

XXIX.—*The Influence of Temperature on the Heat of Chemical Combination.*

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OUR knowledge of the influence which temperature exerts on the heat of chemical combination is at present of the most rudimentary character. It has been established as one of the fundamental principles of thermochemistry that the total heat evolved in the combination of two substances at different temperatures, together with that necessary to reduce the systems in the two cases to the same initial and final temperatures, is a constant quantity—that where  $Q$  and  $Q'$  represent the actual heat evolved during the combination of A with B at  $T$  and  $T'$ , we shall have—

$$Q - C_{AB}(T' - T) = Q' - (C_A + C_B)(T' - T),$$

$C_A$ ,  $C_B$ , and  $C_{AB}$  being the specific heats of A, B, and the compound which they form, respectively. Where the specific heat of the compound is equal to the sum of those of its components, the heat which these develop in combining will be a constant quantity independent of temperature. The labours of Kopp have shown that such a condition exists to a certain extent in the case of most solids, but we are still in ignorance as to whether it is absolutely or only approximately true, whether those variations which have in many cases been observed in the specific heats of solids are regular in their nature, whether, in fine, the compound AB at  $T$  is in every respect the same substance as AB at  $T'$ .

The present investigation shows that this is not the case. It will appear that the relation between the constituent portions of the molecule of a complex solid undergoes a series of modifications as the temperature changes, the result of which is that the variations exhibited in the heat of combination, and consequently in the specific heat also, being conditioned by a different order of circumstances at different temperatures, exhibit irregularities of a very marked character.

As no methods have yet been devised for obtaining very accurate measurements of specific heats through small, or indeed through considerable ranges of temperature, the heat of combination appeared to be the only available means of investigating the subject; in order, however, to invest the determinations of it with a degree of accuracy which would promise any chance of success, it was necessary to confine them within the limits of ordinary atmospheric temperatures, a small range of  $25^{\circ}$  C. only being thus available. Substances which would be most likely to exhibit any variation in the heat of their formation within these narrow limits would be those in which the energy of combination was small. Hydrated salts afford many instances of such a nature, and, consequently, they were chosen as the subjects of this investigation; the heat of hydration presents, moreover, one other material recommendation for the present purpose, in that the number of operations necessary for a determination of it is very limited, and the nature of these is very simple.

Whatever may be the complexity of the reactions occurring when a salt is dissolved in water, it is generally accepted that the difference between its heat of dissolution in the anhydrous and hydrated state gives the heat of combination of the salt with its water of crystallisation,\* provided we first subtract from the second of the above-named quantities the heat absorbed in the conversion of the solid water present into liquid water, for every fact which bears on the question supports the view that in a solid hydrated salt the water is present as a solid, and in the solution of such a salt as a liquid.

The heat of fusion of ice at temperatures other than  $0^{\circ}$  never having been determined experimentally, it must be calculated by means of the specific heats of water and ice; the latter of these has also never been determined for temperatures above  $0^{\circ}$ , and, consequently, some doubt must be felt as to the correctness of the values calculated for the heat of fusion. The present experiments themselves, however, will be found to afford considerable evidence as to the accuracy of these calculated values, and, moreover, any error in them will not affect the main conclusions drawn from this work,

\* This can only be so if the heat of combination of the various atoms composing the salt molecule is unaffected by the combination of that molecule with the water.

inasmuch as such errors would affect the inclination of the curves only, and not their nature. The latent heat of fusion of 1 mol., or 17.96 grams, of water,  $l_m$ , has been calculated from the equation—

$$l_m = (1423.33 + (c - c')T) \text{ cal.},$$

in which the specific heat of water,

$$c = 17.96 + 0.00072T + 0.0000162T^2,$$

and the specific heat of ice,  $c' = 9.052 + 0.0185T$ . The various values of  $l_m$ , which is of course a negative quantity, are represented in Plate VII, and it will be seen that, for the purposes of the present communication, this is practically a straight line.

The heat of combination of a salt with its water of crystallisation, both being in the solid state, will be given by the equation—

$$Q = M_A - (M_H + xl_m),$$

in which  $M_A$  and  $M_H$  represent the observed heat of dissolution of anhydrous and hydrated salt, and  $x$  the number of molecules of water which the latter contains. If, as has hitherto been assumed, the specific heat of a hydrated salt is equal to the sum of that of the anhydrous salt and the water (reckoned as solid water), the value of  $Q$  will be a constant quantity, independent of temperature.

The more important conclusions arrived at in this paper are based on differences so small as to be nearly on a par with those attributable to experimental error; it will, therefore, be necessary to enter considerably into detail to show that they can by no means be attributed to this source.

### *Apparatus and Method Employed.*

The apparatus employed was Berthelot's open calorimeter, and full details as to the method of operation adopted in this research will be found in *Phil. Mag.*, 1886, **21**, 324. It will be sufficient to mention here that, except in some of the earlier experiments, and in some of those at very low temperatures, the temperature of the air was kept constant within about  $0.2^\circ$  of the initial temperature of the calorimetric water. This precaution, which naturally rendered the experiments very tedious, was necessary, in order to reduce the errors inherent in the determination of the rate of cooling to a minimum, and it also obviated any important correction having to be applied on account of the temperature of the salt before dissolution not being identical with that of the water in which it was dissolved.

The rate of cooling (or heating) was determined in every single experiment, and the necessary correction applied, for it was ascertained

that not in one case out of a hundred did the salt dissolve in a space of time sufficiently short to render such a correction superfluous.

The general method of procedure was modified in the case of hydrated sodium sulphate only. The adhesive nature of this salt rendered it impossible to shake it out of the weighing-tube into the calorimeter without causing an inordinate amount of splashing; the following device was, consequently, adopted in one series of experiments (those with sample No. 3095). The salt was weighed out into a very short wide test-tube, of which the water equivalent was known, and the tube with its contents plunged bodily into the water; a platinum wire fused into the bottom of the tube served as a means of holding the tube inverted till its contents had fallen out. It was found, however, that the presence of these tubes in the calorimeter interfered with the agitation of the liquid to such an extent that, at low temperatures, a very long time elapsed before all the salt dissolved. In the experiments with other samples, therefore, the salt was weighed out into the ordinary test-tubes on feet, but instead of being shaken out into the water, it was shaken out on to the flat disc which formed the end of the agitator, and which for that purpose was momentarily raised till flush with the level of the water. All splashing was thus avoided. The raising of the pounder was repeated in each interval, during which the rate of cooling was measured, so that any error due to evaporation from its surface during the process might be allowed for; no additional error appears to have been caused by this operation, as the average variation of duplicate experiments in this series is not greater than that in other cases.

#### *Thermometers Employed.*

Two calorimetric thermometers were at first employed, No. 55,083, with a range of 1—16° C., and No. 55,081, with a range of 10—25°; subsequently another instrument, ranging from 5—21°, was used (No. 56,916), and in a few experiments No. 55,080, a fellow instrument to No. 55,081, as well as No. 55,084, with a range of 0—26°. They were divided into about 38 arbitrary degrees, each of which were subdivided into tenths, these subdivisions being 1·2 mm. apart, and each equivalent to about 0·038° C. In reading them, a pocket lens was employed, and the fractional portions estimated to the twentieth of the marked divisions, one estimation unit, therefore, representing 0·002°. With No. 55,084, these quantities must be doubled, as the range in its case is twice as great as with the others.

These calorimetric thermometers were originally standardised by comparison with a natural standard, but as the work progressed it became apparent that this method was insufficient to afford

the amount of accuracy required, since a small error in the reading of the standard would cause a very appreciable want of concordance in the various instruments. The following expedient was therefore adopted :—All the thermometers were compared with No. 55,084, the range of which embraced those of all the others, and which was thus converted into an “intermediate standard;” as this instrument is about three and a half times as delicate as the natural standard, a corresponding increase in the concordance of the calorimetric instruments was thus attained. It is true that this “intermediate standard” itself had to be standardised by comparison with the natural standard, but any error made in this operation would affect all the calorimetric instruments to the same extent, and would not impair their concordance *inter se*, which was here the consideration of most importance. The results thus obtained were further modified by comparing the calorimetric instruments with each other, this being effected by comparison with No. 56,216, the scale of which overlapped that of all the others to a considerable extent, twelve or more comparisons at different points being made with each instrument, a fall or rise of about 170 mm. ( $2.3^{\circ}$ ) being taken in each observation.

At the same time that this re-standardising was effected, all the instruments were calibrated afresh, and all the several hundred experiments which had been completed were recalculated. Some details as to these calibrations and standardisations will be found in the *Phil. Mag.*, 1886, 21, 180.

In spite of the very great pains which were taken to produce an absolute concordance between the various thermometers, the results were not altogether satisfactory; indeed a certain regularity which appeared in the differences of the results obtained with different instruments, seemed to indicate the existence of some unknown imperfection inherent in the nature of mercurial thermometers, which prevented the attainment of such concordance throughout the scales.

A device was consequently adopted, by means of which not only the same thermometer, but also the same part of the thermometer, was used in every experiment, whatever the temperature might be. This was effected by removing the requisite amount of mercury into the upper chamber of the instrument by the application of heat, thus adjusting its reading to any particular temperature, and rendering two experiments at different temperatures as comparable with each other as if they had been performed at the same temperature: in fact, for the purposes of the present investigation, the errors of calibration and standardisation were thus obviated entirely.\* At the same time, the delicacy of the instruments was increased six- or seven-fold; in two of them (Nos. 62,839 and 63,616) the total range of about 600 mm.

\* A similar device has, I believe, been used by Crafts.

represented  $3.6^\circ$  and  $3.86^\circ$  respectively, each estimation unit ( $0.05$  mm. in this case) being equivalent to  $0.0003^\circ$  only. A full description of these thermometers, together with some peculiarities which they exhibit, and the manner in which these must be guarded against, has been given in the *Phil. Mag.*, 1886, **21**, 330.

### *Quantities Used.*

The relative proportions of salt and water used in all these experiments was 1 mol. of a single salt to 400–420 mols. of water, the actual quantities being  $\frac{3}{4}$ ths of a gram-molecule to 600 c.c.

Chemists have generally preferred to take proportions of water not exceeding  $200\text{H}_2\text{O}$ , but though such a proportion gives twice the temperature disturbance, the larger quantity,  $400\text{H}_2\text{O}$ , would appear to offer greater facilities for very accurate measurements in most cases. The estimation of the rate of cooling is certainly that part of a determination which admits of the largest error, and the employment of  $200\text{H}_2\text{O}$  in these experiments would have increased the rate of cooling beyond the limits within which that rate is practically constant in the case of three of the salts, while in all the cases in which anhydrous salts were dealt with, the larger proportion of salt would have required twice the time pounding and stirring to have effected its dissolution, and would thus have doubled the correction necessary for cooling. Moreover, with the instruments employed, a rise or fall of as much as  $5^\circ$ , which would have occurred in some cases had  $200\text{H}_2\text{O}$  been used, would have limited very materially the range of temperature available for the series of experiments, and would have rendered it impossible to use such delicate thermometers as the last two described.

Another inducement for taking the larger proportion of water will be mentioned when the calculation of results is discussed.

With double salts, the proportion of salt was only one-half of that used in the other cases.

