VI.—*On the Chemical Action of Water on Soluble Salts.*

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In pursuing my researches on chemical affinity among substances in solution, it seemed desirable to ascertain, if possible, what specific chemical action water exerted on a salt. Unfortunately my experiments in this direction have not led to any such conclusive result as I had hoped; yet, during the course of the inquiry, many observations were made which I believe to be new, and some of which I think are not unworthy the notice of chemists.

In order to bring these observations clearly before the minds of others, it may be well to associate them with the leading trains of thought that presented themselves to my own mind during the investigation; and, as in a difficult discussion it is very necessary to examine the simpler before attempting the more complex phenomena, it will be wise to confine the attention first to simple salts, and indeed to begin by trying to ascertain what is the action of water on such a salt *before* it dissolves it.

Anhydrous salts will frequently absorb water, and still remain solid bodies, either amorphous or crystallized. In such a case, the water combined in the solid form is always in atomic relation with the salt itself. The language of chemists implies the general belief

that a certain number of equivalents of water are then simply added to the original salt; yet great heat is often evolved, and a change of colour frequently ensues.*   I know of no reason to think that the water in such a case has been decomposed by the salt (whose composition may be expressed by the general formula MR), and that the resulting solid contains any such compound as MO,HR, though should any one choose to advance such a view he would not be wholly without arguments to support it.

These "hydrated" salts are usually, but not always, soluble in water. When solution does take place, those difficulties, as to their rational composition, of which we have already seen the commencement, increase; for there is now scope for more varied chemical actions, and consequently for a wider range of speculation.   The water may act merely as a solvent; or it may unite without decomposition with the dissolved salt, becoming an integral part of it; or it may exert an action similar to what usually takes place when two binary compounds are united under such circumstances that all the resulting bodies are free to act and react, namely, that reciprocal decomposition ensues, each electro-positive element combining with each electro-negative one in certain proportions; or the ultimate result may be due to two or more of these modes of action in conjunction.

Usually when a "hydrated" salt is dissolved in a minimum of water, nothing is observable beyond a change in its state of aggregation, and the new physical properties, and the absorption of heat resulting from that. No change of colour, as far as I can find, ever ensues. A change in fluorescence may occur.†   There is no atomic relation between the quantity of salt dissolved, and the quantity of water, indeed the ratio varies with the degree of temperature.   Here we *seem* to have the simplest case of solution, such as we necessarily conceive when a salt dissolves in ether, or a fat in an essential oil.

When an anhydrous salt, which will not combine with water to produce a solid compound, dissolves in that liquid, the same phenomena usually present themselves, except that a change in colour

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* For a case in point, and some remarks on it, see my paper "On the Colour of Chloride of Copper in Different States of Hydration."   Quart. Journ. Chem. Soc., viii, 211.
† As in the case of crystallized salts of uranium, which are much more fluorescent than their saturated solutions. See the paper of Prof. Stokes, Phil. Trans., 1852, 517.   This observation, as every other quoted or reasoned on in this communication, has been verified by myself.

may occur; as in the case of red prussiate of potash, which gives a green saturated solution.

Sometimes, however, an evident decomposition ensues, the hydrogen and oxygen of the water combining each with one of the elements of the other binary compound, and the products of this action remaining uncombined.   This is common among the compounds of the non-metallic bodies—as, for instance, the chlorides of phosphorus,—and is not unknown among what are more properly called salts, for instance chloride or nitrate of bismuth, or sulphate phosphate or citrate of ammonia.   In such cases the decomposition makes itself manifest by the separation of the one resulting substance from the other.   The bismuth salt treated with water forms an insoluble subsalt; the compound of ammonia with a polybasic acid gives off some of the volatile alkali when its solution is heated, while the liquid itself becomes acid.   It is certain, however, that in the vast majority of cases of solutions of salts, no such interchange takes place, with the production of a new oxygen and a new hydrogen compound uncombined; if chloride of copper be dissolved, no oxide of copper, or subsalt, is precipitated, and no hydrochloric acid can be boiled off.   Yet it has been contended that a haloid salt in dissolving ceases to be of the constitution MR, and becomes MO, HR; only that the two new products, instead of separating, form one compound body.   When this theory was started, there was supposed to be a wide difference in the essential constitution of haloid and other salts; our views have now changed, and there seems to me now no logical grounds on which, if we consider a haloid salt in solution to be MO,HR, we can stop short and refuse to consider this as the general expression of any salt in solution.

