

XXI. *Experiments on the Heat disengaged in Combinations.*By THOMAS GRAHAM, *Esq.*, *F.R.S.*, &c.

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THE observations, of which an account shall be given in the present paper, are exclusively confined to the heat disengaged in combinations formed in the humid way. The heat disengaged in such combinations is in general easily collected and measured, as it is immediately communicated to a mass of fluid, of which the temperature may be observed with accuracy. The elevation of temperature in an experiment may often, however, be greatly affected by incidental circumstances; such as the liquefaction of the product of the combination, arising from its solution in the water, or other menstruum employed; or the hydration of the compound formed, which so generally occurs with a salt formed by uniting an acid and base; and can rarely, therefore, be taken as the expression of the heat disengaged from the combination without considerable correction.

Thus in a few preliminary experiments to ascertain whether, as has been anticipated, different bases of the same class evolve equal quantities of heat on combining with the same acid, it was found that equivalents of oxides of copper and zinc, and the equivalent of magnesia on dissolving in highly diluted sulphuric acid, evolved respectively $4^{\circ}20$, $5^{\circ}18$, and $11^{\circ}70$. But the sulphates formed are all hydrated salts, and a large portion of the heat was found to be due to the combination of this water, namely $3^{\circ}49$ in the sulphate of copper, $3^{\circ}90$ in the sulphate of zinc, and $4^{\circ}12$ in the sulphate of magnesia. Again, the salts are obtained in solution; now the liquefaction or solution of salts is attended with the absorption of a certain quantity of heat or fall of temperature, namely by a fall of $0^{\circ}66$ in the hydrated sulphate of copper, $0^{\circ}93$ in the hydrated sulphate of zinc, and $0^{\circ}83$ in the hydrated sulphate of magnesia. The last quantities being added to the heat first observed in the solution of the oxides, and the preceding quantities being subtracted from the same heat first observed, we obtain as the corrected determinations of the heat evolved from the combination with sulphuric acid of the oxides enumerated (or rather from the substitution of these metallic oxides for the basic water of the sulphate of water), by oxide of copper $1^{\circ}37$, by oxide of zinc $2^{\circ}21$, by magnesia $8^{\circ}41$; quantities which, so far from being equal, are nearly in the ratio of the numbers 2, 3, and 12. It is obvious, therefore, that experiments to determine both the heat absorbed in the solution of salts, and that evolved in their

hydration, must precede inquiries respecting the heat disengaged in the formation of the salts themselves by the combination of their essential constituents, when the salts are formed in the humid way.

The apparatus employed consisted of a delicate thermometer of small bulb, namely, that used in the wet-bulb hygrometer, as prepared by Greiner of Berlin. Every degree was divided into five parts, each part again was divisible by the eye into five parts, so that observations were made to $\frac{1}{25}$ th of a degree. The degree is that of Reaumur's scale. After trying glass jars and various other vessels, it was found that nothing answered better than a large platinum crucible, which weighed 1201.9 grains, and was capable of containing 5 ounces of water. The thermometer and crucible, with a hollow cylinder of palladium, weighing 207.6 grains, employed as a stirrer, were all the apparatus necessary. Of the salt or other substance experimented upon, a quantity corresponding with its atomic weight, and representing a single equivalent, was always used; and the quantity of water was constant, namely 1000 grains, and relatively large, so as to render the change of the specific heat of the fluid insensible.

The water, crucible, stirrer and thermometer, being the same in all the experiments, the results are strictly comparable. The numbers express the relative quantities of heat disengaged from atomic equivalents of the bodies.

I. *Hydration of Oil of Vitriol.*

1. H O, S O. The protohydrate of sulphuric acid employed was pure, and of density 1.848. The quantity used of this and other substances was always one-twentieth of the number expressing the equivalent taken in grains; that is 30.68 grains of oil of vitriol, the equivalent of the protohydrate being 613.5. It was weighed in an exceedingly thin and light glass spherule, which was afterwards broken in the water, and the acid diffused through the latter. The greater portion of the heat is disengaged in the first two or three seconds after mixture, or its evolution is almost instantaneous. To avoid the loss of heat by communication to the air, during the short time that must elapse before the thermometer in the liquid becomes stationary, the crucible, water and stirrer were previously cooled down so far below the temperature of the air, as the liquid was expected, from a preliminary experiment, to rise on the addition of the acid. The crucible was also placed within a glass jar containing tow, to impede the passage of heat by conduction. I am indebted for several valuable hints on the mode of conducting

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such experiments, to the papers of Dr. Andrews and Professor Hess, who have preceded me in similar investigations.

The rise of temperature in a preliminary experiment, in which the water and crucible were not previously cooled, was $3^{\circ}78$ R. In two other experiments in which the crucible and water were previously cooled before the addition of the acid, the rise was $3^{\circ}88$ and $3^{\circ}85$. The mean of the last results, or $3^{\circ}86$, may therefore be taken as the heat disengaged in the hydration of an equivalent of the protohydrate of sulphuric acid. No perceptible change of temperature occurred on diluting further with water the products of these experiments.

2. $\text{H O}, \text{S O}_3 + \text{H O}$. This is the crystallizable hydrate of sulphuric acid, of density 1.78. 36.3 grains, the equivalent quantity, were mixed with 1000 grains of water, as in the preceding case. The rise of temperature in three experiments was $2^{\circ}40$, $2^{\circ}36$ and $2^{\circ}40$; of which the mean is $2^{\circ}39$.

The dilution of this hydrate gives occasion to the disengagement of $1^{\circ}47$ less heat than the preceding hydrate. It appears, therefore, that in the dilution of the first hydrate or of sulphate of water, $1^{\circ}47$ is due to the combination of the first atom of water, with which it forms the crystallizable hydrate, and $2^{\circ}39$ to combination with all the rest, making together $3^{\circ}86$.

3. $\text{H O}, \text{S O}_3 + 2 \text{H O}$. This is the hydrate of sulphuric acid in the formation of which the greatest contraction is observed to occur. With 41.93 grains, or one equivalent, the rise of temperature on dilution was in three experiments conducted as before, $1^{\circ}88$, $1^{\circ}86$ and $1^{\circ}85$, of which the mean is $1^{\circ}86$. The difference between the heat evolved by the present and the immediately preceding hydrate is $0^{\circ}53$, which is therefore the heat evolved by the addition of the second atom of water to the sulphate of water. It is scarcely one-third of $1^{\circ}47$, the quantity evolved by the first atom.

4. $\text{H O}, \text{S O}_3 + 3 \text{H O}$. With 47.55 grains, or one equivalent of this hydrate, the rise by dilution was in three experiments $1^{\circ}31$, $1^{\circ}31$ and $1^{\circ}27$, of which the mean is $1^{\circ}30$. The difference between the heat evolved by this and the preceding hydrate is $0^{\circ}56$, which is therefore the heat evolved by the addition of the third atom of water to the sulphate of water. Now the second atom evolved $0^{\circ}53$, so that the second and the third atoms of water appear to evolve sensibly the same quantity of heat. This curious result favours the conclusion, that the second and third atoms of water go together; or that the hydration of the sulphate of water here advances by two atoms at a time, and that no intermediate hydrate exists, in a state of solution at least, between $\text{H O}, \text{S O}_3 + \text{H O}$

and $\text{H O, S O}_3 + 3 \text{ H O}$. The last may be represented as $\text{H O, S O}_3, \text{H O} + 2 \text{ H O}$.