### *Experimental Error.*

As the question of experimental error in these experiments has been fully discussed in the *Phil. Mag.*, 1886, **21**, 324, it will be necessary to mention here the general results only.

One estimation unit ( $0.06$  mm.), in the case of the less delicate thermometers, represents 16 cal. in the molecular heat of dissolution of a single salt, while with the two more delicate ones it ( $0.05$  mm.) represents 2.5 cal.

The experimental error where the former were used was found to be  $\pm 18.86$  cal. for every single experiment; of this  $\pm 5.56$  cal. is

due to errors in the calibration and standardisation of the instruments, leaving  $\pm 13.3$  cal. as the error of each experiment, when duplicate determinations at the *same* temperature, and performed with the *same* instruments, are compared. Of this error,  $\pm 5.71$  cal. have been traced to error in reading the instruments, and  $\pm 7.59$  cal. to error in manipulation. In cases where two thermometers were used simultaneously in the calorimeter, the manipulation error is increased to  $\pm 9.53$ .

With the two very delicate instruments, the total probable error of each experiment was only  $\pm 7.42$  cal., this being the error when comparing experiments performed, not only at the same temperatures, but at different temperatures also.

In the case of the double salts, all the above numbers become doubled.

### *Calculation of Results.*

The salt before its introduction into the calorimeter being at very nearly the same temperature as the water, the correction due to the "salt temperature" was generally very small, rarely amounting to one estimation figure of the thermometer. The specific heats from which any such correction was calculated were taken as follows:—

$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ , 0.320;  $\text{Na}_2\text{SO}_4$ , 0.229;  $\text{K}_2\text{SO}_4$ , 0.190;  $\text{Li}_2\text{SO}_4$ , 0.200;  
 $\text{CuSO}_4, 5\text{H}_2\text{O}$ , 0.300;  $\text{CuSO}_4$ , 0.135;  $\text{MgSO}_4, 7\text{H}_2\text{O}$ , 0.380;  
 $\text{MgSO}_4$ , 0.222;  $\text{CuSO}_4, \text{K}_2\text{SO}_4, 6\text{H}_2\text{O}$ , 0.260;  $\text{CuSO}_4, \text{K}_2\text{SO}_4$ , 0.168;  
 $\text{MgSO}_4, \text{K}_2\text{SO}_4, 6\text{H}_2\text{O}$ , 0.264;  $\text{MgSO}_4, \text{K}_2\text{SO}_4$ , 0.170.

Having applied this correction, as well as that due to cooling (or heating) during the dissolution, the heat evolved was calculated from the initial and final temperatures thus obtained, according to the simplified method adopted by Berthelot (*Méc. Chim.*, **1**, 190), which consists in reckoning the number of cubic centimetres of water originally taken as so many grams with a specific heat of 1, and neglecting the salt present. It is true that the specific heat of solutions containing 1 mol. of the salt to  $200\text{H}_2\text{O}$  has been determined for some of the substances here dealt with (Marignac, *Arch. des Sc. de la Bibl. de Genève*, 1876), and that the employment of solutions of that strength would have allowed of the adoption of a more accurate method of calculation in such cases; but even in the few instances where it would have been possible, its application would have been limited to the experiments at one temperature only, since the data for calculating the specific heats at any temperature between  $0^\circ$  and  $25^\circ$  are entirely wanting.

Berthelot shows that in many cases his method introduces but very trifling errors, and gives far more accurate results than are obtained

by assuming the specific heat of dilute solutions to be unity. With solutions as dilute even as those containing  $200\text{H}_2\text{O}$ , it is liable, however, in some cases to lead to serious errors, taking for instance copper sulphate. 23·8 grams of the anhydrous salt would be dissolved in 602·05 c.c.\* (weighing 600·5 grams) at  $24^\circ$ ; the specific heat of such a solution at this temperature is 0·95, and hence its water equivalent will be  $(600·5 + 23·8)0·95$ , or 593·1 grams, whereas according to Berthelot's method, it would be taken as 602·05 grams, thus causing an error of  $\frac{1}{70}$ th. This error, however, is greatly reduced by using more dilute solutions. From Marignac's work on the specific heat of saline solutions (*loc. sup. cit.*), we may conclude that the specific heat of solutions of various sulphates differ from each other to a smaller extent the more dilute they are; that with  $400\text{H}_2\text{O}$  their specific heat will probably be very near  $0·98^\circ$ , and that a rise of temperature of  $1^\circ$  will cause an increase of approximately 0·0001 in this specific heat. Taking now two experiments with copper sulphate with  $400\text{H}_2\text{O}$  at  $24^\circ$  and  $4^\circ$  respectively. At  $24^\circ$ , the water taken would have measured 602·05 c.c., and weighed 600·50 grams. The weight of salt taken would be 11·9 grams. The water equivalent of the solution would be  $(600·5 + 11·9)0·98 = 600·05$  grams, whereas it would have been taken as 602·05 grams, the error, therefore, being  $\frac{1}{300}$ th. At  $4^\circ$  the water taken would be 601·74 c.c., weighing 601·74 grams, and the true water equivalent  $(601·74 + 11·9)0·978 = 600·14$ , that taken 601·74, the error being  $\frac{0·6}{300}$ th. Such errors (and I have taken an instance where it would appear to be larger than in most cases) would often be within the limits of the experimental errors, and, as will be seen, the conclusions drawn in this communication do not depend on the absolute accuracy of the numbers given, but on the relative accuracy of experiments with the same salt at different temperatures (the error in comparing together the above experiments would be only  $(\frac{1}{300} - \frac{0·6}{300}) = \frac{1}{1500}$ th), and on a comparison of the heat of dissolution of the anhydrous and hydrated salts at the same temperature. All the experimental data, however, will be given in full, so that in the event of future work completing our knowledge of the specific heats of saline solutions, these results may be recalculated in a more correct manner.

#### *Preparation of the Salts.*

The method generally adopted in preparing the hydrated salts consisted in recrystallising them very carefully two or three times,

\* I take the volumes which would actually have been used in the present experiments; these are the volumes delivered by the same glass vessel at the various temperatures. No difference would be made in the present calculations were the same volumes taken at every one of the temperatures.



powdering the crystals finely, and washing them with water. This powdering and washing is very necessary in the case of all sulphates containing copper, or any allied metal, since, owing to the dissociation of the salt in solution, any mother-liquor adhering to the crystals will be acid, and this will cause serious errors to arise in the colorimetric determinations. It is also preferable in such cases not to boil the solutions of the salt, since a high temperature greatly increases the amount of this dissociation.

The hydrated salts were invariably sifted, sometimes through a silk sieve.

Considerable difficulty was at first experienced in preparing these salts with exactly the theoretical amount of water, owing to efflorescence. The most satisfactory results were obtained by determining the percentage of water present in the crystallised salt which had been imperfectly dried, and then allowing it to lose whatever excess of water it was found to contain, by exposing weighed quantities of it to the air with constant stirring. It was ascertained that even a large quantity of a salt which retained excess of moisture could, by sifting and mixing, be obtained sufficiently homogeneous throughout to render such a method trustworthy.

To take one instance out of many, a sample of hydrated sodium sulphate weighing 1 kilo. gave on analysis 56.612, 56.611, and 56.596 per cent. of water, numbers which are very closely concordant, although the sample contained a considerable amount of adhering moisture, the theoretical percentage for  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  being only 55.88.

The most accurate and indeed the only satisfactory means of analysing most of the sulphates here dealt with, was found to be a determination of the percentage of water present in them, using very large quantities for each analysis. This method has already been discussed in a previous paper (*Trans.*, 1885, 100), and the analytical results will not be given in the present communication, since, unless the water percentages were found to correspond to the theoretical amount within experimental error (within about 0.03 per cent.), the preparation was rejected.

In the case of a hydrated salt, such as sodium sulphate which parts with its water of crystallisation very easily, it was found necessary to prevent the salt from caking in the bottle in which it was preserved, by constant agitation, for if it cakes some of the water from the crystals in one part of the bottle distils into another part which happens to be slightly cooler, so that the sample is no longer homogeneous. A whole series of experiments was spoilt by neglecting this precaution.

It was found best to preserve the anhydrous salts in small bottles

or sealed tubes, each containing sufficient for only two or three determinations, so that exposure to the air might be avoided as much as possible; in order, however, to make sure that the contents of each bottle or tube were precisely the same as regards their state of purity, it was necessary to put the whole of the sample into a big bottle immediately after its preparation, keep it there with continual shaking for several days, and then after heating it in the bottle itself to a temperature considerably above  $100^{\circ}$ , to transfer it to the smaller vessels.

The experiments were so arranged that different determinations at the same temperature were made after long intervals of time, so that any alteration in the salt, whether of a molecular or of accidental nature, might be detected. In no case was any such molecular alteration observed, and only in one instance (with a sample of copper sulphate) was any difference detected, and that was due to accident.

### *Specimens Used.*

The following are the preparations which were used in the various experiments. For the sake of reference, I have retained the numbers by which they were distinguished when prepared.

*Hydrated Magnesium Sulphate*,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 245.48$ .—This salt when pure neither effloresces nor deliquesces on exposure to air; its preparation, therefore, is very easy. Three different specimens, Nos. 2688, 2756, and 3417, were used in the majority of the experiments, as well as three others in a few cases.

*Anhydrous Magnesium Sulphate*,  $\text{MgSO}_4 = 119.76$ .—Samples 2718 and 2754 were prepared by heating the salt in small quantities in a platinum dish below a red heat. No. 3092 was dehydrated at a temperature of  $250^{\circ}$  only.

*Hydrated Potassium Magnesium Sulphate*,  $\text{MgK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} = 401.4$ .—Prepared by cooling a hot saturated solution of the component sulphates. The details of its preparation in a state of purity are given in this vol., p. 8.

Four different samples were used.

*Anhydrous Potassium Magnesium Sulphate*,  $\alpha\text{-MgK}_2(\text{SO}_4)_2 = 293.64$ .—Five preparations of this salt were made. The difficulty of obtaining it in the anhydrous condition without inducing a change which converts it into a second modification necessitated the employment of samples retaining small quantities of water (except with No. 3039) for which a correction had to be applied. No. 3432 had been somewhat overheated, and gave numbers uniformly 1113 cal. lower than the other samples. This amount was added to experiments with it for convenience in deducing a curve. The peculiarities of this salt,

and those of the corresponding copper compound, formed the subject matter of a communication to the Society, and full details as to most of the specimens here used will be found in this vol., p. 1 *et seq.*

*Hydrated Copper Sulphate*,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 248.64$ .—One specimen only of this salt was used, No. 2736.

*Anhydrous Copper Sulphate*,  $\text{CuSO}_4 = 158.84$ .—Eight different preparations were used. The first one, No. 2729, having been kept in one bottle, was found to have accidentally absorbed a certain amount of moisture, which rendered the numbers yielded by it in the later determinations uniformly 160 cal. lower than those given in the earlier ones. This amount has consequently been added to the later experiments with it, as indicated in Table III. Nos. 3094 and 3401 were preserved in small bottles, and the remaining specimens in sealed tubes. All the specimens were prepared at a temperature between  $200^\circ$  and  $250^\circ$ .