I was unacquainted with any argument of weight in support of this hypothesis; yet, on the other hand, it had never been actually disproved. Analogy, too, led me to view it with some favour, for it seemed reasonable to suppose that water might act like hydrochloric acid, or a similar hydrogen compound, and that possibly an aqueous solution of a salt might resemble a solution of ferric phosphate in hydrochloric acid, which contains portions of both the original salt and the hydracid, mixed with ferric chloride and phosphoric acid.*   The action of HO on MR would by analogy

* See my paper, in the Quart. Journ. Chem. Soc., ix, 152.   Of course water was present in the reaction alluded to there, but I have repeated it in absolute alcohol with a similar result.

result in a reciprocal decomposition, MO and HR being formed—either separate or in combination—while portions of the original HO and MR coexisted in the same solution.

But how was this to be decided? By all analogy it might be anticipated that by increasing the amount of HO more MR would be decomposed, just as the addition of more hydrochloric acid to a solution of ferric phosphate in that acid, produces more ferric chloride and heightens the colour. The action of water when added to a saturated solution of a salt becomes therefore a matter of peculiar interest.

That such an addition of water produces a decomposition is sometimes evident from the separation of a precipitate—and that in several different ways. Thus:—

Pentachloride of antimony, as is well known, though soluble in a small amount of water, is decomposed by a larger quantity, giving rise to hydrochloric acid, and an oxychloride of the composition $SbClO_2$, according to Peligot.

A strong solution of ferric sulphate, if diluted with water, deposits a subsalt, $3Fe_2O_3,SO_3 + 7HO$.*

The intensely blue solution of crystallized ammoniacal nitrate or sulphate of copper in a little water is perfectly clear, but on dilution it becomes turbid from the separation of a subsalt, the quadrobasic sulphate, while free ammonia is perceived in the solution.

Nitrate of bismuth, if slightly acid, dissolves in a little water, but forms a white precipitate, of varying composition, when this is poured into a larger quantity.

In all these cases, the amount of precipitate increases, within certain limits, with the amount of water added. The full action of the water also does not take place instantly. Yet it must be borne in mind that not one of these salts is of simple constitution after the type MR, and that the products of decomposition are never MO, but some new salt of complicated composition. There is this difference too between these cases and all those instances of reciprocal decomposition which are recorded in my paper "On the circumstances modifying the action of Chemical Affinity," that here a large amount of water, many equivalents in fact, is required before any trace of the insoluble compound is formed.

* According to Scheerer, this is $2(3Fe_2O_3SO_3) + 9HO$. but the specimens analyzed by me contained more water.

That the addition of water to a saturated aqueous solution of a salt produces some chemical change is sometimes apparent from a change in colour.   This phenomenon was closely examined.

It might be anticipated, *a priori*, that a certain amount of salt would have the same absorbent effect on a given number of rays of light, whether it were dissolved in much or in little water, and that, as the absorbent power of water is practically *nil*, it would appear to the eye of precisely the same depth and character of colour in the two cases.   And this actually happens in the majority of instances ; but, to perform the experiment, it was, of course, necessary to make the same quantity of light impinge upon the solution before and after dilution, and this required a special con- trivance.   Colourless cylindrical glasses of uniform diameter and of the same size were procured, and they were each closed at one end with a flat plate of glass.   These were placed side by side in a wooden frame (something like that of an ordinary stereoscope), which was painted black within, and so made that it prevented any light from passing into the cylindrical glasses except by the two ends.   This frame was supported in such a manner that the glasses were vertical, with a space of a foot or thereabouts intervening between them and a sheet of white card-board placed beneath. The glasses so situated were of course capable of holding solutions, and it is evident that the light transmitted through them to the eye of an observer standing above must come through the flat ends of the cylinders, which were of uniform size, and equally illumina- ted from the white sheet below.   It is evident, too, that any altera- tion in the bulk of the liquid will not affect the quantity of light that enters by the end of the cylinder ; and that the fact of all experiments being comparative will eliminate all errors that might have arisen from the difference of light at different hours, or any similar cause.   As this little apparatus will be frequently referred to, I will give it a name, and since its principal use is in judging by the eye of the quantity of colour in two solutions, it may be appropriately designated the *Isoscope*.