5. $\text{H O, S O}_3 + 4 \text{ H O}$. With 53·18 grains, or one equivalent of this hydrate, the rise of temperature on dilution was $1^{\circ}05$, $1^{\circ}07$ and $1^{\circ}05$; mean $1^{\circ}06$. The difference between this and the preceding hydrate, namely $0^{\circ}24$, is therefore the heat evolved by the combination of the fourth atom of water with sulphate of water.

6. $\text{H O, S O}_3 + 5 \text{ H O}$. With 58·8 grains, or one equivalent of this hydrate, the rise of temperature on dilution was $0^{\circ}88$, $0^{\circ}88$ and $0^{\circ}85$; mean $0^{\circ}87$. The heat from the combination of the fifth atom of water is $0^{\circ}19$. It is not impossible that the heat evolved from the fifth is the same in quantity as that evolved from the fourth atom of water, and that these two atoms go together like the second and third. The present hydrate of sulphate of water corresponds with crystallized sulphate of copper.

7. $\text{H O, S O}_3 + 7 \text{ H O}$. With 70·05 grains, or one equivalent, the rise was $0^{\circ}68$, $0^{\circ}71$ and $0^{\circ}65$; mean $0^{\circ}68$. The difference between the effect of this and the preceding hydrate is $0^{\circ}19$, which is therefore the heat evolved by the combination of the last two atoms of water, namely the sixth and seventh atoms. This hydrate of sulphate of water corresponds with crystallized sulphate of magnesia.

By the continued hydration of the sulphate of water, the quantities of heat evolved are therefore as follows:—

	Heat evolved.	Hydrate formed.
By first atom of water	$1^{\circ}47$...	$\text{H O, S O}_3 + \text{H O}$.
By second and third atoms together	$1^{\circ}09$...	$\text{H O, S O}_3 + 3 \text{ H O}$.
By fourth and fifth atoms together	$0^{\circ}43$...	$\text{H O, S O}_3 + 5 \text{ H O}$.
By sixth and seventh atoms together	$0^{\circ}19$...	$\text{H O, S O}_3 + 7 \text{ H O}$.
By an additional excess of water	$0^{\circ}68$...	$\text{H O, S O}_3 + 7 \text{ H O} + x \text{ H O}$.

It will be observed that the heat evolved by the first atom is sensibly the same as that evolved by the four following atoms, the quantities being $1^{\circ}47$ and $1^{\circ}52$; the difference between these numbers being within the limits of errors of observation. The same conclusion is drawn from his experiments on the hydration of oil of vitriol by Professor Hess. Supposing the whole heat disengaged in the hydration of sulphate of water to be divided into 23 parts, 9 are evolved by the first atom of water, 9 by the next four atoms, 1 by the following two atoms, and 4 by the remaining excess.

Although the experiments detailed above agree with those of M. Hess in bringing out one curious result, they yet differ from them to an extent which it is difficult to account for in other respects. Thus reducing my results to the same

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scale as those of M. Hess, the comparison is as follows. In the hydration of the sulphate of water,

	Hess.	Graham.
Heat from the first atom of water . . .	2	2
... second atom of water . . .	1	0.72
... next three atoms of water	1	1.35
... additional excess of water	$\frac{1}{5}$	$\frac{1.18}{5}$
		$\frac{5.25}{5}$

8. $\text{H O, S O}_3, \text{H O} + 10 \text{H O}$. An equivalent quantity of this hydrate, or 92.55 grains, was mixed with 969.3 grains of water, the quantity of the latter being diminished so as to make up 1000 grains with the water already in the acid hydrate. The rise of temperature in two experiments was $0^{\circ}.37$ and $0^{\circ}.41$, of which the mean is $0^{\circ}.39$. This hydrate contains four atoms more of water than the last operated upon, and disengages $0^{\circ}.29$ less heat. The heat, therefore, due to the combination of the additional four atoms of water is $0^{\circ}.29$.

9. $\text{H O, S O}_3, \text{H O} + 14 \text{H O}$. Of this hydrate the equivalent, or 115.05 grains, was mixed with 915.6 grains of water, and occasioned a rise of temperature in two experiments of $0^{\circ}.23$ and $0^{\circ}.20$, of which the last was believed to be the most trustworthy result. Hence the four atoms of water last added evolve $0^{\circ}.09$, or about one-third of the quantity evolved by the preceding four atoms of water.

10. $\text{H O, S O}_3, \text{H O} + 24 \text{H O}$. The equivalent of this hydrate, or 171.3 grains, was mixed with 859.4 grains of water, and produced in one experiment a rise of $0^{\circ}.15$. The hydrate was kept for three days before it was diluted in the experiment; for immediately after its preparation the heat which this hydrate yielded on dilution was considerably less than the quantity assigned above to it; indeed not more than $0^{\circ}.06$ in one experiment.

11. $\text{H O, S O}_3, \text{H O} + 36 \text{H O}$. The equivalent quantity of this diluted acid, or 238.8 grains, was mixed within an hour of its preparation with 792 grains of water; the rise of temperature was $0^{\circ}.11$.

12. $\text{H O, S O}_3, \text{H O} + 48 \text{H O}$. The equivalent quantity, or 306.3 grains, was mixed about three hours after its preparation with 724.4 grains of water; a rise occurred of $0^{\circ}.08$. The dilution of the same hydrate twenty-four hours after its preparation was attended with a rise of $0^{\circ}.13$.

The last hydrate is oil of vitriol diluted with nine times its weight of water, yet it was still capable of evolving a sensible quantity of heat by further dilution. The term at which the mixture of acid and water ceases to disengage heat

on a further addition of water, was not observed, but the effect was insensible in a mixture formed of one part of the concentrated acid and thirty parts of water.

II. Hydration of other Magnesian Sulphates.

The heat produced in the hydration of different anhydrous sulphates, compared with oil of vitriol, appears in the following results; equivalent quantities of the anhydrous salts in the solid state being thrown into the same quantity of water, and the rise of temperature observed after the hydration and complete solution of the salts.

Protosulphate of manganese	3°22
Sulphate of copper . . .	3°73
Sulphate of water . . .	3°86
Sulphate of zinc . . .	4°17
Sulphate of magnesia . .	4°33

The most material difference in the circumstances of the experiments is, that while the oil of vitriol was liquid, the salts with which it is compared were necessarily applied in the solid form. The liquefaction of the latter during the experiment, would therefore occasion an absorption of heat of unknown amount, which does not occur in the latter.