*Hydrated Potassium Copper Sulphate*,  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} = 440.78$ .—Two specimens of this salt, prepared in the same manner as the corresponding magnesium compound, were used; one of them, however, in two experiments only.

*Anhydrous Potassium Copper Sulphate*,  $\alpha\text{-CuK}_2(\text{SO}_4)_2 = 333.02$ .—The four different specimens used were prepared by dehydrating the crystallised salt at temperatures between  $115^\circ$  and  $130^\circ$  (*vide supra*).

*Hydrated Sodium Sulphate*,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 321.41$ .—Two different specimens, Nos. 3095 and 3418, were prepared from totally different samples of the commercially pure salt.

*Anhydrous Sodium Sulphate*,  $\text{Na}_2\text{SO}_4 = 141.81$ .—Seven preparations of this salt were examined. No. 3036, prepared by drying the effloresced hydrated salt over sulphuric acid. Nos. 2775 and 3052, samples dried at  $100^\circ$ . No. 3081, dried at  $150^\circ$ . These were all obtained from the same lot of the hydrated salt.

Owing to the excessive degree in which this salt cakes, it was impossible to make any accurate determinations with these samples below  $10^\circ$ . It was found, however, that the anhydrous sulphate precipitated by heating a saturated solution of the salt above  $30^\circ$  dissolved without difficulty, and evolved the same amount of heat as the non-crystalline specimens prepared by efflorescence (see Trans., 1884, 689). Three samples (Nos. 3098, 3407, and 3604) were prepared in this manner from different lots of the hydrated salt.

*Potassium Sulphate*,  $\text{K}_2\text{SO}_4 = 173.88$ .—Four different preparations were made, the finely-powdered salt being sifted through silk, and then heated for many hours at  $200\text{--}250^\circ$ . These specimens did not yield absolutely concordant numbers for their heat of dissolution, due no doubt to the temperature at which they were prepared not being exactly the same (see Trans., 1885, 98). The various results were

reduced to uniformity with those of No. 3603, by adding 18 cal. to those with 2725, — 38 cal. to those with 3428, and — 63 cal. to those with 3613.

*Anhydrous Lithium Sulphate*,  $\text{Li}_2\text{SO}_4 = 109.84$ .—The experiments with this salt do not claim the same amount of accuracy as those with the other salts, as the specimens used were not specially purified. Four samples were prepared by drying the hydrated salt at  $200^\circ$  till constant; No. 3093 appears to give results 81 cal. above those of the other samples, and this amount has consequently been subtracted in Table XII, which contains the results.

A few experiments were performed with the monhydrated sulphates of magnesium, copper, and lithium. Details of the preparation of the four different samples of the first of these will be found in the *Trans.*, 1885, 100. The copper salt, of which one specimen was used, was prepared by heating the crystallised sulphate at  $100^\circ$ .

Two different specimens of the lithium sulphate were used in the different experiments with that salt.

*Calorimetric Results. Explanation of the Tables (p. 291, et seq.).*

All the determinations of the heat of dissolution are collected in the accompanying tables.

The thermometers employed are designated for brevity sake as 80, 81, 83, 84, 16, 39, and 616 respectively.

$w$  is the weight *in vacuo* of the salt taken,  $W$  the water equivalent of the calorimeter and its contents, the actual water being  $601.687 + 0.016T^\circ \text{ C. c.c.}$  (reckoned as so many grams with sp. heat = 1) together with that (if any) which the salt contained.

$T$  is the temperature of the salt before its introduction into the calorimeter, expressed in degrees of the same thermometer as that employed in this latter.

$t$  and  $t'$  are the corrected initial and final temperatures of the calorimetric liquid given in the arbitrary degrees of the thermometers employed, the corrections include\* that due to the temperature of the salt introduced, the cooling (or heating) during its dissolution, the exposure of the column of mercury to the atmospheric temperature, and the calibration correction.

$M$  represents the molecular heat of dissolution of the salt as given by the equation—

$$M = \frac{\left( \frac{t - t'}{t' - t} \right) \alpha WM}{w} ,$$

\* According to the equation  $\frac{(t - T)wc}{W + w}$ ,  $c$  being the specific heat of the salt.

in which  $M$  is the molecular weight of the salt, and  $\alpha$  the mean value of the thermometric degrees in degrees centigrade, these being for—

$$\begin{aligned} 80 &= 0.39633 \\ 81 &= 0.38663 \\ 83 &= 0.38046 \\ 84 &= 0.70659 \\ 16 &= 0.38549 \\ 39 &= 0.06025 \\ 616 &= 0.064161 \end{aligned}$$

The corrections which are applied to  $M$  in certain cases will be understood from what has already been mentioned.

In the case of a hydrated salt, the observed heat of dissolution is represented by  $m$ ,  $M$  being reserved for the "true" heat of dissolution  $= m - xl_m$ ,  $l_m$  being the heat of fusion of 1 gram-mol. of ice.

The last column gives the initial temperature of the experiment in degrees centigrade,  $T$ . Where the mean results to which this temperature applies are deduced from experiments in which the various initial temperatures differed by more than about  $0.08^\circ$ , the centigrade equivalent of each is given in the column under  $t$ .

In most cases, the means are arithmetical means, but in a few instances some determinations have been allowed a smaller weight than others. With hydrated sodium sulphate, experiments with sample 3418 have been allowed twice the value of the others.\*

### *Explanation of the Plates.*

The calorimetric results are given diagrammatically in the accompanying plates; each of these plates contains three curves, one representing the apparent heat of dissolution of the hydrated salt, the second, to which the numbers on the right hand side refer, its "true" heat of dissolution, and the third, to which the numbers on the left refer, the heat of dissolution of the anhydrous salt. The continuous thick lines represent the mean results given in the tables, the others will be explained shortly. The higher the position of a point in any of these curves, the greater is the heat development or the less the heat absorption which it represents.

From the manner in which the curves are arranged, the vertical distance between any points in those representing the heat of dissolution of the salt in its hydrated and anhydrous conditions is proportional to the heat of combination of the salt with its water of

\* Some of the numbers given in these tables will exhibit slight differences from those quoted in previous papers. The present ones are the more accurate, as they depend on a more correct calculation of the scales of the thermometers, and on a larger number of experiments.

crystallisation in the solid state. The values deduced for this latter are represented separately in the curves at the foot of each plate.

*Critical Examination of the Results.*

The most striking and most important feature of these curves is undoubtedly their irregularity. In all of them, there appear more or less sudden breaks, or else they consist of two or more independent curves.

Before discussing them, and the conclusions which may be drawn from them, it will be necessary to show the means which have been taken to make certain that these irregularities cannot be attributed to experimental error, an explanation which will but naturally suggest itself, when it is observed that an appropriate distribution of such an error of less than 100 cal. would cause most of these irregularities to disappear, and that even duplicate experiments at the same temperature will sometimes differ by nearly this amount.

The two thermometers 81 and 83 were alone employed in the first experiments, and the portion of the curves where the irregularities most generally occur, and where they were first noticed, coincides unfortunately with the point where one instrument was substituted for the other (at about 13—15°). The conclusion drawn at first was, of course, that the non-concordance of the instruments was the explanation of these irregularities. Many considerations, however, render such an explanation highly improbable.

(1.) The temperature at which the instruments were changed being notified by a bar across the curves, it will be seen that, although a sudden dip near this point is generally due to the experiments with the highest portion of 83, it is not always so; with  $\text{MgSO}_4$  the dip is due to experiments with 81, while in the case of  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and  $\text{CuK}_2(\text{SO}_4)_2$ , there is no such dip noticeable, and with both  $\text{MgK}_2(\text{SO}_4)_2$  and  $\text{MgK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  the point in question was investigated with both the instruments, and both of them gave identical results.

(2.) Were the irregularities in the curve belonging to the hydrated salt due to errors in the scale of the thermometers, irregularities of an exactly opposite nature would present themselves at nearly the same point in the curve of the anhydrous salt, but the reverse is the case. The depressions or elevations in the one are generally more or less reproduced in the other. If we were to apply corrections to the thermometers such as would reduce any one curve to uniformity, it would only bring into greater prominence the irregularities of the other curves. Besides which, the errors in the calibration curves which would have to be supposed to exist would be out of all proportion to the known magnitude of the probable error from this cause (see *Phil. Mag.*, 1886, **21**, 181).

(3.) The fact that these depressions do not always occur at the same temperature in the different cases, and that others at totally different temperatures exist, would alone be sufficient to disprove their being attributable to such a source.

However, that no proof should be wanting, another thermometer, No. 16, in which this debatable point occurred in the middle of the scale, was introduced, and fresh experiments performed with it. With potassium magnesium sulphate, both hydrated and anhydrous, a whole series were performed in which it was used simultaneously with one of the other instruments; the results with 16 only are (Plate III) represented by a thinner line, and bring out the peculiarities of the curve even more strongly than those with the other thermometers, which form the dotted curve, and in which the individual experiments are marked by crosses. The determinations at  $15^{\circ}$  were repeated thrice with 16, and the mean result here depends on as many as 8 observed values. For the sake of greater security, the experiments with the anhydrous and hydrated salt at the same temperature were performed within half an hour of each other.

With hydrated sodium sulphate (Plate V), 16 was also used, and the results with it are indicated as in the foregoing case. Except at  $12.3^{\circ}$ , where a considerable divergence unfortunately occurs, these results are concordant with those of the other instruments to the most minute details.

Experiments with this thermometer were also performed in the case of hydrated copper sulphate, hydrated magnesium sulphate, and potassium sulphate, and agreed fully with those with the other instruments, as will be seen from the tables, but their number was not sufficient to make it worth while representing them separately in the Plates.

In spite of these results, I did not yet feel satisfied, so remarkable did the facts appear to me; and, consequently, started fresh series of experiments with two instruments, 80 and 82, companion ones to 81 and 83, together with a third new one, 84, embracing all the temperatures required; what experiments were done with them were confined chiefly to potassium sulphate, and will be found to be thoroughly concordant with the others. But before the work with these had progressed very far, the idea occurred of using the same portion of the same instrument, and that a very much more delicate one, for every experiment. All doubt as to the irregularities being due to imperfections in the thermometers were thus set at rest effectually. This instrument, 39, which has been described above, was applied in the case of hydrated magnesium sulphate, anhydrous copper sulphate, potassium sulphate, and anhydrous sodium sulphate (Plates I, II, V, and VI); except with the latter salt, the results with



it only are represented separately by thin lines; the dotted curves representing those with the other instruments, and as will be seen they bear out in every case the conclusions which had been arrived at with the others, the results with 83 would appear to be generally rather high in comparison with those of 39, but the main features of the two are identical. The dotted curve given with copper sulphate refers to three experiments with No. 616.

Such, then, are the means I have taken for assuring myself of the correctness of these observations. But it is impossible by a mere description in outline, or by the synoptical view presented by experiments massed together in tables or diagrams, to convey any adequate conception of the strength of this assurance: of how the few experiments which first had exhibited any irregularity were repeated over and over again, after long intervals of time, with different instruments and with different samples; of how often the work, after being laid aside as complete, would slowly assume the appearance of a phantom conjured up by imperfections in the instruments, and of how often, having been begun all over again, such an idea would be dispelled, and conviction in the accuracy of the results enforced with double power. And now, it is only after having fully investigated all the imperfections of thermometers themselves, having obtained some more delicate and more perfect instruments than any yet produced, and having devised a method of using them which obviates the greater part of the experimental error, that I venture to bring the results before this Society.