For the purpose of determining whether the addition of water to a saturated solution of a salt causes it to absorb more or less light, the solution to be examined was divided equally between the two cylindrical glasses, so that when they were looked through from above they appeared identical in colour ; water was then added to one of them, and if any change was effected by it, it became at once visible by comparison with the other.   It was found neces-

sary to avoid focusing the eye at any particular part of a solution, when diluted so as to be very deep, but a little practice will soon enable the observer to avoid this, especially when the solutions are looked at from some considerable distance (five or six feet) above them.   It is desirable also to place the head in such a position that the line joining the two eyes shall be at right angles to the line joining the two glasses, for if each eye be immediately over one of the glasses, a slight fallacy results, apparently from the unequal strength of the two eyes.   The accuracy with which slight differences in intensity of colour may be observed, varies with the nature of the colour, the degree of illumination, and doubtless the sensitiveness of the observer's eye.   In my case I can generally detect, under ordinary circumstances, a variation of 1 in 50.   Differences in the *character* of the colour are, of course, easily recognized.

In this manner, the saturated solutions of many simple salts were examined, and where the saturated solution was too intensely coloured to be practically available, a slightly diluted solution was placed in each glass, and with one of them additional water was mixed.   The following salts appeared to be unaffected by water, as to their power of absorbing the rays of light:—

Ferrous sulphate.	Terchloride of gold.
Ferric nitrate.	Terbromide of gold.
Ferric meconate.	Protochloride of platinum (in
Ferric comenate.	hydrochloric acid).
Ferric comenamate.	Bichloride of platinum.
Ferric gallate.	Bichloride of palladium.
Nitrate of nickel.	Chromate of potash.
Nitrate of cobalt.	Ferrocyanide of potassium.
Sulphate of copper.	Ferridcyanide of potassium.
Chloride of chromium.	Nitroprusside of sodium.
Acetate of chromium.	Sulphindigotic acid.
Chromate of chromium.	Sulphindigotate of ammonia.
Nitrate of uranium.	Carbazotate of copper.
Chloride of uranium.	Pentasulphide of potassium.
Sulphate of ceric oxide.	

Some dissolved salts were found to vary in the intensity of their colour, but not in the character of it, on dilution, thus:—

Ferric acetate became considerably darker.
Ferric tartrate became slightly paler.
Chromic sulphate (green modification) became paler.

Many dissolved salts were found to vary in the character of their colour, according to the state of dilution, thus :—

Ferric chloride becomes more yellow, that is to say, passes from a red orange to an orange yellow.

Ferric citrate becomes paler and more yellow.

Ferric sulphocyanide changes from an intense and pure red to orange, and on further dilution to yellow ; but when this colour makes its appearance a decomposition manifests itself by the formation of a yellow precipitate.*

Chloride of nickel passes from a yellow to a blue green.

Iodide of nickel suffers a similar change, though when strong it does not transmit so much light as the chloride does.

Chloride of cobalt becomes paler and of a more decided pink.

Iodide of cobalt passes from a deep green to pink.

Acetate of cobalt becomes slightly paler, and assumes somewhat of a yellower tint.

Sulphocyanide of cobalt passes from a magnificent purple blue through every shade of purple till it becomes of the ordinary red or pink colour of cobalt salts in solution.

Chloride of copper passes from green to blue.

Bromide of copper suffers a similar change.

Acetate of copper becomes much paler, and passes from a greenish to a more pure blue.

Permanganate of potash becomes paler and of a redder purple.

Chromic acid passes from red to an orange brown, then to a purer orange, which becomes paler on further dilution.