1. *Sulphate of Magnesia*.—The same mode of experimenting was followed and apparatus used as in the preceding experiments with oil of vitriol. On dissolving the equivalent quantity, 77·35 grains (one-twentieth of 1547·02), of the crystallized salts in 960·6 grains of water, a fall occurred in three experiments of 0°·96, 0°·90 and 0°·89, of which the mean is 0°·92. In these experiments, the water contained in the crystals, which amounts to 39·4 grains, was deducted from the 1000 grains of water usually employed to dissolve the salt; but if this quantity of water is supposed to be added, the mean result would become 0°·88.

The salt was made certainly anhydrous by exposure to an incipient red heat for a considerable time, and the equivalent quantity, 37·98 grains, in the state of a fine powder, was thrown into 1000 grains of water. It did not cake, and was dissolved completely by stirring in about one minute and a half. The rise of temperature in two experiments was 4°·30 and 4°·36, of which the mean is 4°·33. To this must be added the heat lost by the liquefaction and solution of the hydrate formed.

Rise on solution of $Mg O, S O_3$	4°33
Fall from solution of $Mg O, S O_3 + 7 H O$	0°92
Whole heat disengaged by $Mg O, S O_3$.	$\overline{5^{\circ}25}$

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Mg O, S O₃, H O. It is not easy to obtain the sulphate of magnesia with exactly one atom of water. The salt first operated upon retained, after being dried by an oil-bath, at 400° to 100 sulphate of magnesia only 14·14 water, instead of 14·81, the single equivalent. The hydrate was therefore $\frac{2}{2}$ H O. The heat evolved by the solution of 43·35 grains, an equivalent quantity of this hydrate in two experiments, was 3°·06 and 3°·9, of which 3°·08 may be taken as the mean.

Another portion of the same sulphate less strongly dried, retained to 100 sulphate of magnesia 15·75 water, which is $1\frac{1}{7}$ H O. The results from the solution of 43·93 grains, the equivalent of this hydrate, were 3°·03, 2°·98 and 2°·93, of which the mean is 2°·98. The mean of the two sets of experiments, or 3°·03, probably does not differ far from the truth.

Rise on solution of Mg O, S O₃, H O . . . 3°·03

Fall on solution of Mg O, S O₃, + 7 H O . . . $\frac{0°·92}{7}$

Whole heat disengaged by Mg O, S O₃, H O $\frac{3°·95}{7}$

The anhydrous salt disengaged 5°·25, while the protohydrate disengages 3°·95; the difference, or 1°·30, is therefore the heat disengaged by the combination of the first atom of water with sulphate of magnesia. It thus appears that of the whole heat evolved in the complete hydration of sulphate of magnesia, as nearly as possible one-fourth is due to the combination of the first atom of water, one-fourth of 5°·25 being 1°·31.

2. *Sulphate of Zinc.*—The equivalent quantity of the crystallized salt, 89·59 grains, contains 39·38 water, and was therefore dissolved in 960·6 water. The fall of temperature in two experiments was 1°·01 and 0°·98, of which the mean is 1°·00. This sensibly exceeds the cold produced by the solution of crystallized sulphate of magnesia, which is 0°·92. The difference has a real foundation, and is not the consequence of errors in experiment; for in two other sets of observations on the same salts made in glass, and which may be compared with each other, although not with the preceding experiments, the results were for sulphate of magnesia 0°·85, 0°·80 and 0°·83, of which the mean is 0°·83; for sulphate of zinc 0°·97, 0°·91, 0°·92, of which the mean is 0°·93; greater cold occasioned by the solution of sulphate of zinc than of sulphate of magnesia, by the first experiments 0°·08, by the last experiments 0°·10.

Of sulphate of zinc, carefully dried and made perfectly anhydrous, the equivalent quantity, 50·22 grains, was dissolved in 1000 grains of water, with the exception of a mere trace of flaky matter. The rise in one experiment was 4°·20; in another 4°·15; mean 4°·17. The results then are,—

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Rise on solution of Zn O, S O ₃	4 ^o ·17
Fall on solution of Zn O, S O ₃ + 7 H O	1 ^o ·00
Whole heat disengaged by Zn O, S O ₃	5 ^o ·17

There is the same difficulty in obtaining the protohydrate of sulphate of zinc exactly definite, as the corresponding hydrate of sulphate of magnesia. The hydrate operated upon contained to 100 sulphate of zinc 11·99 water, instead of 11·207, which is a single equivalent. The equivalent quantity, 56·21 grains, was dissolved in 1000 grains of water, and occasioned a rise of temperature in two experiments of 2^o·34 and 2^o·33. As the rise for the anhydrous salt was 4^o·17, the deficiency from the hydrate, 4·17 - 2·34 = 1^o·83, is due to the quantity of water already combined in the salt of the experiment. But this deficiency cannot be entirely ascribed to a single atom of water, as the combined water exceeded that proportion as 11·99 to 11·21. It is difficult to find proper elements for the necessary correction, but we may probably reduce the amount of deficient heat to 1^o·71, that is, as 11·99 to 11·21, without any considerable error. Hence

Rise on solution of Zn O, S O ₃ , H O	2 ^o ·45
Fall on solution of Zn O, S O ₃ + 7 H O	1 ^o ·00
Whole heat disengaged by Zn O, S O ₃ , H O	3 ^o ·45

The difference between the heat disengaged by the protohydrate and the anhydrous salt, or the heat due to the combination of the first atom of water, namely 1^o·71, is almost exactly one-third of the whole heat disengaged in the hydration of sulphate of zinc; one-third of 5^o·17 being 1^o·72. The quantities of heat disengaged by sulphate of zinc in the two conditions specified, are therefore as 4 to 6.

3. *Sulphate of Copper.*—The equivalent quantity of the ordinary crystallized salt, containing 5 H O, namely 77·97 grains, was dissolved in 1000 grains of water, with a fall of temperature in three experiments of 0^o·67, 0^o·65 and 0^o·68, of which the mean is 0^o·67. This and other more sparingly soluble salts were pounded fine and sifted; the solution took place with stirring within one minute.

Of the anhydrous salt, 49·84 grains, the equivalent quantity, were dissolved in 1000 grains of water, with a rise in two experiments of 3^o·72 and 3^o·74. Hence the results for the anhydrous salt are,—

Rise on solution of Cu O, S O ₃	3 ^o ·73
Fall on solution of Cu O, S O ₃ + 5 H O	0 ^o ·67
Whole heat disengaged by Cu O, S O ₃	4 ^o ·40

The protohydrate was prepared by drying the crystallized

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salt by a nitre-bath; it retained to 100 sulphate of copper 11.83 water, instead of 11.29 water, the single equivalent. The equivalent quantity, 55.72 grains, was dissolved in 1000 grains of water, with a rise in two experiments of $2^{\circ}.15$ and $2^{\circ}.13$. The result is $3.73 - 2.14 = 1^{\circ}.59$ for the combined water. This hydrate contained $1\frac{1}{2}$ H O.

