric sulphocyanide. This experiment is of importance, not because there was much doubt, *à priori*, that the condition of a double salt in solution is the same whether it has ever been crystallized or not, but because at first sight some experiments recorded by Professor Graham seem to point to the opposite conclusion. He found, in respect to the salt above mentioned, and the sulphate of magnesium and potassium, that the double salt was more diffusible than its mixed constituents.* Yet this seems to be the case only when the solutions are freshly prepared and in the cold, and the discrepancy probably arises solely from the slowness of the action by which uniformity is ultimately produced.

When there are several salts with the possibility of solid matter forming, the ultimate result may indeed be influenced by the order

* Phil. Trans., 1850, 22.

in which they are mixed. Thus, in the experiment above narrated, with chloride of sodium and sulphate of magnesium compared with chloride of magnesium and sulphate of sodium, it was only when the salts were mixed together beforehand that they equally reduced the iodide of platinum and potassium. When they were added one after the other to the red salt, a deposit of platinum separated in the one case, though not in the other. This, however, is not a real exception to the general rule, which only refers to salts actually in solution.

Extension of M. Margueritte's experiment.

M. Margueritte has shown,* by a number of instances, that if a salt MR is less soluble in water than another salt M'R', or than MR' or M'R, the addition of M'R' causes a larger quantity of it to be dissolved. One instance is that of chlorate of potassium, which is more soluble in a solution of chloride of sodium than in pure water. Now, from the law of reciprocal decomposition (of which this is a result), it was foreseen that after a single equivalent of the more soluble salt M'R' had exerted its influence, a second equivalent would produce an additional effect, though to a smaller extent, and so on. On trying the experiment, this was found to be the case. 129 grm. of chlorate of potassium and 59 grm. of chloride of sodium were taken as equivalent proportions.

Chlorate of Potassium.	Chloride of Sodium.	Water required for solution.	Decrease for each equiv. of Chlor. Sodium.
1 equiv.	0	2493 meas.	0
1 „	1 equiv.	2208 „	285 meas.
1 „	2 „	2060 „	148 „
1 „	4 „	1910 „	75 „

If a compound MR is rendered more soluble by the presence of another compound M'R', the addition of either MR' or M'R will precipitate it from its saturated solution.

This is also a necessary consequence of the law of reciprocal decomposition: for the MR' or M'R will produce more MR, and the liquid is incapable of holding any more of this compound in solution. In a former paper, I examined one particular case

* Comptes rendus, xxxviii, 304.

of this general law, namely, when a salt insoluble in water dissolves in an aqueous solution of an acid; and the law was found to hold good in every instance except one. That apparent exception was in the case of ferric phosphate dissolved in hydrochloric acid, from which a precipitate was not obtained by the addition of phosphoric acid; but I have since found that phosphate of iron, freshly prepared by double decomposition, and well washed, dissolves in phosphoric acid, and thus the anomaly is fully explained. I have lately observed another apparent exception in the case of phosphate of calcium dissolved in hydrochloric acid, and this admits of another explanation, for the tribasic phosphate dissolves in three equivalents of the acid; therefore, if on the addition of phosphoric acid, any chloride of calcium be decomposed, the hydrochloric acid set free will suffice to dissolve the phosphate of calcium produced.

But in all these cases the compound MR was a salt scarcely soluble in water, and the more powerful solvent was an acid. Neither of these conditions is indispensable for the result. The following experiments will illustrate the general law in cases where 1st, the compound MR is soluble in water, though not so soluble as $M'R'$, $M'R$, or MR ; 2nd, where $M'R'$ is a neutral salt as well as MR .

1st—Sulphate of silver was dissolved in weak nitric acid; to a part of the solution nitrate of silver, and to another part sulphuric acid was added, with the production in each case of the crystalline sulphate.

Again, it was found that chloride of sodium had deposited from a solution of sulphate of sodium in hydrochloric acid; the liquid, which of course was saturated with the salt, and contained likewise free hydrochloric and sulphuric acids, and no doubt sulphate of sodium, was divided into two portions, and from each a crystallization of chloride of sodium was obtained by the addition, respectively, of sulphate of sodium and hydrochloric acid.