That these changes of colour are due to the action of the water, and not to any merely physical cause, is proved by the fact that dilution with alcohol does not occasion them. Chloride of copper, for instance, dissolves in absolute alcohol of a bright green colour, and chloride or sulphocyanide of cobalt of a magnificent bluish purple, but when examined by the isoscope, these solutions are found to be unaffected by the additions of more absolute alcohol, either in respect to the intensity or the character of their colour. If water be added to the alcoholic solution, the change of colour ensues more or less perfectly according to the relative amount of the two liquids ; and if alcohol be added to a somewhat dilute

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* This decomposition has been investigated by Dr. Claus; see Annal. Chem. u. Pharm. July, 1856. He seems to be unaware that the sulphocyanide may be diluted till it appears of a yellowish orange, without any precipitate forming, even after many days.

aqueous solution of these salts, the primary colour is more or less restored. Ferric sulphocyanide, however, seems to form an exception. A very large quantity of absolute alcohol produces the same change in the colour of this substance that a much smaller quantity of water does, and on long standing, a little yellow substance separates. I do not believe that this depends on any water in the alcohol itself; for that employed by me was of specific gravity 790, and it is hard to conceive that any trace of water should leave the strongest alcohol to act upon a salt, and effect a change which usually requires its presence in overpowering quantity.

A glance at the list of salts which change colour on the addition of water will suffice to show that they consist of little else than acetates, and a peculiar group of "haloid" salts, namely, compounds of chlorine, bromine, iodine, and sulphocyanogen, with iron, and the allied metals, nickel, cobalt, and copper.

These changes of colour, though consistent with the idea of the water added to a saturated solution decomposing more of the original salt MR, and thus forming more MO,HR, are very far from proving that hypothesis. They may be attributed to the formation of a higher hydrate; and other hypotheses might easily be invented. It seemed, however, a matter of interest to try whether the change of colour produced by water in a solution of such a salt as acetate of copper was analogous to the change that takes place on the addition of another hydrogen compound, for instance, hydrochloric or sulphuric acid* Now, in both cases, a reduction of the colour ensues; and in the case of the acid, it takes place in a diminishing ratio, that is, each addition of acid has a smaller effect (as compared with its quantity) than the preceding. Does the action of water exhibit a similar ratio?

Experiments were performed to determine this. A portion of a saturated solution of acetate of copper was divided equally between the two vertical glasses of the isoscope. The one was kept as a standard; to the other a known amount of the same saturated solution was added, and as that of course increased the colour, water was added till it was brought down again to that of the standard. The ratio between the amount of water added and the amount of coloured salt which it could render invisible, so to speak, gave what was required. Two experiments were made with the same solution.

* Phil. Trans. 1855, pp. 222, 223.

Orig. amount of Acetate of Cop per Solution.	Amount of Acetate of Copper solution added.	Water required.		Reducing effect of each addition of Water.	
		Exp. I.	Exp. II.	Exp. I.	Exp. II.
Pts.	Pts.	Pts.	Pts.	Per cent.	Per cent.
100	8	60	..	13·3	
100	16	116	..	14·3	
100	24	180	..	12·5	
100	32	244	..	12·5	
100	40	..	330	..	12·1
100	48	352	405	14·8	10·7
100	56	..	535	..	6·1
100	64	596	615	6·5	10·
100	72	..	790	..	4·6
100	80	980	975	4·2	4·3
100	88	..	1180	..	3·9
100	96	1500	1440	3·1	3·1

Both these experiments indicate that the effect of additional quantities of water is in a decreasing ratio, at least, after the addition of four or five times its bulk of water to the saturated solution, about which point the two experiments show a certain irregularity and discrepancy. About this point, also, the change to a somewhat purer blue takes place.

On mixing water with a solution of ferric acetate, the colour is considerably deepened, but on standing awhile, the solution becomes nearly as pale as originally.

The following series of observations was obtained with ferric sulphocyanide :—

Orig. amount of Ferric Sulphocyanide Solution.	Amount of Sulphocyanide Solution added.	Water required.	Reducing effect of each addition of Water.
Pts.	Pts.	Pts.	Per 100 pts.
100	10	24	4·2
100	20	44	5·0
100	40	80	5·5
100	60	128	4·2
100	80	204	2·6
100	100	296	2·2
100	120	384	2·3
100	140	468	2·4
100	160	556	2·3
100	190	692	2·2

Within the range of these observations, which, as may be supposed, did not commence with a saturated solution, and which terminated long before the salt became yellow, there is evidently more than one change of ratio in the reducing effect of successive additions of water. The ratio at first increases, then rapidly decreases, and attains a kind of uniformity, which, however, seems to show another but very slight rise and fall.