After being dried still further on an oil-bath at 370° , it consisted of 100 sulphate of copper and 11.44 water, or was $1\frac{1}{3}$ H O; the salt was now almost white, the green tint being barely perceptible. The equivalent quantity of the last salt, 55.54 grains, was dissolved in 1000 grains of water, but somewhat more slowly and with greater difficulty than the preceding salt. The heat evolved in two experiments was $2^{\circ}.09$ and $2^{\circ}.07$, which instead of exceeding falls short of the preceding results. The deficiency of heat in the last experiments is remarkable, and is in some measure, but I believe not fully, accounted for by the slowness of the solution. Giving a preference to the first results, and deducting $\frac{1}{2}$ nd part for the excess of water above one atom already combined with the salt, there remains $1^{\circ}.47$ for the heat due to the combination of the first atom of water. The result for the protohydrate is,—

Rise on solution of Cu O, S O₃, H O . . . $2^{\circ}.26$

Fall on solution of Cu O, S O₃ + 5 H O . . . $0^{\circ}.67$

Whole heat disengaged by Cu O, S O₃, H O $2^{\circ}.93$

One-third of $4^{\circ}.40$, the whole heat evolved in the hydration of sulphate of copper, is $1^{\circ}.466$, which is as nearly as possible the result obtained above for the first atom of water. The ratio is the same as in the sulphate of zinc, while in the hydration of the sulphate of magnesia the heat evolved by the first atom of water was one-fourth of that evolved by the whole. It may be inferred from the experiments on oil of vitriol, that it approaches more closely to the former salts than to sulphate of magnesia in this character, although a rigid comparison cannot be made, as we are unacquainted with the fully hydrated sulphate of water in a crystalline form, and cannot therefore estimate its heat of liquefaction.

4. *Protosulphate of Iron*.—Of the crystallized salt containing seven atoms of water, the equivalent quantity, 86.39 grains, dissolved in 1000 grains of water in two experiments with a fall of 1° and $1^{\circ}.04$. Allowing for the 39.38 grains of water introduced by the salt in addition to the thousand grains employed, these results become $1^{\circ}.04$ and $1^{\circ}.08$, of which the mean is $1^{\circ}.06$.

Fall on the solution of Fe O, S O₃ + 7 H O... $1^{\circ}.06$.

The protohydrate of sulphate of iron, formed by drying

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the crystallized salt in air at a temperature approaching 400° , was found to be nearly insoluble in cold water. The anhydrous sulphate was more soluble, but not sufficiently so for the determination of its thermal relations.

5. *Protosulphate of Manganese*.—The crystallized salt employed contained five atoms of water. The equivalent quantity, 75.47 grains, of the crystallized salt was dissolved in 972 grains of water at 59° Fahr., with a fall of temperature in two experiments of $0^{\circ}.11$ and $0^{\circ}.13$ R., of which the mean is $0^{\circ}.12$.

Of the same salt made anhydrous by heat, the equivalent quantity, 47.35 grains, was dissolved in 1000 grains of water at 60° Fahr., with a rise in two experiments of $3^{\circ}.20$ and $3^{\circ}.24$ R.; mean rise $3^{\circ}.22$.

Rise on solution of Mn O, S O ₃	$3^{\circ}.22$
Fall on solution of Mn O, S O ₃ + 5 H O	$0^{\circ}.12$
Whole heat disengaged by Mn O, S O ₃	<u>$3^{\circ}.34$</u>

The crystallized salt being well dried at a temperature not exceeding 400° Fahr., was found to retain a quantity of water in combination, which slightly exceeded a single equivalent, namely in the proportion of 5.82 grains to 5.62 grains, in 52.97 grains of the hydrated salt. The heat evolved in the solution of the equivalent quantity, 52.97 grains, of this protohydrate by 1000 grains of water was in two experiments $1^{\circ}.80$ and $1^{\circ}.78$, of which the mean is $1^{\circ}.79$.

Rise on solution of Mn O, S O ₃ , H O	$1^{\circ}.79$
Fall on solution of Mn O, S O ₃ + 5 H O	$0^{\circ}.12$
	<u>$1^{\circ}.91$</u>

It follows that the heat evolved by the combination of the first atom of water with sulphate of manganese is $3^{\circ}.34 - 1^{\circ}.91 = 1^{\circ}.43$. This result approaches to $1^{\circ}.47$, the heat evolved by the combination of the first atom of water with sulphate of copper. The small depression of temperature produced by the solution of crystallized protosulphate of manganese is remarkable, and distinguishes this salt from the other magnesian sulphates. This salt alone of the class forms a thick solution, when highly concentrated, and crystallizes with difficulty. It was also observed that the protohydrate of sulphate of manganese does not dissolve easily in cold water; the quantity of the protohydrate employed in the experiments narrated above requiring to be agitated with the water for two and a half minutes, before the liquid ceased to be turbid and the salt was entirely dissolved. The anhydrous sulphate of manganese was dissolved quickly and with ease.

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III. *Sulphates and Chromates of the Potash family.*

1. *Sulphate of Potash.*—Good crystals of this salt were reduced to powder and sifted. The solution of the equivalent quantity, 54·55 grains, in 1000 grains of water, which took place in thirty seconds, was attended by a fall of temperature in two experiments of 1°·50 and 1°·52, of which the mean is 1°·51.

Fall on solution of K O, S O_3 . . . 1°·51.

The same quantity of sulphate of potash was dissolved in a mixture of 300 water-grain measures of dilute sulphuric acid of density 1·1 mixed with 700 grains of water. The dry acid in the mixture amounted to 36 grains; a single equivalent is represented by 25 grains. The solution was quite as rapid, or more so, than in pure water; the fall of temperature 2°·04; the difference of 0°·53 is probably connected with the formation of bisulphate of potash.

2. *Chromate of Potash.*—The solution of the equivalent quantity, 62·09 grains, of this salt in 1000 grains of water, was attended with a fall of 1°·18 in water.

Fall on solution of K O, Cr O_3 . . . 1°·18

When dissolved in an equal quantity of the same dilute sulphuric acid as was used with sulphate of potash, the solution became red from the formation of bichromate, and only a very slight change of temperature occurred, namely a fall of 0°·08.

3. *Bichromate of Potash.*—The fused salt was used, as it is easily reduced to a fine powder, and half the equivalent quantity used, as the whole equivalent is not dissolved by 1000 grains of water at 57° Fahr., the temperature of the experiments. The solution of 47·34 grains, half the equivalent quantity, was attended with the same fall of 1°·98 in two experiments. No sensible change of temperature occurred on diluting this solution. In the dilute sulphuric acid used with the two preceding salts, the fall on the solution of half an equivalent of bichromate of potash was 2°·00, or sensibly the same as in pure water. The fall of temperature for a whole equivalent of bichromate of potash will therefore be 3°·96.

Fall on solution of K O, 2 Cr O_3 . . . 3°·96

The heat of liquefaction of bichromate of potash is therefore very considerable. It appears to be the same in quantity as that of *nitrate of potash*. The equivalent quantity of the latter salt, 63·25 grains, was dissolved in 1000 grains of water, with a fall of 3°·86. The temperature of this solution was further reduced 0°·10, by dilution with another 1000 grains

of water; so that by the solution of an equivalent quantity of this salt in the same proportion of water as was employed for the solution of an equivalent of bichromate of potash, a fall of temperature of $3^{\circ}\cdot96$ is produced. In a second experiment the whole fall of temperature on the solution of an equivalent of nitrate of potash was $3^{\circ}\cdot95$.