### *Hydrates in Solution.*

A cursory inspection of these curves will show that many of them must be still very imperfect. The changes in them are often confined within such narrow limits that, but for the chance selection of some particular temperature for an experiment, this change would never have been detected. The number of observations which would be necessary to establish satisfactorily the precise form of all the lines would be enormous; and it must, therefore, be remembered that, with the materials at present available, numerous as are the complications exhibited, they may in reality be far more so.

Considering, in the first place, what conclusions may be drawn from the examination of any one curve by itself, it will be seen that in no case is the heat of dissolution, whether of a hydrated or anhydrous salt, capable of being represented by a straight line, as is generally assumed (see Berthelot, *Ann. Chim. Phys.*, **29**, 310), nor even by a single curve (except perhaps in the case of  $\text{Na}_2\text{SO}_4$  and  $\text{CuK}_2(\text{SO}_4)_2$ , though probably not so in either of these cases). With some of the an-



hydrous salts taken, this discontinuity might be attributed to variation in their heat of combination with those molecules of water with which they are associated in the solid form, but with hydrated salts no such explanation is possible, and we will take these, therefore, as presenting the more simple problem.

At certain points, then, in these curves there is a more or less sudden increase in the heat developed, and it seems impossible to account for such an increase in any way except by the formation of some new and higher hydrate.

What is generally termed the "hydrate" theory of solution may probably be incapable of giving a full explanation of all the phenomena of dissolution, but it is, I think, proved by overwhelming evidence that many salts in solution do exist in a state of combination with water, and it is highly probable that the hydrates which are there present are often of a higher order than those known in an isolated or solid form; that such is the case with the so-called hydracids and alkalis, Berthelot's researches on the heat developed when they are diluted with varying amounts of water have shown, and they have also shown that the same substance may form more than one such hydrate under different conditions, whilst under intermediate conditions these different hydrates coexist in a state of partial dissociation. The same state of things would appear to hold good in this case as regards salts, the agent which determines their formation being heat instead of excess of water. From a study of any of these curves, it would seem that as the temperature rises the amount of the particular hydrate present reaches a maximum at a certain point and then diminishes, thus producing a curve, when a further rise induces a different state of equilibrium, and another hydrate begins to form causing a fresh development of heat.\*

This explanation, the only one which seems possible, involving the idea that an increase of temperature favours a higher combination between a salt and water, will at first sight appear to be opposed to our general ideas on the subject; but it must be remembered that we ought to have no general ideas on this subject at all, for we have no general knowledge on which to found them. We know, in the case of sodium sulphate and a few other salts, that a certain temperature,

\* Instead of the amount of the hydrate, or the number of water molecules constituting it, being the variable quantity, it might be the energy with which the water in any *one* hydrate is combined with the salt. But this I consider to be improbable, for, as will be shown below, the temperatures at which an *increase* in the heat of dissolution of a salt occurs, are those at which a *decrease* in the energy of combination of the salt with its water of crystallisation takes place; moreover, any increase in this latter quantity is very small in comparison with the *general* increase in the heat of dissolution of a salt as the temperature rises, and could not afford any explanation of it.

generally a high one with reference to the salt in question, favours the dissociation of the salt from the water with which it is combined while in solution, or rather, that the balance of the many forces which the temperature influences results in the dissociation of the hydrate: but whether this be so in all cases, or whether it holds good also for the temperatures far below the melting point of the salt or the boiling point of the solution, we know not, and in the face of this absence of all evidence to the contrary, the present experiments must be accepted as proof. A striking point in favour of such a view is found in the case of sodium sulphate itself, where, instead of having any increased development of heat at about  $14^{\circ}$  and  $23^{\circ}$ , as in other cases, none occurs after  $8^{\circ}$ , that is, at a temperature  $26^{\circ}$  below that at which the affinity of the salt for water is known to diminish; the minor irregularities which occur in this curve at higher temperatures being probably due to experimental errors.

One case which was investigated with great care was that of potassium sulphate, owing to its being an anhydrous salt in every condition as far as is known, and one which, judging by the large absorption of heat on its dissolution, possesses but small affinity for water. As many as 58 experiments, many of them with two thermometers, were made; the delicate instrument 39 was used in 18 cases, and the results with it fully confirmed the previous ones, both as to the existence of a dip at  $14^{\circ}$ , where eight separate determinations were made, and as to the curvature of the line above and below this point (Plate VI). Only at  $19^{\circ}$  are the experiments not altogether concordant, and it may be that another dip occurs here, the curvature between this point downwards to  $14^{\circ}$  being more marked so as to pass through the experiment at  $16.9^{\circ}$ . However this may be, the existence of at least two curves and therefore two different hydrated conditions seems certain. (The results with thermometer 39, below about  $13^{\circ}$ , give results uniformly lower than those with the other thermometers, as has already been noticed.) Side by side with the potassium sulphate curve in Plate VI is given that of lithium sulphate, as well as a reproduction of that of anhydrous sodium sulphate. These three curves will be seen to exhibit no stronger resemblances to each other than they do to those of less closely allied salts. Lithium sulphate, like the potassium salt, shows a dip at about  $14^{\circ}$ , but in other respects the two cases are dissimilar, especially at the lower temperatures, while sodium sulphate differs from both of them, the portion at  $14^{\circ}$ , and indeed that from  $12$ — $17^{\circ}$ , being somewhat higher, rather than lower, than the rest of the curve. It will have been seen that a considerable number of experiments were performed in the case of this salt, Table IX.

The experiment with lithium sulphate at  $23^{\circ}$  is not in accordance

with the rest of the curve; for this, a sample of the salt was employed which was not used in any other experiments, and it may have differed from the other samples in purity; none of the experiments, indeed, with this salt can be regarded as being of such an accurate nature as those with the other salts (see p. 271).

No conclusions can be drawn as to the universality of a dip in the curves at about  $14^{\circ}$ . It occurs in most of the present cases, it is true, but it must be remembered that we are dealing with salts all belonging to the same class, and that in the one which differs most from its congeners—sodium sulphate—such a dip as we have just said is absent; the precise point also at which it occurs is not identical in every case, and the peculiarities which the various curves exhibit at other temperatures are quite sufficient to differentiate them.

The salt which exhibits the greatest number of changes, and one in which these changes have been well established, is hydrated potassium magnesium sulphate (Plate III). The heat of dissolution of this salt between  $2^{\circ}$  and  $24^{\circ}$  constitutes no less than three complete curves, together with the beginning of a fourth one, the temperatures where minima heat developments are observed being  $2^{\circ}$  (perhaps lower in this case),  $7.5^{\circ}$ ,  $15^{\circ}$ , and  $24.3^{\circ}$ . The increase which occurs after the latter temperature caused the case of magnesium sulphate to be investigated at these higher temperatures also, and an analogous rise was discovered, beginning, however, at a lower point, about  $22^{\circ}$ . But magnesium sulphate, unlike its double salt, exhibits no minimum point at  $7.5^{\circ}$ , the heat developed from  $14^{\circ}$  down to  $3^{\circ}$  forming but one continuous curve. It should be remarked that the same confidence cannot be placed in the experiments at very low temperatures as in the other cases, the great difficulty of keeping the temperature of the laboratory constant within a few degrees of zero, and the great effect which the presence of the operator has on the temperature of the calorimeter, rendering the operations less trustworthy.

The curves formed by the copper salts (Plates II and IV) differ very considerably from those of the magnesium salts; the changes which occur are much more abrupt in their nature; those of hydrated copper sulphate, and of the hydrated double sulphate would appear to consist of a series of straight lines rather than curves, and the true heat of dissolution of hydrated copper sulphate is affected by temperature to a considerably smaller extent than is magnesium sulphate, or indeed any of the other salts examined. It must be noticed, however, that, with the exception of anhydrous copper sulphate, these copper salts were not investigated so fully as the magnesium ones.

It is somewhat remarkable that in no case does any marked change appear at  $4^{\circ}$ , the temperature of the maximum density of water.

It is curious that the extent to which the *apparent* heat of dissolution of all three of the hydrated single sulphates varies with the temperature is very small, it being in some cases practically constant for a considerable range of temperature. This, however, is not so with the double sulphates; it would appear as if the potassium sulphate which is present in them still retained its individuality to a considerable extent, its heat of dissolution when combined in the double salt being affected in the same way, though not to the same extent, as when in the free state.

The true "molecular" nature of these double salts is also brought into prominence by the fact that in order to render the curves of their heats of dissolution analogous to those of the single salts, we must, as has been done in these tables, represent the heat evolved on half the scale only. We would almost appear to be dealing with two molecules instead of one, and thus getting a double rate of variation as the temperature falls or rises.\*

It should also be remarked that what is here called the "true heat of dissolution" of both hydrated copper sulphate and hydrated magnesium sulphate is a positive quantity of no mean value, and that such a quantity even does not represent what is in reality the "true" heat of dissolution of the hydrated salt; for from it should be subtracted the heat of fusion of the salt itself, at present an unknown quantity. If the heat thus evolved be due to the combination of the already hydrated salt with more water—and it is difficult to find any other explanation of such an evolution—either this additional water must be considerable in amount, or else the energy with which it is combined must be great, and bear no small ratio to that with which the water of crystallisation is combined.

The series of curves referring to any particular salt are of too rough a character, and their precise meaning too imperfectly understood, to render it profitable to draw further conclusions from them; but with more complete data and more perfect knowledge, it would evidently be possible by prolonging them to obtain numeric values of the heat of formation of each fresh hydrate, and it would appear possible, if not probable, that this heat would not bear any very inconsiderable ratio to that of the formation of the known hydrates, it being thus unnecessary to imagine that the new ones are of a much more complicated character than those already known.

The occurrence of these successive changes in the constitution of a salt in solution, involving successive developments of heat, will involve also successive variations in the specific heat of the solution,

\* This is in reality a consequence of the heat of formation of these salts being affected to only a small extent by temperature, and hence also of their specific heats being practically equal to the sum of those of the constituent sulphates (see p. 288).

too small no doubt to be rendered apparent by the imperfect means which we possess at present for its direct estimation, but none the less certain notwithstanding. We thus have a curious picture of the temperature of a saline solution rising under the influence of a constant source of heat, not with a regular motion, but in a series of pulsations, recurring at irregular intervals, often considerably less than  $10^{\circ}$  apart.

### *Water of Crystallisation.*

We now pass to a consideration of those conclusions which may be drawn from a comparison of the curves of a salt in the hydrated and anhydrous condition. The difference between the quantities which they represent give the heat of combination of the salt with its water of crystallisation; this, it must be clearly understood, refers simply to the *known solid hydrate*, and is entirely independent of the combinations existing in solution.

The results are given in the lower diagrams in the various plates. An inspection of these will show that the heat of this combination is not a constant quantity, it does not even vary in any regular manner, but resembles in nature the heat of dissolution of a salt.