The irregularity of these results rather militates against the idea of water acting on salts in the same way as a hydracid.

A still stronger argument against this hypothesis was found on a comparison of the rays absorbed by dilute and strong solutions of those salts that vary in the character of their colour according to the amount of water. It invariably happens that the dilute solutions, while they transmit every ray that was transmitted by a strong solution of the same salt, transmit also some that were absorbed by it. To take a particular instance, blue sulphocyanide of cobalt absorbs at once those rays of the prismatic spectrum which lie about the fixed line D; the red sulphocyanide transmits them perfectly: hence it may be concluded that after a certain dilution no more blue sulphocyanide is left, a conclusion at variance with the supposition that HO acting on CoCsy (blue salt) produces CoO,HCsy (red salt) + HO + CoCsy, the amount of the last substance diminishing as the water increases, but never entirely disappearing. The nature of the absorption indicates rather that the strong solution contains the compounds present in the dilute solution *plus* some other; and a close prismatic examination of the 'haloid' salts that change colour has furnished me with a remarkable confirmation of this view. It is founded on the fact deduced by *a priori* reasoning in my paper on the use of the prism,* and demonstrated in a more recent paper,† that " when two bodies combine, each of which exerts a different influence on the rays of the spectrum, the one constituent will absorb certain rays, and the other certain other rays, and the dissolved salt itself will transmit only those rays which are not absorbed by either, or in other words, only those which are transmitted by both." Now strong solutions of ferric chloride, chloride and bromide of copper, chloride and iodide of nickel and of cobalt, exhibit not only the absorption due to the respective metals, but another absorption which can be identified with that produced by the halogens themselves when simply dissolved in water; while, when these solutions are diluted, they cease to produce this second absorption, and give precisely the same prismatic image as any compound of the same base with a colourless acid. This is explained in detail with figures in the paper already referred to.† It is certainly a suggestive fact, and shows, I think, most clearly, that there is some difference of arrangement among the elements of the dissolved salt and the water, according to their proportional

* Quart. Journ. Chem. Soc. April, 1857.   † Phil. Mag. Dec. 1857.

amount, and the degree of temperature; but what is that diffe-rence? The peculiar absorbent power exerted by bromine shows itself in the green solution of bromide of copper, but there is certainly no free bromine present, and it will hardly avail us to suppose that such a solution contains the true CuBr, and that the change of colour on dilution arises from the formation of a compound of oxide of copper with the colourless hydrobromic acid; for there would still remain the question—why should bromine affect the light when in combination with copper, while it does not do so when combined with hydrogen, or potassium, or indeed any other metal beyond this particular group and the congeners of gold? Besides anhydrous bromide of copper, which certainly has the greatest claim to be considered CuBr, is not green but black.

DOUBLE SALTS.

The action of water on double salts is a still more complicated problem, for beside all the questions that arise in respect to simple salts, there is the additional inquiry—whether water separates the two constituents of which the double salt is composed. This latter question, however, is more capable of decision than some previously discussed.

That a double salt is not always resolved into the two simple salts which we suppose constitute it, requires no elaborate proof. The iodide of platinum and potassium dissolves easily in water, though the iodide of platinum itself is insoluble; while, on the other hand, the potassio-chloride is sparingly soluble, though each of the chlorides supposed to be contained in it dissolves readily in water.

It is very conceivable, however, that in some cases a partial decomposition may take place; indeed some of Professor Graham's experiments seem to indicate this. He states,[*] that when alum, or bisulphate of potash, is diffused, one of the constituents passes out of the cell in greater quantity than the other. Now if these double salts are partially decomposed by the water, this is precisely what might be anticipated; and there is nothing else than water present to decompose them.

Should water exert such an action, it might be expected that the action would be increased by the addition of more water.

* Phil. Trans., 1850, p. 19.

There are cases in which water, when added in above a certain amount, does decompose a double salt. Thus colourless crystals of the iodide of mercury and potassium will dissolve in a little water, but the addition of a larger quantity causes the separation of the insoluble yellow iodide of mercury; and water added to a saturated aqueous solution of sulphocyanide of silver and potassium gives a curdy precipitate of sulphocyanide of silver.* In each case the more water is added the more complete the decomposition.