Fall on solution of K O, N O_5 $3^{\circ}\cdot96$

It is possible that this coincidence is not accidental, but depends on a thermal equivalency of N O_5 and $\text{Cr}_2 \text{O}_6$, the acids united with potash in these two salts. If the single equivalent of nitrogen in nitric acid be divided by three, or considered three atoms instead of one, as has been inferred on other grounds, then the acid constituents of both salts will contain the same number of atoms, namely eight; and the bichromate of potash, which has hitherto appeared so anomalous among salts, be assimilated to the nitrate of potash.

4. *Terchromate of Potash*.—Of this salt 63·63 grains, or one-half of the equivalent quantity, were dissolved easily and entirely by 1000 grains of water, with a fall of $1^{\circ}\cdot63$. But the terchromate of potash changes colour when thrown into water from decomposition, being resolved in a great measure into bichromate of potash and chromic acid, both of which are soon dissolved, the last more rapidly than the first.

Half an equivalent of this salt was dissolved, with a fall of $1^{\circ}\cdot28$, in 1000 water-grain measures of dilute nitric acid, of specific gravity 1·1453. But in this menstruum also, the terchromate appeared to be decomposed with separation of chromic acid, although to a much less extent than in the preceding experiment. In a liquid, however, already charged with the salt, like the last, an additional quantity may be dissolved without further decomposition. Half an equivalent of the salt was dissolved in that liquid with a fall of $1^{\circ}\cdot14$, which is a fall of 2·28 for a whole equivalent of the salt. The capacity for heat of the solution in question does not (I believe) differ materially from that of 1000 grains of water.

Fall from solution of K O, 3 Cr O_3 $2^{\circ}\cdot28$

Half an equivalent of the crystallized *biphosphate of potash*, or 42·68 grains, was dissolved in 1000 grains of water, with a fall of $1^{\circ}\cdot12$, which gives $2^{\circ}\cdot24$ for the whole equivalent.

Fall from solution of $2 \text{ H O, K O, P O}_5$ $2^{\circ}\cdot24$

A corresponding proportion of the crystallized *binarsenate of potash*, or 56·38 grains, were dissolved by 1000 grains of water, with a fall in one experiment of $1^{\circ}\cdot13$, and in another of $1^{\circ}\cdot18$. In a third experiment the solution of a whole equi-

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valent of this salt, or 112·75 grains, was attended by a fall of temperature of $2^{\circ}\cdot 15$. A greater discrepancy is observable in the results obtained from this than from most other salts, which appeared to arise from the full depression of temperature not occurring at the moment of solution, but a small portion of it being produced in a gradual manner for three or four minutes after the solution. The mean of the three observations gives $2^{\circ}\cdot 26$ for the equivalent quantity of the salt.

Fall from solution of $2 \text{ H O} \cdot \text{K O}, \text{As O}_5$. $2^{\circ}\cdot 26$

The thermal properties of these two salts are interesting in relation to the terchromate of potash. The latter salt contains 14 atoms, which is also the number of atoms in both biphosphate and binarsenate of potash, if the equivalents of phosphorus and arsenic be supposed, like that of nitrogen, to represent three atoms.

Potash being common to the terchromate and biphosphate of potash, there remain, on subtracting that constituent from both salts, three equivalents of chromic acid equivalent in some sense to one equivalent of phosphoric acid together with two equivalents of water. This statement respecting phosphoric acid, recalls the view which has lately been proposed by M. Wurtz of the constitution of the hypophosphites, in which the two atoms of water which they all contain are supposed not to be basic, but to form part of the acid; a neutral hypophosphite being represented by $\text{R O} + \text{P O}, \text{H}_2 \text{O}_2$, or rather by $\text{R O} + \text{P O}_3 \text{H}_2$. For we are here representing biphosphate of potash as $\text{K O} + \text{P O}_7 \text{H}_2$, corresponding with the terchromate of potash $\text{K O} + \text{Cr}_3 \text{O}_9$, in which P is equivalent to Cr_3 , and $\text{O}_7 + \text{H}_2$ to O_9 . The two atoms of water, however, may be replaced by a strong base in a biphosphate, but not in a hypophosphite. The relations of these salts show a progressive and imperceptible passage of the basic elements of a salt into constituents of its acid, and the existence of intermediate conditions of the elements in question, which we may well conceive although our chemical formulæ fail to enable us to denote them; these formulæ being adapted only for the expression of the extreme conditions.

Of anhydrous *chromic acid* an equivalent, 32·59 grains, was dissolved by 1000 grains of water with a rise of $0^{\circ}\cdot 51$. A second equivalent, dissolved in the previous solution, produced a rise of only $0^{\circ}\cdot 38$. The relations of this acid to water are therefore very different from those of sulphuric acid.

5. *Sulphate of Soda*.—In removing the hygrometric water which the crystals of this salt generally contain in large quantity, by pressure in blotting-paper, the salt is apt to lose a

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little of its combined water. The crystallized salt contained as determined by analysis, to 100 sulphate of soda, 121·5 water, instead of 126·1 water, which are ten equivalents. The equivalent quantity of the fully hydrated salt is 100·85 grains, but of the salt under examination only 98·79 grains. The last quantity, which contains 54·2 grains of water, was dissolved in 946 grains of water in half a minute, with a fall of 4°·43. The fall is almost entirely due, as will immediately appear, to the liquefaction of the combined water of the salt, of which the quantity liquefied in the experiment was 54·2 grains instead of 56·2, the ten equivalents. The fall of 4°·43 increased in the proportion of 54·2 to 56·2, becomes 4°·59.

Fall on solution of $\text{Na O, S O}_3 + 10 \text{ H O}$. . . 4°·59.

The same quantity of the salt was dissolved in the diluted sulphuric acid of the experiments with the previous salts, with a fall of 5°·00; which, corrected in the same manner as the last result, gives a fall of 5°·19 for the equivalent of the salt. Hence the fall on the solution of the sulphate of soda in dilute sulphuric acid is 0°·60 greater than in pure water; a circumstance connected probably with the formation of bisulphate of soda.

Sulphate of soda was made anhydrous by a strong heat, without being fused. The solution of the anhydrous salt is difficult, owing to the instantaneous formation of a hard coherent mass when the salt is thrown into water, which it requires two or three minutes to break up and dissolve. Very little change of temperature occurs. A rise took place in one experiment of 0°·10. In another experiment, in which the salt was added in a gradual manner with constant stirring, there was less caking, and the solution more rapid, although it still required two minutes. A rise occurred of 0°·18. The last experiment is most to be depended upon. The results for the sulphate of soda will therefore be,—

Rise on solution of Na O, S O_3	0°·18
Fall on solution of $\text{Na O, S O}_3 + 10 \text{ H O}$	4°·59
Whole heat disengaged by Na O, S O_3	<u>4°·77</u>

The last number represents the heat evolved in the formation of a solid hydrate of sulphate of soda containing ten atoms of water; it is remarkable how little it exceeds the heat disengaged in the crystallization of the same salt, or the fall observed on the solution of the crystallized salt. It appears as if water abandoned little more than its heat of fluidity on combining with dry sulphate of soda to form a solid hydrate.

