

L.—*Examination of Substances by the Time Method.*Part I. *Hydrates.*

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 β -Double Salts.

IN a former paper (*Chem. Soc. J.*, 1877, **2**, 381,) an account was given of the method by which the thermal dissociation of a hydrated salt may easily be followed, and it was shown that the isomorphous salts of different metals, although alike in their statical relations, were widely different in their behaviour when undergoing decomposition. As mentioned in that paper, an examination of double salts, the deportment of whose constituents in the free state was known, would be likely to throw some light on the nature of such compounds in showing how

much the combination affected the affinity of the salts for their water of crystallisation. As I have now finished the examination of a sufficient number of double salts to draw some general conclusions, I have the honour of laying the results before the Society.

Since the above paper was published a large number of experiments have been made regarding the effect of variation of the rate of passage of the air over the salt, and also the state of comminution of the salt itself on the rate at which the moisture is evolved, and the following conclusions arrived at. First, when the air is passing in such quantity that it is in sufficient excess to keep the mixture of air and moisture above its dew point at the coolest part of the apparatus, the results are constant, that is to say, any greater flow of air does not increase the amount of moisture carried over, but any considerable decrease in the rate causes a diminution in the quantity of moisture given off. Secondly, as most of the salts examined fuse partially on heating, the effect of pulverisation was nil, and even in those which do not fuse, the difference of rate of evolution of moisture in a coarse powder as compared with a fine one is scarcely discernible. Still all the salts experimented upon were pulverised to apparently the same state of fineness.

The first double salt examined was that of magnesium and zinc, $\text{MgZn}(\text{SO}_4)_2 \cdot 14\text{H}_2\text{O}$, which, owing to the water of crystallisation remaining the same as in the uncombined salts, offers special facilities for examining the effect of combination upon the affinity of the salts for their water. In a double salt, where one salt replaces the water (or a part of it) in the other, the results would have a special and not a general bearing. As an example of how the work was done, I give the original numbers of the determination of this double salt.

Purity of Salt.—Pure sulphates were prepared by two crystallisations, and the double salt then formed by adding saturated cold solutions to each other in the proportions required, and allowing the salt to crystallise over a sulphuric acid desiccator. The crystals obtained were large, and after being dried and crushed, and then air-dried, were analysed by determining their water of crystallisation. 2·4267 grams of salt were heated to about 500°C ., and cooled and weighed, when 1·1475 gram was found to be the loss, equal to 47·39 per cent., the theoretical amount being 47·26. This being nearly pure, the drying tube was weighed, some salt placed in it, and the decomposition carried on, with the following results:—

Tube and salt....	26·1375
Tube	21·9540
	<hr/>
	4·1835

Time.			H ₂ O evolved.	Gram per minute.
—	Drying tube A	50·3720	—	—
—	„ B	48·4745	—	—
5'	„ A	50·4845	0·1125	0·0225
15	„ B	48·9505	0·4760	0·0317
20	„ A	51·3775	0·8930	0·0446
15	„ B	49·1115	0·1610	0·0107
15	„ A	51·3915	0·0140	0·0093
45	„ B	49·1180	0·0065	0·0001
<hr/> 1 h. 55 m.			<hr/> 1·6630	

Or in total time and percentage, as stated in my former paper, we have—

Temperature 100°.