2nd—Where the solvent is a neutral salt. Chloride of lead was found to dissolve freely in acetate of sodium. Such a solution, saturated with the chloride, was prepared: it was divided into two parts; to the one neutral acetate of lead, and to the other chloride of sodium, was added, and in each case after awhile chloride of lead separated.

It appears, therefore, that the more general expression of the law deduced from theory, and given at the head of this section, is

confirmed by experiment. Yet it is not to be expected that in every case the precipitate will actually make its appearance; for the formation of a double salt or the special solvent powers of the compound added may be a disturbing influence, and may give rise to anomalous exceptions.

Action of Acid Solvents, and Reciprocal Decomposition in Alcohol instead of Water.

When ferric phosphate was dissolved in hydrochloric acid, the paleness of the solution, and the increase of colour on the addition of more acid, both rendered it evident to the eye that the whole of the iron was not in the state of chloride. Indeed, a comparison of the colour gave ground for the belief that in a saturated solution, at least as much as 85 per cent. of the iron is actually held dissolved as phosphate in the acid present.* It became interesting to see whether this solvent action would take place in the absence of water; and if so, whether the same proportion between the different salts would be maintained. For this purpose, a solution of hydrochloric acid in absolute alcohol was prepared, and its power of dissolving dry ferric phosphate was tried. It dissolved a great deal, assuming a pale yellowish-green colour. Thus, one question was answered; but there still remained the inquiry whether the proportions of the several salts in solution were the same as when the experiment was made in water. This received a reply in the negative, showing that the nature of the liquid influenced the reciprocal action for a comparison of the solution with one of ferric chloride in absolute alcohol showed that a very large quantity—probably 95 per cent.—of the iron must have been present as phosphate. Again, the alcoholic solution became much darker when diluted with water, which is not the case with the ferric chloride itself dissolved in alcohol. Another experiment made with this solution of the phosphate was the following:—a portion was divided into two equal parts; to the one was added some of the hydrochloric acid dissolved in alcohol, to the other the same bulk of pure alcohol. At first the two appeared of the same colour, but after awhile that containing the large excess of hydrochloric acid became decidedly deeper.†

* See Chem. Soc., Qu. J., ix, 152.

† Some of the experiments described in this and the preceding section were brought forward at the meeting of the British Association at Leeds, in 1858, but the subject has been more fully worked out since.

Testimony from Diffusion Experiments.

I have already published* an account of an experiment showing that, from a mixture of equivalent proportions of chloride of sodium and nitrate of barium there diffused the four substances in such relative proportions as could only be explained on the assumption that each of the two acids had distributed itself between the two bases.† Professor Graham, in his recent paper "On Liquid Diffusion applied to Analysis," has described two experiments of a similar character; the one made with a mixture of chloride of potassium and sulphate of sodium, the other with equivalent proportions of chloride of sodium and sulphate of potassium; but the results are not so conclusive in favour of the law of reciprocal decomposition, for the numbers do not differ widely from such as might be given if all the chlorine were in combination with the potassium, and all the sulphuric acid with the sodium. Yet the accordance is not perfect, and the distribution of the four elements may be very different. One thing is conclusively shown by the perfect accordance of the two experiments, namely, that, in the words of Graham, "The acids and bases are indifferently combined, or that a mixture of chloride of potassium and sulphate of sodium is the same thing as a mixture of sulphate of potassium and chloride of sodium, when the mixtures are in a state of solution."‡

A Method of Quantitative Determination by means of Circular Polarization.

An argument in support of the law of reciprocal decomposition has already been drawn from an experiment made by Bouchardat,§ while examining the circular polarization of camphoric acid. He found that certain camphorates rotate the plane of polarization less than the acid itself, and that when one of these salts was supersaturated with hydrochloric acid, the solution did not exhibit so much polarizing power as it would have done had the whole camphoric acid been set free. Unfortunately, the experiment was not made with equivalent proportions of the different substances, and hence it has no quantitative value.

* British Association Report, 1860, and Chem. News, Aug. 11th, 1860.

† The relative proportions in the diffusate expressed in equivalents were—sodium 1,253, chlorine 1,175, barium 812, nitric acid 892.

‡ Phil. Trans., 1861, 197.

§ Comptes rendus, xxviii, 319.

It occurred to me, however, that interesting numerical results might easily be obtained by taking advantage of the fact that different compounds of the same body rotate the plane of polarization differently; and just to test the possibility of this, I have made some determinations with two substances belonging to very different groups—nicotine and tartaric acid.