Sulphate of soda, which had been allowed to effloresce in

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dry air between 50° and 55° Fahr. for a week, consisted of dry salt 100 and water $0\cdot46$. The equivalent quantity of this salt, which is so nearly anhydrous, or $44\cdot81$ grains, was dissolved in 1000 grains of water with a very slight change of temperature, namely a rise of $0^{\circ}\cdot05$.

6. *Sulphate of Ammonia*.—Of the hydrated salt crystallized by spontaneous evaporation in air, which contains one atom of water of crystallization, the equivalent quantity, $47\cdot03$ grains, was dissolved in 1000 grains of water with a fall of temperature in three experiments of $0^{\circ}\cdot65$, $0^{\circ}\cdot64$ and $0^{\circ}\cdot61$, of which the mean is $0^{\circ}\cdot63$.

Fall on solution of $\text{N H}_4 \text{O}$, $\text{S O}_3 + \text{H O}$. $0^{\circ}\cdot63$.

The salt was obtained anhydrous by drying at 248° Fahr.; it was granular and crystalline, and neutral to test paper. The equivalent quantity, $41\cdot41$, produced a fall in three experiments of $0^{\circ}\cdot51$, $0^{\circ}\cdot53$ and $0^{\circ}\cdot49$; of which the mean is $0^{\circ}\cdot51$.

Fall on solution of $\text{N H}_4 \text{O}$, S O_3 . . . $0^{\circ}\cdot51$.

A sensible but very small reduction of temperature, not exceeding $0^{\circ}\cdot02$, occurred on mixing the solution of sulphate of ammonia with an equal bulk of water at the same temperature.

Dissolved in the diluted acid, consisting of a mixture of 300 water-grain measures of sulphuric acid of density $1\cdot1$ and 700 grains of water, the equivalent, $41\cdot41$ grains, of the anhydrous salt produced a fall of temperature in two experiments of $1^{\circ}\cdot17$ and $1^{\circ}\cdot14$; of which the mean is $1^{\circ}\cdot16$. Hence the fall is greater on the solution of the sulphate of ammonia in dilute sulphuric acid than in water, by $0^{\circ}\cdot65$. The fall of sulphate of soda was also greater by nearly the same amount, $0^{\circ}\cdot60$, and of sulphate of potash by $0^{\circ}\cdot53$, when these salts were dissolved in the same dilute acid instead of water.

IV. *Double Sulphates*.

1. *Bisulphate of Potash*.—Of the usual double sulphate of water and potash crystallized in rhombohedral crystals, an equivalent quantity, $85\cdot23$ grains, was dissolved in 1000 grains of water, with a fall in two experiments of $1^{\circ}\cdot96$ and $1^{\circ}\cdot95$. The same salt was fused by heat and pounded; it dissolved afterwards with a fall of $1^{\circ}\cdot94$ and $1^{\circ}\cdot90$ in two experiments. The cold upon solution of this salt appears to be the same before and after fusion. The result is,—

Fall on solution of H O , $\text{S O}_3 + \text{K O}$, S O_3 . $1^{\circ}\cdot95$.

I was anxious to compare with this salt the anhydrous bi-

sulphate of potash of M. Jacquelin, which is described as being capable of dissolving in water without decomposition. One equivalent of sulphate of potash was accordingly dissolved in two equivalents of oil of vitriol, with the aid of heat, and an abundant crop was obtained on cooling of a salt in small silky crystals. As these appeared to be the salt in question, an equivalent quantity, or 79.60 grains, was dissolved, and a fall observed of $1^{\circ}90$. The result not differing from that of the former salt, the preparation of the anhydrous salt was repeated. The spongy mass of thin prismatic crystals obtained in a second experiment was pressed, dissolved again in water, crystallized and pressed again. The salt was still in minute prisms. The solution of 39.8 grains, half the equivalent quantity, was attended with a fall in two experiments of $0^{\circ}91$ and $0^{\circ}95$; or, for a whole equivalent, $1^{\circ}86$. Of the same salt, before the second solution, half an equivalent produced a fall of temperature of $0^{\circ}96$; or, for the whole equivalent, $1^{\circ}92$. These results are identical with those formerly obtained with the hydrated bisulphate, if allowance be made for the smaller quantity of the salt employed, a circumstance which excited a doubt as to the composition of the prismatic salt. The product of the second crystallization was accordingly analysed; 19.30 grains of it gave 32.34 grains of sulphate of barytes, equivalent to 11.12 sulphuric acid, or 57.59 per cent.; 22.53 grains of the crystals lost no weight at 150° , but lost 0.24 water, or 1.02 per cent., by cautious fusion. The proportion of acid in the salt is greatly under that of an anhydrous bisulphate, namely 62.98 per cent., while it approaches sufficiently near that of the hydrated bisulphate, 58.74 per cent. The process of M. Jacquelin has not therefore given an anhydrous bisulphate of potash in my hands, and none of my experiments favours the existence of such a salt; the silky prismatic crystals which I obtained being nothing more than an unusual form of the sulphate of water and potash.

2. *Bisulphate of Soda*.—An equivalent quantity, 75.27 grains, of one and the same specimen of this salt, dissolved in three experiments with a fall of $0^{\circ}40$, $0^{\circ}28$ and $0^{\circ}17$. It did not dissolve so easily as the bisulphate of potash, possibly from partial decomposition and formation of a portion of neutral sulphate of soda. The same supposition will explain the want of agreement among the results. Taking the mean of the results,—

Fall on solution of H O , $\text{S O}_3 + \text{Na O}$, S O_3 . $0^{\circ}28$.

The fall of temperature observed on dissolving bisulphate
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of potash in water approaches that observed on dissolving the neutral sulphate of potash in dilute sulphuric acid, the first being $1^{\circ}95$ and the second $2^{\circ}04$. But it is doubtful if the fall in the second case can be ascribed simply to the immediate formation and solution of bisulphate of potash, when the sulphate of potash and dilute sulphuric acid are mixed and dissolved together. In the formation of bisulphate of potash we have both the substitution of sulphate of potash for the second atom of water of the sulphate of water, and the throwing off of all the remaining water combined with the sulphate of water in hydrated sulphuric acid, bisulphate of potash containing no water of crystallization. Now as a great deal of heat was disengaged by this additional water on originally combining with the sulphate of water, we should expect heat again to be assumed by that water on becoming free, or cold to be produced.

3. *Sulphate of Magnesia and Potash.*—An equivalent quantity of the crystallized salt, namely 126.28 grains, containing 33.75 grains of water of crystallization, was dissolved in 976.2 grains of water at 52° Fahr., with nearly two minutes' stirring; a fall of temperature was observed of $2^{\circ}30$ R. The experiment was repeated with the same result. But a slow rise of temperature was afterwards observed to occur in the solution, independent of any external influence, which in the course of four minutes amounted to $0^{\circ}20$ R. This is not the only salt in which the fall of temperature on solution is immediately followed by a slight but sensible rise.