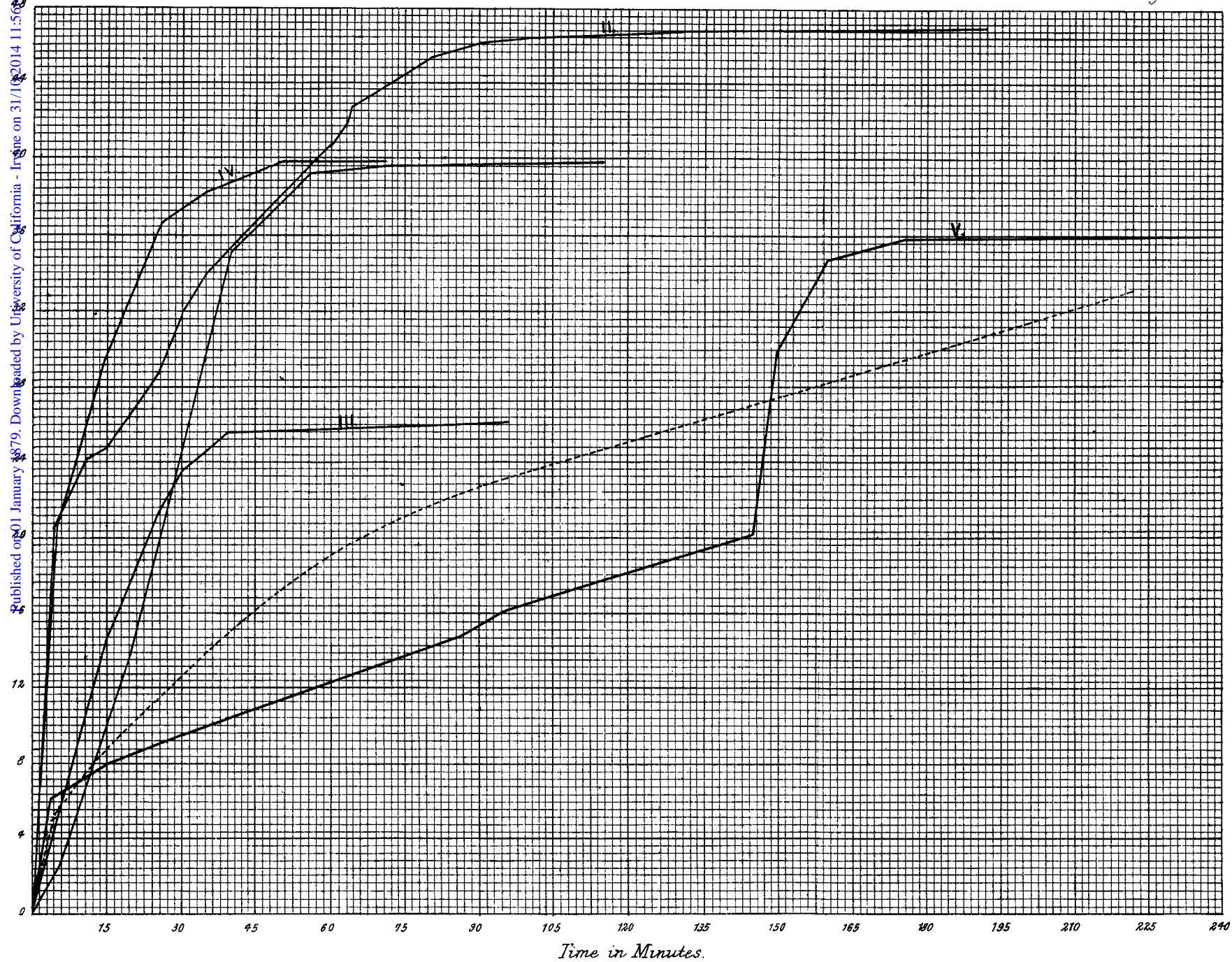
Intervals.	Time.		Loss per cent.	Per cent. per minute.
5'	5'	2·69	2·69	0·54
15	20	11·37	14·06	0·75
20	40	21·35	35·41	1·07
15	55	3·82	39·23	0·25
15	70	0·33	39·56	0·02
45	115	0·15	39·71	0·003

The tube containing the dehydrated salt was found to weigh 24·4715 grams, showing a loss of 1·6660 gram: hence 0·0030 gram had escaped unabsorbed. This being a loss of only 0·16 per cent., was considered correct enough for the object aimed at; in fact the loss was sometimes greater, and yet did not sensibly affect the curve. The course of this decomposition is shown graphically in Curve I. I have also drawn as a dotted line the theoretical course of a mixture of magnesium and zinc sulphates, calculated from the curves given in my former paper. The following table shows the difference between the rate of decomposition of a mixture of the two salts and that of a combination:—

Evolution of H₂O at 100°.

Minutes.	Mixture, MgSO ₄ ·7H ₂ O + ZnSO ₄ ·7H ₂ O.	Compound, MgZn(SO ₄) ₂ ·14H ₂ O.
5'	5·34 per cent.	2·69 per cent.
20	10·51 „	14·06 „
40	14·95 „	35·41 „
55	18·38 „	39·23 „
70	20·68 „	39·56 „
115	24·78 „	39·71, finished.
240	34·65, finished.	