Nicotine gives a strong left-hand rotation, but when combined with hydrochloric acid it entirely loses this power.* A solution of known strength gave a rotation of -14° : it was mixed with an equivalent proportion of chloride of ammonium; the two odours of nicotine and ammonia were perceptible in the mixture, and when it was examined with the polariscope it indicated only -10.5 .

Hence it may be concluded, that sufficient nicotine to produce the wanting -3.5° of rotation had entered into combination with hydrochloric acid displacing of course an equivalent amount of ammonia. These numbers happen to have the common divisor 3.5 . The four substances must therefore have been present together in solution in very nearly, if not exactly, the following proportions:



The experiment was repeated with chloride of sodium in place of chloride of ammonium. A rotation of -28° was reduced to that of -25° indicating the following composition for the mixture:



As the nicotine has decomposed less chloride of sodium than chloride of ammonium, and its absolute tendency to unite with the hydrochloric acid must have been the same in both experiments, it follows that the soda must have a greater tendency to combine with the hydrochloric acid than the ammonia has, as compared with their tendency to remain in combination with water alone. In combination with hydrochloric acid 3 equivalents of ammonia, in fact, balance themselves against the nicotine, and as many as 8.3 equivalents of soda are required to do the same.

It is evident that the above experiment might be repeated with innumerable other salts, and tables of respective affinity might thus be drawn up. The method is also available for experimenting on the influence of the quantity of any of the constituents.

Tartaric acid gave results which are not so easily understood. It has already been observed that equivalent proportions of the isomorphous tartrates of potassium and ammonium have an equal

* Indeed, when the acid was in great excess, Wilhelmy's observation of a slight indication of right-handed polarization seemed to be confirmed.

influence on the polarized ray, and the same appears to be true of the sodium-salt. The amount of rotation is increased by the alkali, and apparently independently of whether it exists in the state of the neutral or acid-salt: thus:—

Tartaric acid	= +10°
„	+ 1 equivalent of sodium (bitart.)				= +20·5
„	+ 2 equivalents	„		(neut. tart.)	= +31°

Tartaric acid was mixed with an amount of citrate of sodium, sufficient to form the bi-tartrate of sodium, if it should decompose it entirely. The polariscope showed that a partial decomposition had ensued. Additional portions of the citrate were added, and an additional production of the tartrate resulted in each case. The numbers were—

Tartaric acid	= +10°
„	+ $\frac{1}{2}$ citrate of sodium	..		= +14·4
„	+ 1	„	..	= +18·5
„	+ 2	„	..	= +23°

This result is in strict accordance with what was theoretically expected: the sodium has distributed itself between the two acids in certain proportions; namely, 8·5 to the tartaric, and 12·5 to the citrate, when equivalent proportions were employed; and when more citrate of sodium was added, more tartrate was produced.

Now, citric and tartaric are analogous acids, and perhaps the above is the true explanation of the phenomena observed; but when other salts of sodium were employed, results were obtained which showed some effect on the polarized ray that is not to be accounted for by such simple decompositions. Thus, with acetate of sodium—

Tartaric acid	= +10°
„	+ 1 equivalent of acetate of soda				= +22°
„	+ 2	„	„		= +28°
„	+ 3	„	„		= +31°

When two or three equivalents of the acetate were employed, the results obtained are intelligible enough, but why should a single equivalent of acetate of sodium produce a greater increase of rotation than a proportionate amount of hydrate of soda would have done?

But there are greater anomalies still. When nitrate sulphate,

or chloride of sodium, or chloride of ammonium is added to tartaric acid it actually reduces the rotating power. Thus:—

Tartaric acid	= + 10°
„	+	1 equiv.	nitrate of sodium	..	= + 7°	
„	+	2 equiv.	„	„	..	= + 5°
„	+	2 equiv.	sulphate of sodium	..	= + 8°·5	
„	+	2 equiv.	chloride of sodium	..	= + 3°·5	
„	+	2 equiv.	chloride of ammonium		= + 4°	

With sulphate of ammonia, a very slight increase of rotation was obtained.*

The cause of these phenomena has not yet been ascertained. It evidently will interfere with the use of tartaric acid for the purpose intended; but, doubtless other substances besides nicotine might be found to give trustworthy indications.