This salt was made anhydrous by a low red heat to which it was exposed for upwards of two hours, but was not fused. When the salt was thrown into water after this ignition, it gave a liquor which remained white and milky for two or three minutes, but the salt finally dissolved without residue. The rise of temperature on the solution of a whole equivalent of the anhydrous salt, or 92.53 grains, was $1^{\circ}57$; on solution of one-half of an equivalent, or 46.26 grains, $0^{\circ}80$; which gives $1^{\circ}60$ for the whole equivalent.

Rise on solution of $\text{Mg O, S O}_3 + \text{K O, S O}_3$. . .	$1^{\circ}60$
Fall on solution of $\text{Mg O, S O}_3 + \text{K O, S O}_3 + 6 \text{H O}$	$2^{\circ}30$
Whole heat disengaged by $\text{Mg O, S O}_3 + \text{K O, S O}_3$	$\frac{3^{\circ}90}{\quad}$

The crystallized sulphate of magnesia and potash, dried by a nitre-bath, was found to retain 18.32 water to 100 anhydrous salt. Now 18.24 water represents 3 H O; the crystallized salt has consequently lost one-half of its water, retaining only three atoms. Of this salt, an equivalent quantity, or

109·4 grains, were dissolved in 1000 grains of water, with a fall in three experiments of $1^{\circ}35$, $1^{\circ}30$ and $1^{\circ}35$, of which the mean is $1^{\circ}33$.

Fall on solution of Mg O , $\text{SO}_3 + \text{K O}$, $\text{SO}_3 + 3 \text{H O}$ $1^{\circ}33$.

The fall on the solution of this hydrate is less than on the solution of the former, by the heat disengaged in the combination of the salt with the deficient three atoms of water. The heat disengaged by the union of the salt with the first three atoms of water comes therefore to be $2^{\circ}93$, and with the second three atoms of water $0^{\circ}97$, making together $3^{\circ}90$. Hence as nearly as possible three times as much heat are disengaged by the first three atoms of water as by the last three atoms.

4. *Sulphate of Magnesia and Ammonia*.—The solution of an equivalent quantity, 113·13 grains, of the crystallized salt in 1000 grains of water was attended by a fall of temperature, in two experiments, of $2^{\circ}20$ and $2^{\circ}15$, of which the mean is $2^{\circ}17$. If dissolved in 976·2 grains of water, like the potash salt, the fall would have been about $\frac{1}{30}$ th more, or $2^{\circ}24$.

Fall on solution of Mg O , $\text{SO}_3 + \text{NH}_4 \text{O}$, $\text{SO}_3 + 6 \text{H O}$ $2^{\circ}24$.

The fall on the solution of the corresponding potash salt was $2^{\circ}30$.

5. *Protosulphate of Iron and Ammonia*.—The solution of 122·17 grains, the equivalent quantity of the crystallized salt in 1000 grains of water, was attended with the same fall of $2^{\circ}20$ in two experiments. But this determination should be increased by $\frac{1}{30}$ th, like the last; the fall then becomes $2^{\circ}27$.

Fall on solution of Fe O , $\text{SO}_3 + \text{K O}$, $\text{SO}_3 + 6 \text{H O}$ $2^{\circ}27$.

6. *Sulphate of Manganese and Ammonia*.—In two experiments 61·20 grains of the crystallized salt, being one half of the equivalent quantity, were dissolved in 983 grains of water with a fall of $1^{\circ}11$ and $1^{\circ}13$; or $2^{\circ}24$ for a whole equivalent. Fall on solution of Mn O , $\text{SO}_3 + \text{NH}_4 \text{O}$, $\text{SO}_3 + 6 \text{H O}$ $2^{\circ}24$.

It thus appears that the heat of liquefaction of the four crystallized double salts, sulphate of magnesia and potash, sulphate of magnesia and ammonia, sulphate of iron and potash, and sulphate of manganese and ammonia, is sensibly the same.

7. *Sulphate of Zinc and Potash*.—The fall on the solution of half an equivalent, 69·26 grains, of the crystallized salt in 1000 grains of water, was in three experiments $1^{\circ}33$, $1^{\circ}27$ and $1^{\circ}30$, of which the mean is $1^{\circ}30$. The fall for a whole equivalent, 138·52 grains, is therefore $2^{\circ}60$.

This salt was made anhydrous by a heat little short of redness, without being fused Half an equivalent, 52·39 grains,

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was dissolved in 1000 grains of water with a rise of temperature of $0^{\circ}\cdot83$ and $0^{\circ}\cdot87$ in two experiments, of which the mean is $0^{\circ}\cdot85$. The rise for a whole equivalent, $104\cdot77$ grains of the salt, is therefore $1^{\circ}\cdot70$.

Rise on solution of $\text{Zn O, SO}_3 + \text{K O, SO}_3$	$1^{\circ}\cdot70$
Fall on solution of $\text{Zn O, SO}_3 + \text{K O, SO}_3 + 6 \text{ H O}$	$2^{\circ}\cdot60$
Whole heat disengaged in the hydration of } $\text{Zn O, SO}_3 + \text{K O, SO}_3$ }	$4^{\circ}\cdot30$

8. *Sulphate of Copper and Ammonia*.—Of the crystallized salt, $62\cdot45$ grains, or one half of the equivalent quantity, were dissolved in 983 grains of water with a fall of temperature of $1^{\circ}\cdot33$ and $1^{\circ}\cdot28$ in two experiments; giving $2^{\circ}\cdot63$ for the whole equivalent.

Fall on solution of $\text{Cu O, SO}_3 + \text{N H}_4\text{O, SO}_3 + 6 \text{ H O}$. $2^{\circ}\cdot63$.

The fall on the solution of the two immediately preceding salts is therefore sensibly the same.

9. *Protosulphate of Iron and Potash*.—Of this salt in small but well-defined crystals, $67\cdot66$ grains, one half of the equivalent quantity, were dissolved in 983 grains of water with a fall, in two experiments, of $1^{\circ}\cdot25$ and $1^{\circ}\cdot22$; or for the whole equivalent $2^{\circ}\cdot47$.

Fall on solution of $\text{Mn O, SO}_3 + \text{K O, SO}_3 + 6 \text{ H O}$. $2^{\circ}\cdot47$.

10. *Sulphate of Zinc and Ammonia*.—Of the crystallized salt half an equivalent, $62\cdot64$ grains, was dissolved in 983 grains of water with a fall of $1^{\circ}\cdot37$ and $1^{\circ}\cdot36$.

Fall on solution of $\text{Zn O, SO}_3 + \text{K O, SO}_3 + 6 \text{ H O}$. . $2^{\circ}\cdot73$.

11. *Sulphate of Copper and Potash*.—The solution of half an equivalent of the crystallized salt, $69\cdot07$ grains, in 1000 grains of water, was attended with a fall in two experiments of $1^{\circ}\cdot54$ and $1^{\circ}\cdot50$; or for the whole equivalent of the salt, $138\cdot14$ grains; the fall is $3^{\circ}\cdot08$ and $3^{\circ}\cdot00$, of which the mean is $3^{\circ}\cdot04$.