Two conclusions can be arrived at by a glance at these numbers;



first, that where a *mixture* would leave the compound $\text{MgZn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ with evolution of 33.75 per cent. of moisture, the two salts when combined leave a residue $\text{MgZn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, with evolution of 40.50 per cent. of moisture, that is, the individuals of the compound hold only one-half of the moisture they can retain when free; and second, that the decomposition is finished in one-half of the time. It thus appears that those two salts in combining have expended one-half of the affinity of the anhydrous salt for its water of crystallisation, and that their combination has been effected in much the same manner as any case of pronounced chemical action. It will be seen from Curve No. I that at first the rate is a little lower than the mixture, but this is due to accidental causes; at 20 minutes the rate is once and a half as quick, while at 40 minutes the rate is more than twice. It is then at one minute reduced to double, and at 115 minutes is less than double. This alteration of the ratio of the rates is caused by the curious property of zinc sulphate in giving off its moisture at an increasing rate, and as the curve occurs in shorter time, the increase takes place at an earlier stage.

The next salt examined was the double sulphate of iron and magnesium, which, as the decomposition curves of the constituents are very similar, seemed likely to offer a good illustration of the effect of combination. The salt was prepared by the same method as the magnesium-zinc salt, and contained 48.25 per cent. of moisture, this being estimated in an atmosphere of hydrogen. The calculated percentage is 48.09. The following table gives the results of its thermal decomposition :—

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
5'	5'	20.94	4.19
5	10	23.86	0.58
5	15	24.84	0.19
5	20	26.79	0.39
5	25	29.09	0.46
5	30	31.99	0.58
5	35	34.07	0.41
10	45	36.47	0.24
5	50	37.87	0.28
5	55	39.41	0.30
5	60	40.64	0.24
<i>Carried on with P_2O_5.</i>			
5	65	42.07	0.28
15	80	45.54	0.23
10	90	46.16	0.06
10	100	46.41	0.02

Carried on with P_2O_5 .

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
15'	115'	46.60	0.01
15	130	46.78	0.01
30	160	46.89	0.003
30	190	47.01	0.003

As the total water contained in the substance was 48.25, and as the substance on being weighed after decomposition showed a loss of 47.46, we have here the case of a salt giving up all its water at 100° , while its constituents would have retained 3 mols. between them, the magnesium salt two, and the iron one, and we have another confirmation of the law that two salts in combining weaken their affinities for their water of crystallisation, as the water is evolved in one-half of the time. Curve No. II graphically depicts the decomposition.

An interesting case for examination is afforded by the double salts formed by copper sulphate, which, although in the free state a pentahydrate, takes up 2 mols. of water in combining with heptahydrates, forming double salts of the formula $M''M''(SO_4)_2 \cdot 14H_2O$. As copper sulphate had not yet been examined, its decomposition was done with the following results:—

Temperature 100° .

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
15'	15'	14.45	0.96
5	20	17.29	0.57
5	25	21.16	0.77
5	30	23.48	0.46
10	40	25.54	0.11
10	50	25.60	0.01
10	60	25.70	0.01
15	75	25.95	0.01
10	85	26.14	0.02
10	95	26.20	0.006

The decomposition of this salt was carried no further, the rate decreasing so much that it showed the well known fact of the retention of 1 mol. of water at 100° .

The curve No. III shows that when 2 mols. (14.33 per cent.) of water have been driven off, the rate decreases till 3 mols. have been given off, when the rate shows a quick and continuous decrease till the fourth mol. has been evolved. The curve points to the existence of the two hydrates, $CuSO_4 \cdot 3H_2O$ and $CuSO_4 \cdot 2H_2O$ before the greenish-white monohydrate is reached.

To show the agreement between experiments made at different times with the same salt by this apparently rough method of investi-

gation, I give two other determinations of copper sulphate taken at random from several I have done.