There appears in the first place to be a general tendency towards an increase in the energy with which the salt and water are combined, and such a tendency is in full accordance with the fact already observed of higher hydrates being formed in solution as the temperature is increased. It may be objected that here at any rate we know that a rise of temperature favours loss of water with a solid hydrated salt; but this knowledge, if it can be called such, is derived from experiments at considerably higher temperatures than any here dealt with, and, as far as I know, in none of these observations has the effect of temperature only, or the influence of temperature on the one factor, with elimination of its effects on other concomitant factors, been ascertained. When a salt is heated in air under ordinary conditions, it may be the increased avidity for moisture with which the air becomes endowed, and not any dissociating influence of the temperature itself, which causes the salt to part with its water. Or the loss may occur not because the energy with which it is combined is diminished, but because other tendencies, those towards different arrangements of the atoms in the molecule, for instance, are increased. In the present experiments such possibilities, however, are eliminated, since their results depend on the difference between two quantities which in every respect but one are precisely similar; in every case we have identical initial and final states; such experiments, therefore, are the only ones which can be admitted as evidence on the subject, and the evidence which they bear is not, I

think, much opposed to our general and unauthorised notions on the question, when we remember the lowness of the temperatures with which we are dealing, and when we notice that in the case of sodium sulphate, an increase in these temperatures, low as regards a thermometer, but high as regards the salt, causes a rapid *fall* instead of *rise* in the energy of the combination after about  $15^{\circ}$ .

In addition to all this, it must be pointed out that we are but observing in the case of these so-called molecular compounds a condition which has been well established in the case of many atomic compounds. A sufficiently high temperature will dissociate the constituents of water; but, nevertheless, the heat of their combination (the water being in the gaseous state) *increases* with the temperature, or does so at any rate at all those temperatures where we have any knowledge of the specific heats of the substances concerned. It is quite possible, and, indeed, unless some great changes in specific heats occur, must often be, that, even when a substance is actually partially dissociated, the heat of combination of its constituents in those compound molecules still existing, is *greater* than it is at lower temperatures when no dissociation exists; the heat and the energy of the combination of the constituents being, as a matter of fact, but one of the many factors which determine this dissociation.

It must be borne in mind that the variations in the heat of combination of the salt with its water cannot be looked upon as being so accurately determined as those of the heat of dissolution of the hydrated salt, for they depend on the values of two quantities instead of one. It would be rash to state that the break at  $14^{\circ}$  in the case of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  for instance (Plate I), is not due to experimental error; it is but faintly marked in the mean curve, and by taking the different results of the different thermometers its appearance is very much altered; moreover, the number of determinations with the anhydrous salt were not large.

With copper sulphate (Plate II), however, it is otherwise. The heat of combination between  $2^{\circ}$  and  $23^{\circ}$  is represented by two complete curves and a portion of a third; the curves are steep, and throughout there is a tendency towards a rapid increase in the heat of combination. The first curve, that extending from  $2^{\circ}$  to  $9^{\circ}$  (and to a certain extent the second curve also), will be seen to be due chiefly to the peculiarities exhibited in the heat of dissolution of the anhydrous salt, and, in spite of the large number of determinations which were made between  $4^{\circ}$  and  $9^{\circ}$  with this salt, I cannot feel altogether satisfied as to it. The results with the delicate thermometer 39 (the thin line) reduce considerably the curvature at  $6^{\circ}$  which was given by the other instruments (the thick dotted line); but still it is well marked, and it should be remarked that an extra precaution was generally taken here of using

the salt contained in any one of the sealed tubes in which it was kept at two or three *different* temperatures, and performing the experiments consecutively. Three experiments performed with the most perfect thermometer (616, the thin dotted line) exhibited no curvature at all, but they are inexplicable by the side of the others, and the general inclination of the curve. Of the existence of a second curve from  $9-17^{\circ}$ , and a portion of a third one from  $17-23^{\circ}$ , there can, however, be no doubt. A marked similarity also appears between the various curves; allowing for experimental irregularities, the inclination of the rising and falling portions of each is the same, while a gradual increase in extent prevails throughout them.

Coming now to the double salts, it will be found that similar irregularities exist in the case of potassium magnesium sulphate (Plate III). The heat of combination is represented by one curve from  $4-11^{\circ}$ , by another less abrupt one from  $11^{\circ}$  to about  $19^{\circ}$ , from which point a third curve would seem to start; the results with thermometer 16 are given in the thin line side by side with those of the other instruments (the dotted line), and it will be seen that while they exaggerate some of the features, they make others less apparent, and show clearly the futility of insisting on every minute detail in the curves, and the necessity for considering their general bearings only.

With this salt, however, and also with sodium sulphate, more weight may be attached to the results at present under discussion than in the case of the other salts, for the curves of both the hydrated and anhydrous salts were investigated with the same degree of care. With the magnesium potassium sulphate the extra precaution was adopted in one series of experiments of effecting the determinations with the hydrated and anhydrous compound as nearly as possible at the same time.

With potassium copper sulphate (Plate IV) we have a line of a totally different nature to that of the corresponding magnesium salt; a short sharp curve exists between  $13^{\circ}$  and  $15^{\circ}$ , which would be looked upon with suspicion, were it not that this temperature evidently forms a starting point for a different order of conditions; the inclination of the line being totally different after it from what it is before. The straightness of the two portions of the line is remarkable, as also is the abruptness of the change; this abruptness appears throughout to be a characteristic of the copper salts in contradistinction to those of magnesium.

It should not be forgotten that the scale on which these curves of the double sulphates are represented is only half that used for the single salt, their peculiarities are therefore diminished. They will be found in Plate VII on the larger scale.



The only other case to mention is that of sodium sulphate (Plate V), and here we have a curve of a very different character from those of the other salts. There is a sharp increase in the heat of combination from  $5^{\circ}$  to  $8^{\circ}$  followed by as sharp a decline, another slight rise occurs afterwards as far as  $13^{\circ}$ ; after this, the heat remains constant for the next two or three degrees, and then declines regularly to the end, instead of rising as it does in most of the other cases. Such I interpret the nature of this curve to be: if we take the results of thermometer 16 at  $12^{\circ}$ , where there is unfortunately some error with one of the instruments, and use it on all the details exhibited at higher temperatures, we should get the excrescence at  $8^{\circ}$ , repeated in a less marked manner at  $12^{\circ}$ , and again more feebly still at  $16\cdot5^{\circ}$ , with a shadow of a third repetition at  $21^{\circ}$ ; but although the results of the different instruments are remarkably concordant (except at  $12^{\circ}$ ), the variations causing the irregularities at the higher temperatures are so slight that they may be attributed to experimental error, though, it is true, the number of experiments at each point is considerable; at any rate it is safer not to insist on their actual existence.

The curve of the anhydrous salt was examined with special care in the case of sodium sulphate in order to ascertain whether it exhibited any peculiarities at those temperatures where the hydrated salt did so, but no such resemblance even of the faintest description could be traced anywhere. Indeed, the only indication which exists of the anhydrous salt not giving a continuous curve throughout is that the portion between  $12^{\circ}$  and  $17^{\circ}$  is decidedly higher than the rest of the line.

The experiments with the monohydrated sulphates quoted in Table XIII are too few in number to give much weight to any conclusions drawn from them, but, such as they are, they tend to show that the same irregularities exist in the heat of formation of the lower hydrates as in that of the higher ones. The copper salt, however, is the only one where the temperature was varied sufficiently for such purposes.

The following are the values which may be deduced in the various cases:—

(1.) For  $\text{CuSO}_4 + \text{H}_2\text{O}$  (solid)—

At  $13\cdot00^{\circ}$ , 5615 cal.; at  $17\cdot83^{\circ}$ , 5743 cal.; and at  $22\cdot88^{\circ}$ , 5914 cal., numbers showing a rapid increase in the heat of combination with the temperature, as with the pentahydrated salt, though not at a regular, but at an increasing rate, this rate being  $26\cdot5$  cal. per degree between the first and second temperature, and  $33\cdot8$  between the second and third.

(2.) For  $\text{MgSO}_4 + \text{H}_2\text{O}$  (solid)—

7012 cal. at  $22\cdot3^{\circ}$ .



(3.) For  $\text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$  (solid)—

At  $13.8^\circ$ , 1267 cal.; and at  $12.97^\circ$ , 1417 cal. Mean, 1342 cal. at  $13.39^\circ$ ;

to this latter, however, no very special value is to be attached (see p. 271).

Here, then, we have a series of changes analogous to those taking place in saline solutions, but more remarkable, inasmuch as the substances which exhibit them undergo no change in centesimal composition.

That changes of temperature bring about changes in the constitution, not only of complex molecules such as those of hydrated salts, but of the more simple bodies which are termed atomic compounds, as well as of the elements themselves, is already well known in some few cases; but the universality of these changes, and the frequency of their occurrence, is a totally new feature.

Our ideas of the stability of a compound must be considerably modified; we must recognise that the substance which we are dealing with at one temperature may be totally different in constitution from the same substance at a temperature only  $10^\circ$  higher or lower. These changes can only be attributed to alterations in the relations between the various atoms or molecules in the hydrated salt. They cannot be explained by changes in the grouping of the many molecules which (probably) act as physical units, for the nature of the determinations eliminates entirely the influence of any such changes. These variations in the heat of combination of the components of the molecule will, as in the case of solutions, necessitate slight corresponding changes in the specific heat of the substance, and we shall consequently have the temperature of the salt under a constant source of heat, rising in an undulatory instead of a regular manner.

One other very important feature remains to be noticed. On referring to the plates, it will be seen that the high portions in those curves which represent the heat of combination of the salt with its water of crystallisation, coincide with the low portions in those representing the heat developed in the dissolution of that salt, and *vice versa*; the stronger the energy with which the few molecules of water in the solid salt are retained, the smaller is the number of molecules in the liquid hydrate. It would appear as if a rise of temperature causes an increase in the energy of the combination of the water with the salt up to certain point, but that a further increase, instead of raising this energy still higher, takes a different direction, and endows the salt with a capacity for taking up a larger number of molecules; but inasmuch as the amount of water held is now greater, each individual portion of it is held with diminished

energy. Such would appear to be the case, but it is not possible to affirm it with confidence, for we are not studying the salt in the same state in both cases; in one case it is in the solid, and in the other in the liquid condition; but another instance of a like nature, not open to such objections, will be brought forward shortly, and the strong presumptive evidence which we have here for supposing the relations between certain portions of a molecule to be influenced by a further addition to it, is one which is certainly in accordance with our general ideas on "atomic" compounds, and one which I have elsewhere (*J. Chem. Soc.*, Abstr. of Proceedings, 1885-6, 112) argued on other grounds to hold good with reference to water of hydration.

It will follow from the fact that the heat of combination of a salt with its water is not a constant quantity, that the specific heat of the hydrated salt is not exactly equal to the sum of those of the anhydrous salt and water (solid) in it. This conclusion will hold good even if we assume an error to have occurred in the number taken for the specific heat of ice at these high temperatures (see p. 262), for, not to mention the irregularities in the curves themselves, the application of a correction in this latter, such as would reduce the curve (*i.e.*, that of the heat of combination) to a horizontal line in one case, would only increase its divergence from such a line in another (*cf.* the latter portions of the copper sulphate and sodium sulphate curves).