As double salts in a crystallized condition sometimes differ considerably in colour or shade from the simple salt of that base to which the colour is due, it was thought that if an increasing decomposition by water took place, it would make itself visible by a change of colour or shade when a strong solution was diluted in the isoscope. It was found, however, that the solution of a double salt containing a coloured constituent, has, generally speaking, precisely the colour and shade of that constituent; thus 200 grms., or one equivalent, of crystallized sulphate of copper and ammonia, gives precisely the same chromatic appearance when dissolved in water as 125 grms., or one equivalent, of crystallized sulphate of copper. Thus it was impossible to derive any information from the fact, that a solution of that salt, or the corresponding potash salt, or potash chrome alum, or the sulphate of nickel and potash, did not change in colour when diluted. The double chloride of platinum and potassium, the double iodide of the same, the analogous gold salt, and the hydrochlorate of chloride of gold, are also unaffected in colour by the further addition of water. What is more to the point is this—that the red bichromate of potash does not pale in colour on dilution, or become more yellow, as would be the case were more of the free acid and the neutral potash salt formed; and the bicomenamate of iron, which is red, remains unchanged, although the neutral salt is purple, and the comenamic acid itself colourless.

On the other hand, instances are not wanting of double salts, the solutions of which change colour on dilution. Thus, the compounds of chloride of copper with chloride of sodium, chloride of ammonium, chloride of platinum, or hydrochloric acid, though green when dissolved in the minimum of water, become blue on dilution, just as chloride of copper itself does; but they require a larger amount of water to produce the change than is requisite in the case of the simple salt. Red potassio-chromic oxalate varies

* Described by Gössman, Ann. Pharm. Oct. 1856.

in intensity of colour by dilution, becoming sometimes paler, and at other times darker. The strong solution of white iron alum becomes redder on dilution, and Rose * has shown this to be due to the formation of a slightly soluble basic salt.

If a double salt be resolved on solution more or less into its simple salts, each of these will assuredly obey the law of reciprocal decomposition with any other salt that may be present. That this reciprocal action does take place between an ordinary and a double salt is beyond question; but that the elements of the latter have separated to produce it, is not so easily ascertained. One form of the experiment, however, occurred to me that seemed to be of a somewhat crucial character. Acetate of copper is of a much deeper blue than an equivalent amount of the sulphate, and this last, as stated above, is identical in colour with the double potash salt. If on mixing the sulphate of copper and potash with the acetate, the double salt should preserve its integrity, it is not very easy to conceive of a reciprocal decomposition, for the acetate itself is strictly monobasic, but if the double salt should separate to any extent, the free sulphate of potash will certainly suffer reciprocal decomposition with the acetate of copper, and as a portion of the copper will then be combined with sulphuric acid, a reduction of the colour will ensue. Accordingly, two equal portions of acetate of copper solution were mixed in the isoscope, the first with an equivalent of sulphate of copper, the second with an equivalent of double sulphate of copper and potash. The second mixture appeared somewhat lighter in shade than the first, and on the addition of three equivalents to each, the second became of a distinctly purer and paler blue. A similar experiment was made with the intensely scarlet bromide, and the pale yellow hydrochlorate of the chloride of gold. The addition of the latter compound reduced the colour of the bromide, though of course the mixture contained a larger amount of gold than the scarlet solution. It may be objected to this reaction that there probably exists a hydrobromate of the bromide of gold analogous to the chlorine compound; but that will not account for the reduction of colour, since the addition of hydrobromic acid to the neutral bromide does not render the solution paler.

In respect, then, to double salts it may be concluded that some are resolved by water more or less into two distinct salts, while

* Pogg. Ann. lxxxiii, 132.

others preserve their integrity in solution; but what determines
this difference does not yet appear.

In respect to the general question of the chemical action of
water on a soluble salt, I feel that no satisfactory conclusion has
yet been arrived at; the idea that a reciprocal decomposition takes
place between the two compounds has received no confirmation
from my inquiry, unless in exceptional cases.   The results rather
militate in my opinion against that supposition, and tend to con-
vince me more and more that the actual state of a dissolved salt
is beyond the expression of any of our formulæ.