Intervals.	Total time.	I. Loss per cent.	Per cent. per minute.
10'	10'	10.95	1.095
10	20	17.17	0.622
10	30	23.52	0.635
10	40	25.62	0.210
10	50	25.72	0.010
10	60	25.81	0.009
25	85	26.18	0.010
10	95	26.22	0.004
II.			
15	15	14.04	0.936
10	25	21.08	0.704
25	50	25.54	0.179
20	70	25.82	0.014
25	95	25.99	0.007
10	105	26.01	0.000
5	110	26.07	0.000

This will suffice to show to what extent the process may be relied upon, and on plotting these two tables as curves they will be found to be coincident with the curve given for the former table.

The first double salt of copper sulphate examined was the compound with magnesium sulphate, $\text{CuMg}(\text{SO}_4)_2 \cdot 14\text{H}_2\text{O}$, with the following results. See also Curve IV.

Temperature 100°.

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
5'	5'	20.38	4.07
10	15	29.45	0.91
10	25	36.50	0.70
10	35	38.22	0.17
15	50	39.72	0.10
20	70	39.94	0.01

Here we see that the 2 mols. of water which the copper sulphate took up in addition to its real water came off together with 2 mols. from each of the salts in the first five minutes. Here again we see a confirmation of the fact that half the affinity of the salt for its water is lost in the combination, because each salt gives up 2 mols. instead of one in the first five minutes, besides the extra water of the copper sulphate, a loss of 6 mols. requiring 20.32 per cent. The water is also evolved in half the time or at double the rate, and the residue contains only 2 mols. of water.

The next salt examined was the compound of copper sulphate with zinc sulphate, $\text{Cu}_3\text{Zn}(\text{SO}_4)_4 \cdot 28\text{H}_2\text{O}$, in which as the zinc predominates we ought to find a curve approximating much more closely to the zinc curve than to the copper. This salt was chosen for the reason that it would show whether the force holding the zinc salt to its water was diminished by one-half or only by one-fourth, as the first would mean that the compound was a combination of 1 zinc mol. with the copper, and the two other zincs with each other, while the second would indicate that the three zincs were equally united with the copper. The following are the results. Curve V.

Temperature 100°.

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
5'	5'	6.18	1.23
5	10	7.10	0.17
5	15	7.94	0.17
10	25	8.92	0.098
30	55	11.84	0.097
30	85	14.80	0.098
10	95	16.01	0.121
20	115	17.72	0.085
30	145	20.14	0.081
5	150	29.64	1.90
10	160	34.79	0.515
15	175	35.78	0.066
30	205	35.92	0.005
30	235	35.95	0.000

By a comparison of these numbers with the curves of copper and zinc, we see that as in the magnesium-copper salt the first few molecules are given off very easily, doubtless owing to the evolution of the two molecules in excess in the copper sulphate, and that the residue contains fully five molecules of water, seeming to approximate to the body $\text{CuZn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O} + 2\text{ZnSO}_4 \cdot 2\text{H}_2\text{O}$, that is, the state of the salt when decomposing seems to be a simple double sulphate of copper and zinc associated with two molecules of zinc sulphate. The two zinc sulphate molecules seem to have been little affected by the combination, as they return nearly the same amount of moisture which they do in the free state. As was to be expected, the weak affinity with which the water of the double salts is held, the curves show few sudden changes to mark out various hydrates, but curve No. V shows the individuality of the zinc salt showing plainly in spite of its combination with copper.

It may be objected that it is not known that a mixture of two salts on being heated would give off the moisture at a rate which

is the mean of the two, and in most cases this cannot be proved, as the salts fuse on being heated, and will thus form a combination. However, neither the copper nor the magnesium salt fuses on being heated, so a mixture of these two sulphates was treated as the double salt had been, with the following result:—

Temperature 100°.

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
5'	5'	6·04	1·21
20	25	14·15	0·405
10	35	17·07	0·584
30	65	25·92	0·295
30	95	28·74	0·094
30	125	29·82	0·036
30	155	30·00	0·006
30	185	30·09	0·003

Comparing this with the table on page 461, we see that the moisture in the true double salt is given off at a rate fully twice as fast as that from the mixture, showing that by combination the affinity of the anhydrous salt for its water of crystallisation has been weakened.

Conclusion.—Two hydrated salts in forming a double salt containing the normal amount of water, expend one half of the affinity of the anhydrous salt for its water of crystallisation in combining with each other, showing that the formation of double salts is comparable with other forms of chemical action.

My thanks are due to Mr. David Stewart for his kind aid in assisting me in these experiments.