The general tendency exhibited in the majority of cases being in the direction of an increase of the heat of combination with a rise of temperature, it follows (p. 260) that the specific heat of the hydrated salt will be somewhat *less* than the sum of those of the solid water and anhydrous salt. It is difficult, however, to speak with any certainty of these "general tendencies," for the range of temperatures in the present experiments is very small in comparison with that through which the salt is capable of existing.

An inspection of the numbers given for the specific heats of salts, and the great differences in those obtained by different observers, will make it apparent why any direct determinations of these specific heats should have failed in elucidating these facts.

It will be necessary to stop for a moment to enquire what effect a more accurate method of calculation, and a more perfect knowledge of the data on which those calculations were based, might have on the general conclusions arrived at here.

To begin with, it is only by assuming sudden alterations in the specific heat of an anhydrous salt, or of ice, that the alterations in the curves here given could be eliminated. Such alterations would involve similar conclusions as regards the constitution of the salt (or of ice), as we have here drawn as to that of the hydrated salt, and would thus be but a poor explanation. The fact that the curves of

the true heat of dissolution of the hydrated salt preserve a course so nearly parallel to those of the anhydrous salts in most cases, and that they converge to a considerable extent in the case of sodium sulphate (the only case in which we have extraneous reasons for expecting that they would converge, *i.e.*, that a rise in the temperature would diminish the energy with which the solid salt retains its water), is strong evidence that the water in a crystallised salt is *solid* water, and that in the dissolved salt is liquid water, and also that the numbers which we have taken for the heat of fusion of this solid water are very near the truth.

Secondly, what would be the general drift of the error caused by taking the volume of the solution as being equivalent to so many grams with a sp. heat of unity instead of basing the calculations on the actual sp. heat of the solution. On p. 267, where copper sulphate was taken as an instance, the error being greater in its case than in any other, it was shown that, as far as we could judge from the very imperfect data at our disposal, whatever the error in the actual quantities might be, the relative error in the comparison of two experiments at  $4^{\circ}$  and  $24^{\circ}$  respectively, would be but  $\frac{1}{1500}$ th; the sp. heat of the solution at the latter temperature by comparison with the sp. heat at the former would be under-estimated by that amount. Referring to Plate II, we see that 16700 cal. is the heat of dissolution of the anhydrous salt as given at  $24^{\circ}$ , it therefore ought to have been  $\frac{1}{1500}$ th greater, *i.e.*, 16810 cal.; in the same way, the apparent heat of dissolution of the hydrated salt should have been -2820 instead of -2800, giving for its "true" heat of dissolution 5340 instead of 5360; the correction of the calculations would thus give  $(16810 - 5340 = )$  11470 cal., as the heat of combination of the solid with its water, instead of  $(16700 - 5360 = )$  11340 cal. which was the value taken. A more correct method of calculation would thus only bring out into stronger prominence the increase in this latter quantity as the temperature rises.

Lastly, these experiments themselves have shown the existence of a more subtle source of error, and one which it is impossible to allow for. The initial temperature of the water is that at which the dissolution must be regarded as being effected, the final temperature serving only as a means of measuring the heat developed; but the proper use of this final temperature depends on our knowledge of the sp. heat of the solution between it and the initial temperature, and, owing to the variations here exhibited in this, it will not be the same for the interval from  $t$  to  $t'$  when  $t'$  is higher than  $t$ , as it is for a like interval when  $t'$  is below  $t$ , *i.e.*, when dissolving the anhydrous and hydrated salts at the same initial temperatures we shall generally be using liquids possessing different sp. heats in the

two cases. Taking as an instance experiments at  $16^\circ$  with potassium magnesium sulphate, and remembering that it is the curve of the hydrated salt which gives a representation of the sp. heat of the solution, this point  $16^\circ$  occurs where the curve is rising, *i.e.*, where an increased development of heat and, therefore, a diminished sp. heat, is brought about by an increase in temperature. In the experiment here with the anhydrous salt, the *rise* measured from  $16^\circ$  to (say)  $17^\circ$  will have corresponded to a *smaller* development than the *fall*, measured in the case of the hydrated salt, from  $16^\circ$  to  $15^\circ$ , the former quantity will have been over-estimated, and the latter under-estimated, the individual experiment should have been plotted at the points marked A and B respectively; these in each case will be *lower* in the diagram, and, if the fall measured is of the same extent as the rise measured, they will be lower to the same extent, thus making no difference in the distance between them, *i.e.*, in the heat of the combination of the salt with its water as deduced from them. In other cases, where the rise and fall measured were not equal, an error will have occurred from this cause which may have resulted in the exaggeration or diminution of the peculiarities of this curve, but it will probably have been of very small extent, and will have affected the general nature of the curve but slightly.

#### *Heat of Formation of Double Salts.*

The experiments which have already been described afforded the means for the determination of another quantity, namely, the heat of combination of two sulphates to form the double sulphates,  $\text{MgK}_2(\text{SO}_4)_2$  and  $\text{CuK}_2(\text{SO}_4)_2$ , in the solid state. Where  $x$  represents this amount, and  $M$  the molecular heat of dissolution of the two single and double sulphates—

$$x = (M_K + M_{Mg}) - M_{MgK} - N,$$

in which  $N$  represents the heat developed on mixing solutions of the constituent sulphates. This latter quantity has been measured by various physicists, and has been given by them as *nil* in the case of both copper sulphate and magnesium sulphate. A few fresh determinations of it are given in Table XIV. In order to render these determinations more accurate, blank experiments were interspersed with the others, and a small correction, which would appear to be generally necessary, owing to loss or gain of heat while the solutions were being mixed, was thus made.

The results bear out fully the conclusions of former experimenters as to the value of  $N$  being negligible, and consequently the heat of combination of the two sulphates in the double salt will be the difference between the heat of dissolution of the anhydrous double salt, and the

sum of those of its constituents in the anhydrous state also. The various values thus deduced for these quantities at different temperatures are plotted out into curves in Plate VII.

The general features shown in the case of the magnesium salt is that of two curves meeting at about  $14^{\circ}$  where the heat of combination is at a minimum; the portion between  $2^{\circ}$  and  $6^{\circ}$  would appear to form part of another curve; but in this case, more than in previous ones, we must not insist too stringently on the details which the lines exhibit, as each point in them is dependent on the correct estimation of three separate quantities, each of which is of considerable magnitude.

With the copper salt, we find a minimum reached at about the same temperature,  $14^{\circ}$ , the heat of combination decreasing gradually, and perhaps regularly, up to this point, after which it again increases, but at a very much greater rate.\*

Here then, with the components of a double salt, we have the same remarkable variations in the energy of combination as we have between a salt and its water of crystallisation, and similar conclusions may be drawn from them.

Side by side with these curves are given those which represent the heat of combination of the same double salt with its water of hydration (drawn to the same scale as the former), and a comparison of the two leads to important conclusions. It will be seen that, with no exceptions other than what may be attributed to experimental error, the temperatures at which the one quantity attains a maximum is the temperature at which the other attains a minimum. This is very strikingly displayed in the cases of both salts, and fully bears out the conclusion which was drawn above, that the relationship between any two parts of a complex molecule is influenced by any change in the other parts of it. Here we appear to have a principle of compensation carried out between the various parts of the solid molecule, just as in the former case an increase of affinity exhibited by a salt in taking up a further supply of water, seemed to leave it but a smaller amount to be expended on that already attached to it.

Although this principle of intramolecular compensation may be more confidently affirmed from these experiments with the double salts than it was with the hydrated salts, it can yet be regarded only as strongly probable, and not absolutely proved: even here we are not dealing with the same molecule in both cases, for the heat of hydration

\* Owing to a clerical error in a previous communication (this vol., 7 and 15), the heat of dissolution of copper sulphate was quoted as being 600 cal. less than it should have been, and the heat of formation of the double salt was consequently under-estimated to the same extent. The present numbers contain also some further corrections of an unimportant nature (see foot note, p. 272).

is measured in the hydrated salt, whereas the heat of combination of the other constituents is measured in the anhydrous salt. It is difficult to conceive, however, any means whereby a nearer approach to positive evidence could be obtained.

It will be noticed that with both pairs of curves in Plate VII, the one individual curve is determined from two quantities, and the other from three quantities, and that of these quantities one only (the heat of dissolution of the anhydrous salt) is common to the two; thus the data on which these two curves are based are to a considerable extent independent of each other.

### *Summary and Conclusion.*

The main points of the present communication may be summarised as follows:—

1. The heat of dissolution of a salt at different temperatures is not represented by a straight line, but by a curve, or generally by a series of curves.

2. Each of these curves probably indicates the formation and existence of some fresh hydrate in the solution.

3. The formation of higher hydrates as the temperature rises would not appear to hold good when we approach a temperature which is near the melting point of the solid hydrated salt, as in the case of sodium sulphate.

4. From the constant variations in the thermal phenomena attending dissolution at different temperatures, it follows that the specific heats of saline solutions exhibit similar variations, remaining constant, or even varying at a uniform rate, throughout very limited ranges only.

5. The heat of combination of a salt with its water of crystallisation in the solid state undergoes similar series of changes.

6. From this it follows that the specific heat of such a salt is not a constant quantity, and that it is not exactly equal to the sum of that of the anhydrous salt and the solid water present, but is generally somewhat less.

7. The general tendency between 2° and 23° is towards an increase in the energy with which the water is combined.

8. Any temperature at which a higher hydrate is formed by a salt in solution, is marked by a *decrease* in the heat of combination of the salt with its water of crystallisation in the solid state.

9. The heat of combination of two sulphates to form a double salt is subject to variations of the same nature as that of the combination of a salt with water.

10. The variations in the heat of combination of the two salts is

attended by variations of an opposite sign in the heat of combination of the double salt and the water combined with it.

11. Most of the salts here investigated show some points of similarity in the curves which they yield, but each possesses specific peculiarities.

12. The peculiarities exhibited by a single salt appear to be reproduced to a certain extent in the double salts which they form, illustrated by the rise in the curves of both the magnesium salts at about  $22^{\circ}$ , and the character of abruptness displayed in the case of both the copper salts.

In drawing these conclusions care must be taken that they be not understood in too general a sense. The temperature of  $14^{\circ}$  appears, for instance, to correspond so often to a depression in the curves, that we might be led to attribute this depression to changes undergone by the water molecules themselves at this temperature; but it must be remembered that the salts which have been investigated belong not only to the same type, the sulphates, but chiefly also to the same class of that type, and that the one which differs most from the others in its nature (sodium sulphate) exhibits a totally different behaviour at this temperature; and even those salts which are most similar in their nature exhibit very marked differences at many temperatures in the heat of their dissolution.

It would indeed have been more satisfactory to have examined a greater variety of salts, and this would have been done had not the work been begun with a different object in view, and had it not progressed a considerable way towards its conclusion before its more important bearings became apparent. It is my hope, however, to extend the work at some future time, though the laborious and trying nature of it may prevent my doing so for some time; no form of apparatus has at present been devised whereby such experiments as these would not suffer in accuracy by being performed at temperatures other than that of the surrounding air, and the absolute dependence of one's work on the atmospheric conditions of a changeable climate, the great waste of time which its changes entail, together with the hardship of working for days together at temperatures but a few degrees above zero, and on other occasions in an atmosphere superheated some  $20^{\circ}$  or  $25^{\circ}$  by burning gas, and the constant attention requisite in maintaining these temperatures for a long period of time, render the work of a most laborious and unenviable description.