The crystallized salt was made anhydrous by a heat short of redness, which had the effect of causing it to frit but did not fuse it. The solution of $52\cdot2$ grains, half an equivalent, in 1000 grains of water, was attended by a fall in two experiments of $1^{\circ}\cdot01$ and $0^{\circ}\cdot96$; or for a whole equivalent, $2^{\circ}\cdot02$ and $1^{\circ}\cdot92$, of which the mean is $1^{\circ}\cdot97$.

Rise on solution of $\text{Cu O, SO}_3 + \text{K O, SO}_3$	$1^{\circ}\cdot97$
Fall on solution of $\text{Cu O, SO}_3 + \text{K O, SO}_3 + 6 \text{ H O}$	$3^{\circ}\cdot04$
Whole heat disengaged in hydration of } $\text{Cu O, SO}_3 + \text{K O, SO}_3$ }	$5^{\circ}\cdot01$

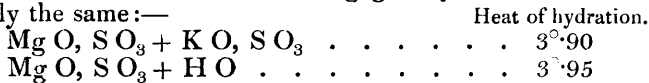
The fall on the solution of the preceding crystallized double salt is $3^{\circ}\cdot04$, while the fall on the solution of its constituents dissolved separately is $1^{\circ}\cdot51$ for the sulphate of potash, and

0°·67 for the hydrated sulphate of copper, making together 2°·18, which is less by 0°·86 than the former. The fall on the solution of the crystallized double sulphate of zinc and potash approaches more closely to the united falls of its constituents dissolved separately, the former being 2°·60 and the latter 1° + 1°·51 = 2°·51. The fall on the solution of the crystallized double sulphate of magnesia and potash is 2°·30; the united falls of its constituent salts 0°·92 + 1°·51 = 2°·43. No perceptible change of temperature was observed when the solutions of a pair of these salts are mixed to form the double salt; which is in accordance with the conclusion of Dr. Andrews, that no heat is evolved in the combination of salts.

I have not, however, succeeded in obtaining any direct proof of the formation of the double sulphates on mixture. To a solution of 77·97 grains, or one equivalent, of crystallized sulphate of copper in 1000 grains of water, 41·41 grains, one equivalent, of sulphate of ammonia dried at 234° were added and dissolved. The fall on the solution of the last salt was 0°·56, or the same as when the salt is dissolved in pure water. No change took place in the colour of the solution of the copper salt. The last salt was selected for this experiment because it appears more disposed to form double salts than even the sulphate of potash.

In certain cases, a double salt is formed on using a bisulphate, while it is not with the neutral sulphate; as in the formation of sulphate of zinc and soda, from sulphate of zinc and bisulphate of soda, but not from sulphate of zinc and neutral sulphate of soda. To a solution of 85·23 grains, or the equivalent, of crystallized bisulphate of potash in 1000 grains of water, 89·59 grains, or the equivalent, of crystallized sulphate of zinc were added and dissolved, with a fall of 1°·00, or the same as in pure water. To a similar solution of bisulphate of potash, 77·35 grains, or one equivalent, of crystallized sulphate of magnesia were added and dissolved, with a fall of 0°·86; the same fall also as on the solution of the latter salt in pure water. Yet the double salts crystallized out readily from both of these solutions.

I have formerly represented the anhydrous sulphate of magnesia and potash as corresponding with the protohydrated sulphate of magnesia. Now both these salts assume six atoms of water, and the heat then disengaged by the two salts is nearly the same:—



When the corresponding salts of zinc are compared, the same equality is not observed, but other relations appear.

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	Heat of hydration.
Zn O, S O ₃ + K O, S O ₃	4°·30
Zn O, S O ₃ + H O	3°·45
Zn O, S O ₃	5°·17

These quantities of heat and the quantity disengaged by the anhydrous sulphate of zinc, have a remarkable relation among themselves; if they be all divided by 0°·86, we have

	Ratios of heat of hydration.
Zn O, S O ₃ + H O	4°·01
Zn O, S O ₃ + K O, S O ₃	5
Zn O, S O ₃	6°·01

The quantity of heat disengaged by the first atom of water on uniting with sulphate of zinc is 1°·71. If it had been only half that quantity, or 0°·86, and had the deficient 0°·86 been evolved by the combination of the six following atoms, in addition to the heat they actually evolve, then the heat disengaged by the six atoms of water which unite with protohydrated sulphate of zinc, and by the double sulphate of zinc and potash, would be the same in both salts, as it is the same in the two corresponding salts of magnesia.

The heat evolved by the corresponding copper salts with their ratios, is as follows:—

	Heat of hydration.	Ratios.
Cu O, S O ₃ + H O	2°·93	4°
Cu O, S O ₃	4°·40	6°
Cu O, S O ₃ + K O, S O ₃	5°·01	6°·86

It is to be observed, however, that while the protohydrate of sulphate of copper combines with only four atoms of water, the sulphate of copper and potash combines with six atoms; the usual comparison cannot therefore be made between these two salts.

The principal numerical results of the paper are exhibited in the following tables:—

1. Heat absorbed by equivalent quantities of crystallized salts on dissolving in water.

Sulphate of magnesia	7 H O	0°·92
Sulphate of zinc	1°·00
Protosulphate of iron	1°·06
Sulphate of copper	5 H O	0°·67
Sulphate of manganese	0°·12
Sulphate of magnesia and potash	6 H O	2°·30
Sulphate of magnesia and ammonia	2°·24
Sulphate of manganese and ammonia	2°·24
Sulphate of iron and ammonia	2°·27
Sulphate of iron and potash	2°·47

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Sulphate of zinc and potash . . .	6 H O	2°·60
Sulphate of copper and ammonia	2°·63
Sulphate of zinc and ammonia	2°·73
Sulphate of copper and potash	3°·04
Sulphate of soda	10 H O	4°·59
Sulphate of potash	anhydrous	1°·51
Sulphate of ammonia	0°·51
Chromate of potash	1°·18
Bichromate of potash	3°·96
Nitrate of potash	3°·96
Terchromate of potash	2°·28
Biphosphate of potash	2 H O	2°·24
Binarsenate of potash	2°·26
Sulphate of water and potash . . .	anhydrous	1°·95

2. Heat disengaged in the complete hydration of anhydrous salts.

Sulphate of magnesia	5°·25
Sulphate of zinc	5°·17
Sulphate of copper	4°·40
Sulphate of manganese	3°·34
Sulphate of magnesia and potash .	3°·90
Sulphate of zinc and potash . . .	4°·30
Sulphate of copper and potash . .	5°·01

3. Heat disengaged by the combination of the first atom of water in the magnesian sulphates.

Sulphate of water	1°·47
Sulphate of copper	1°·47
Sulphate of manganese	1°·43
Sulphate of magnesia	1°·30
Sulphate of zinc	1°·71

Simple relations are observed between the quantities of heat disengaged by the sulphates of magnesia and zinc, which appear to belong to one class, while the sulphates of water, copper and manganese belong to another class.