TABLE I.—*Heat of Dissolution of Anhydrous Magnesium Sulphate.*  $\text{MgSO}_4 = 119.76$ ;  $\frac{3}{40} \text{ mol.} = 8.982 \text{ grams.}$

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t' - t$ .	M.	T.
1. 2718 .....	9.098	614.27	81	33.18	32.201	38.836	6.635	20743	22.320.
2. 2754 .....	9.007	614.27	81	35.40	32.306	38.890	6.584	20792	
3. 2718 and 2754	8.974	614.27	81	35.80	32.416	38.927	6.511	(20637)	
4. 2754 .....	8.417	614.20	81	19.71	19.835	25.880	6.045	20425	17.52
5. 2718 .....	10.783	614.15	81	12.92 (14.685)	12.497	20.128	7.631	20139	14.773
6. 3092 .....	8.974	614.16	81	12.34 (14.85)	12.9215	19.288	6.3665	20178	
7. 2718 .....	9.039	613.91	81	13.08 (13.44)	9.268	15.6635	6.3955	19480	
8. 2718 .....	9.106	613.91	81	13.24 (13.44)	9.301	15.712	6.411	20013	
9. 2754 .....	9.128	613.91	81	12.70 (13.44)	9.267	15.711	6.444	20068	
10. 2754 .....	9.021	613.91	81	12.81	9.196	15.539	6.343	19988	13.43
11. 2718 .....	10.885	614.13	81	8.88 (13.37)	8.8935	16.563	7.4695	20051	
12. 2754 .....	9.043	614.07	83	25.79	25.024	31.443	6.419	19860	10.53
13. 2754 .....	8.813	614.00	83	13.10 (5.96)	13.0315	19.152	6.1205	19429	5.98
14. 2718 .....	9.105	614.15	83	14.37 (6.00)	13.076	19.391	6.315	19410	
15. 2718 .....	10.157	613.94	83	7.68	3.208	10.086	6.878	18943	2.23
16. 2754 .....	8.947	613.97	83	3.07	2.0835	8.106	6.0225	18830	1.80



TABLE II.—Heat of Dissolution of Heptahydrated Magnesium Sulphate.  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 245.48; \frac{3}{40} \text{ mol.}$

= 18.411 grams.

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t - t'$ .	m.	$7l_m$ .	M.	T.
1. 3610	18.539	617.92	39	41.02	39.954	32.1345	7.8205	-3843	-11460	7622	24.63 C.
2. 3610	18.509	617.90	39	40.38	41.641	33.8695	7.7715	-3834			
3. 2756	18.238	617.47	81	33.28	32.2605	31.0545	1.206	-3875			
4. 2756	18.470	617.59	81	33.47	32.2625 (22.32)	31.0145	1.248	-3960			
5. 2756	18.408	617.56	81	34.28	32.411	31.183	1.228	-3910	-11315	7411	22.278
6. 3610	18.554	617.89	39	40.22	40.457 (22.215)	32.587	7.870	-3865			
7. 3610	18.519	617.87	39	41.18	40.448	31.5015	7.9465	-3909			
8. 3610	18.498	617.83	39	40.63	40.333	32.408	7.825	-3853	-11180	7319	19.99
9. 3610	18.563	617.86	39	41.33	40.386	32.502	7.884	-3869			
10. 2756	18.629	619.61	16	22.21	19.8805	18.6725	1.208	-3822			
				—	30.127	28.883	1.241	-3915			
11. 3610	18.530	617.79	39	41.34	40.850	33.626	7.828	-3848	-11028	7165	17.543
12. 3610	18.527	617.79	39	39.74	40.563	33.3415	7.8255	-3847			
13. 3608	18.410	617.73	39	40.00	40.677	33.815	7.859	-3880			
14. 3608	18.558	617.82	39	40.13	40.4965	33.513	7.9805	-3910			
15. 3608	18.421	617.74	39	41.77	40.5945	32.6585	7.936	-3915			
16. 3608	18.511	617.79	39	41.57	40.0665	33.1325	7.874	-3867	-10968	7083	16.507
				16.80	16.973	15.7615	1.2115	-3896			
17. 3416	18.272	619.09	16	—	27.174	25.969	1.201	-3850			
				—	12.9695	11.714	1.2555	-3984			
18. 2756	18.464	617.44	81	12.54	13.140	11.896	1.244	-3954			
19. 2756	18.436	617.44	81	12.60	13.1805	11.950	1.2305	-3909			
20. 2756	18.447	617.44	81	12.91	13.1805	11.9705	1.193	-3993	-10871	6915	14.828
21. 2756	17.478	616.38	16	12.65	23.3595	22.1535	1.206	-4025			
				—	41.086	33.1175	7.9785	-3924			
22. 3608	18.456	617.72	39	42.86	41.086	33.1175	7.9785	-3924			

TABLE II.—(continued.)

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t - t'$ .	m.	$7l_m$ .	M.	T.
23. 2756	17.503	618.66	83	32.92	33.041 (13.57)	31.838	1.203	-3971			
			16	—	19.837	18.655	1.182	-3954			
24. 2756	18.072	618.92	83	27.97	31.657 (13.05)	30.399	1.258	-4024			
			16	—	18.480	17.242	1.238	-4012	-4013	6759	13° 139 C.
25. 3608	18.424	617.64	39	41.47	40.546 (13.13)	32.3665	8.1795	-4014			
26. 3608	18.533	617.69	39	40.43	40.646 (12.815)	32.3995	8.2465	-4025			
27. 3608	18.416	617.60	39	42.66	40.872 (11.39)	32.6775	8.1945	-4044			
28. 3608	18.514	617.69	39	40.60	40.3885 (10.78)	32.1835	8.205	-4029			
29. 3608	18.404	617.64	39	41.00	40.586 (7.32)	32.423	8.163	-4030		6649	11.187
30. 2756	18.281	617.30	83	25.81	25.5125	24.2895	1.253	-3952			
31. 2688	19.726	634.34	83	19.52	16.840 (7.35)	15.4825	1.3575	-4077			
32. 2688	18.295	617.12	83	19.82	16.615 (7.4)	15.325	1.290	-4064			
33. 3416	15.520	617.55	83	17.12	16.968 (3.04)	15.877	1.091	-4054	-4036	6389	7.41
34. 2678	18.797	617.38	83	19.82	16.929 (7.7)	15.641	1.288	-3951			
35. 2678	18.896	617.62	83	19.92	17.742 (2.93)	16.4295	1.3125	-4007			
36. 2756	18.347	617.26	83	14.03	13.097	11.7895	1.3075		-4108	6234	6.00
37. 2756	16.217	616.11	83	2.84	5.3095	4.1165	1.193	-4233	-4202	5952	2.98
38. 2756	18.469	617.27	83	7.44	5.119	3.785	1.336	-4170			

TABLE III.—Heat of Dissolution of Anhydrous Copper Sulphate.  $\text{CuSO}_4 = 158.84; \frac{3}{40} \text{ mol.} = 11.913 \text{ grams.}$ 

Sample.	w.	W.	Therm.	$\tau$ .	t.	$t'$ .	$t' - t$ .	M.	T.
1. 2729	11.810	614.27	81	34.40	33.753	38.932	5.179	16543 + 160	
2. 2729	12.018	614.27	81	34.42	33.835	39.044	4.999	16618	22.92C.
3. 2729	12.008	614.29	81	34.84	33.863	39.107	5.244	16351 + 160	
4. 3094	11.923	614.29	81	34.50	33.9445	39.208	5.2635	16475 + 160	
5. 2729	11.940	614.82	81	22.55	21.6205	26.7595	5.139	16654	
6. 3094	11.861	614.82	81	22.65	21.6215	26.7515	5.130	16235	
7. 2729	11.958	614.11	81	16.10	19.582	24.6925	5.1105	16314	17.96
8. 3094	11.840	614.17	81	21.84	16.8035	21.850	5.0465	16118	
9. 2729	11.873	614.17	81	18.36	16.8565	21.921	5.0645	16076	16.36
10. 3401	12.063	614.16	81	13.29	13.662	18.771	5.109	16089	
11. 3401	12.095	614.18	81	13.58	13.623	18.758	5.135	15974	15.135
12. 2729	11.747	614.10	83	32.70	33.016	38.002	4.986	15752 + 160 = 15912	
13. 3094	11.599	614.10	83	33.98	33.1615	38.146	4.9845	15955	
14. 3401	11.791	614.10	83	33.12	33.2465	38.311	5.0645	15940	
15. 3401	11.951	614.10	83	33.02	33.011	38.152	5.141	15964	13.57
16. 3401	11.921	615.93	83	38.05	33.014	38.104	5.090	15866	
17. 3609	11.990	614.39	81	—	9.619	14.607	4.988	15791	
18. 2729	11.900	614.01	83	13.97	11.853	44.2855	32.4325	15941	
19. 2729	11.928	614.10	83	34.08	30.4725	35.562	5.0895	15870	
20. 3413	10.987	614.08	83	28.95	30.2765	35.3045	5.028	15643 + 160 = 15803	12.56
21. 3413	11.931	614.08	83	28.19	26.3975	31.4765	5.079	15724	
22. 3413	11.952	614.08	83	27.58	26.789	31.836	5.047	15697	
23. 3413	11.994	614.08	83	26.65	26.661	31.685	5.024	15599	
24. 3414	11.945	614.05	83	25.52	25.4415	31.638	5.1005	15771	
25. 3414	11.988	614.05	83	25.71	25.4725	30.491	5.0495	15687	
26. 3414	11.907	614.05	83	26.10	25.5085	30.5365	5.064	15676	10.88
27. 3414	11.946	614.05	83	26.02	25.4225	30.5315	5.023	15655	
28. 3609	12.009	614.34	39	13.41	11.450	30.4585	5.036	15644	
29. 3609	11.844	614.34	39	13.21	11.910	43.139	31.689	15622	
						43.156	31.246	15648	

TABLE III—(continued.)

Sample.	w.	W.	Therm.	r.	t.	t'.	t' - t.	M.	T.
30. 3612	12·042	608·44	616	13·67	14·648	46·621	29·973	15435	
31. 3611	12·059	608·18	39	9·49	12·085	44·074	31·989	15440	
32. 3609	11·876	614·32	39	12·92	11·812	42·9745	31·1625	15429	
33. 3609	11·859	614·32	39	16·06	12·182	43·299	31·117	15458	
34. 3609	11·979	614·32	39	13·11	11·776	43·340	31·564	15491	
35. 3609	12·265	614·39	39	8·02	11·690	44·5165	32·8265	15502	15450 8° 951C.
36. 2729	11·865	614·05	83	20·37	20·819	25·7475	4·9285	15427	
37. 2729	11·773	614·05	83	20·56	20·8595	25·7585	4·8980	15439	
38. 2739	12·059	614·05	83	20·78	20·880	25·8605	4·9805	15451	
39. 3094	11·987	614·05	83	21·37	20·7105	25·7015	4·991	15450	
40. 2729	11·875	614·00	83	14·26	14·170	19·0355	4·8645	15200 + 160 = 15360	
41. 3427	12·025	614·00	83	13·22	14·107	19·0735	4·9665	15325	
42. 3612	12·047	608·40	616	13·28	13·9005	43·412	29·6115	15239	
43. 3611	11·493	608·14	39	11·89	12·6085	42·9245	30·316	15352	
44. 3611	11·968	608·14	39	12·76	12·395	43·736	31·341	15241	
45. 3611	11·970	614·28	39	6·28	11·518	42·586	31·068	15258	
46. 3609	11·874	614·28	39	14·63	12·119	42·980	30·861	15279	
47. 3609	12·047	614·28	39	12·71	12·5405	43·734	31·2935	15276	
48. 2729	11·910	614·00	83	15·42	12·826	17·666	4·840	15169 + 160 = 15329	
49. 3094	11·958	614·00	83	15·81	12·769	17·683	4·914	15345	
50. 3401	10·360	614·35	83	9·99	10·077	14·284	4·207	15076	
51. 3612	11·984	608·37	616	13·49	14·076	43·212	29·146	15079	
52. 3609	11·535	608·11	39	12·26	12·421	42·1425	29·7215	15066	
53. 3611	11·945	608·11	39	10·02	12·143	42·979	30·836	15024	
54. 3401	10·900	614·33	83	8·74	7·591	12·0015	4·4105	15022	
55. 3413	12·073	613·96	83	5·34	6·6375	11·456	8·8185	14808	
56. 2729	11·838	613·95	83	1·63	3·183	7·8545	4·6715	14647 + 160 = 14807	
57. 3401	11·808	613·95	83	1·68	2·512	7·210	4·698	14762	14785 2·092

TABLE IV.—Heat of Dissolution of Pentahydrated Copper Sulphate.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 248.64; \frac{3}{40} \text{ mol.} = 18.648 \text{ grams.}$ 

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t - t'$ .	m.	$5l_m$ .	M.	T.
1. 2736	17.508	614.43	81	33.54	33.6585	32.830	0.8285	-2795	-8110	6312	22.9 C.
2. 2736	18.241	614.69	81	34.61	33.792	32.927	0.865	-2802	-8060	5279	21.75
3. 2736	18.105	616.63	16	30.56	30.821	29.997	0.826	-2760	-8060	5279	21.75
4. 2736	18.326	614.59	81	18.81	41.079	40.238	0.841	-2802	-7921	5159	18.51
5. 2736	18.500	614.66	81	19.61	22.551	21.691	0.860	-2772	-7878	5131	17.47
6. 2736	18.742	614.82	81	22.28	21.611	20.9785	0.877	-2801	-7833	5037	16.44
7. 2736	18.574	616.72	81	22.43	21.840	20.9785	0.8615	-2717	-7777	4920	15.12
8. 2736	18.756	616.51	16	16.90	19.683	18.831	0.852	-2720	-7718	4806	13.71
9. 2736	18.826	616.52	81	16.96	29.929	29.0575	0.8715	-2774	-7645	4757	12.07
10. 2736	18.637	614.60	83	16.90	16.984	16.0985	0.8855	-2798	-7516	4545	9.00
11. 2736	18.555	614.57	83	13.29	27.196	26.309	0.887	-2794	-7385	4347	5.95
12. 2736	18.729	616.51	16	13.29	12.5935	12.6805	0.9135	-2876	-7237	4113	2.66
13. 2736	18.464	616.30	83	35.77	23.782	22.878	0.904	-2838	-7227	4000	2.49
14. 2736	18.194	614.46	83	35.77	33.3965	32.466	0.9305	-2903			
15. 2736	19.165	614.80	83	32.95	33.354	32.428	0.926	-2901			
16. 2736	18.471	614.51	83	32.95	33.426	32.4745	0.9515	-2963			
17. 2736	18.854	614.61	83	16	20.2045	19.291	0.9135	-2882			
18. 2736	18.197	614.37	83	28.24	29.128	28.2195	0.9085	-2869			
19. 2736	17.867	614.18	83	22.97	15.972	15.063	0.909	-2908			
			83	20.27	21.1225	20.1965	0.926	-2958			
			83	20.75	20.7995	19.8165	0.983	-2983			
			83	20.75	12.8875	11.924	0.9635	-3032			
			83	1.75	13.052	12.0645	0.9875	-3045			
			83	2.67	4.355	3.355	0.978				
			83	2.67	3.837	2.844	0.993				

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Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t' - t$ .	M.	Correc- tion.	M corrected.	T.
1. 3432	11.240	614.30	81	36.73	37.1605	39.008	1.8475	11475	+ 1113	12588	24.22 C.
2. 3054	11.067	614.27	81	28.70	32.117	33.9495	1.8325	11559	+ 417	11976	12065
3. 3054	11.094	614.27	81	28.88	32.1875	34.0385	1.851	11648	+ 417	12045	12039
4. 2796	11.184	614.27	81	36.36	32.324	34.234	1.910	11925	+ 120	11989	12055
5. 3000	11.049	614.27	81	35.00	32.0625	33.9515	1.889	11935	+ 54	12159	12039
6. 2796 and 3006	11.011	614.27	81	32.77	32.230	34.134	1.904	12071	+ 87	12104	12039
7. 3039	11.140	614.27	81	31.53	32.2315	34.163	1.9315	—	—	11949	12027
8. 3039	11.027	614.27	81	32.19	32.2285	34.116	1.8875	—	—	11991	21.01
9. 3432	11.139	615.97	81	28.84	28.859	30.590	1.731	10878	+ 1113	11734	11719
10. 3432	11.045	615.95	16	24.79	24.881	26.501	1.676	10621	+ 1113	11705	19.48
11. 2796 and 3006	11.089	614.23	81	—	35.140	36.801	1.661	10592	+ 1113	11480	18.775
12. 3432	11.168	615.92	16	23.33	23.044	24.8685	1.8245	11537	+ 87	11462	11471
13. 3432	11.077	614.18	81	20.37	19.676	21.330	1.654	10367	+ 1113	10966	16.24
14. 2796 and 3006	11.088	614.14	81	15.65	29.916	31.572	1.656	10349	+ 1113	10855	14.94
15. 3432	11.021	615.88	16	12.54	16.499	18.1115	1.6125	10161	+ 87	11019	10963
16. 3432	11.009	615.86	83	35.96	13.178 (14.96)	14.9085	1.7305	10922	+ 1113	10928	10950
17. 3432	11.104	615.83	16	—	23.268 (14.91)	24.824	1.5395	9777	+ 1113	10966	10973
18. 3432	10.961	615.81	83	32.38	36.578 (14.93)	38.173	1.595	9978	+ 1113	10819	10764
19. 3432	10.993	615.77	16	—	23.353	24.890	1.537	9743	+ 1113	10709	10403
20. 3432	11.042	615.74	83	27.36	18.4625	19.9895	1.527	9596	+ 1113	10399	9919
21. 2796 and 3000	11.172	614.01	83	20.25	27.474	28.952	1.478	9286	+ 1113	10407	9719
22. 2796 and 3000	11.079	614.01	83	16.88	14.336	15.796	1.460	9294	+ 1113	9931	9559
23. 3432	11.216	613.97	83	—	21.0895	22.494	1.4045	8818	+ 1113	9908	8992
24. 2796 and 3006	10.726	613.95	83	16.88	8.024	9.4065	1.3825	8795	+ 1113	9744	8585
			83	17.032	4.026	18.408	1.376	8581	+ 1113	9694	
			16	—	4.026	5.392	1.366	8631	+ 1113	9598	
			83	14.50	14.8825	16.430	1.5475	9511	+ 87	9520	
			83	14.84	14.7765	16.2985	1.522	9433	+ 87	9520	
			83	8.41	8.235	9.522	1.287	7879	+ 1113		
			83	7.63	4.1895	5.517	1.3275	8498	+ 87		

TABLE VI.—*Heat of Dissolution of Hexhydrated Potassium Magnesium*

Sample.	w.	W.	Therm.	$\tau$ .	t.	t'.
1. 3433	15·340	612·28	81	36·74	37·272	35·7375
2. 2789	14·865	612·15	81	31·08	32·148	30·618
3. 2789	14·481	612·04	81	31·66	32·284	30·7955
4. 2775	14·731	613·87	81	29·15	29·542	28·019
			16	—	39·786	38·2725
5. 3433	15·086	613·87	81	28·84	28·8435	27·277
			16	—	39·089	37·5285
6. 3433	14·607	613·72	81	24·76	24·856	23·3425
			16	—	35·127	33·591
7. 2789	15·214	611·16	81	23·49	23·157	21·579
8. 2789	14·876	612·05	81	20·63	20·642	19·085
9. 3433	15·074	613·82	81	20·10	20·279	18·712
			16	—	30·532	28·942
10. 3433	15·032	613·79	81	15·93	16·488	14·870
			16	—	26·723	25·090
11. 2789	14·843	611·00	81	14·97	15·133	13·514
12. 2775	15·834	611·00	81	14·87	15·132	13·526
13. 2789	15·028	613·77	81	13·21	13·613	11·9785
			16	—	23·8125	22·166
14. 2789	14·919	612·00	81	13·72	13·161	11·511
15. 2789	14·350	611·85	81	13·16	13·058	11·4825
16. 3433	14·608	613·65	81	12·10	13·054	11·443
			16	—	23·2495	21·627
17. 3433	14·873	613·68	83	36·19	36·631	34·980
			16	—	23·397	21·7685
18. 3433	15·282	613·78	83	32·08	31·644	29·917
			16	—	18·464	16·7785
19. 3433	14·768	613·62	83	27·51	27·509	25·8175
			16	—	14·371	12·7235
20. 2789	14·871	611·83	83	23·80	23·9175	22·182
21. 3433	15·403	613·75	83	20·06	20·954	19·138
			16	—	7·8885	6·0935
22. 3433	14·708	613·54	83	16·50	17·033	15·262
			16	—	4·024	2·258
23. 2789	14·989	611·88	83	13·25	13·6465	11·826
24. 2789	15·029	612·14	83	13·69	13·7155	11·8815
25. 3433	15·318	611·96	83	12·88	12·606	10·7355
26. 3433	15·238	611·91	83	8·13	8·014	6·144
27. 2789	14·934	611·80	83	7·45	3·771	1·915



*Sulphate.*  $\text{MgSO}_4, \text{K}_2\text{SO}_4, 6\text{H}_2\text{O} = 401.40; \frac{3}{80} \text{ mol.} = 15.053 \text{ grams.}$

$t - t'$	$m.$	$6l_m.$	M.	T.	
1.5345		-9512	-9803	+ 291	24° 25 C.
1.530	-9788				
1.4885	-9769	-9777	-9700	- 77	22.29
1.523	-9849				
1.5135	-9759				
1.5665	-9900	-9835	-9645	- 190	21.13
1.5605	-9833				
1.5135	-9875				
1.536	-9994	-9935	-9554	- 381	19.47
1.578		-9851	-9522	- 329	18.82
1.557	-9951				
1.567	-9910	-9962	-9468	- 494	17.74
1.590	-10026				
1.618	-10261	-10293	-9389	- 904	16.24
1.633	-10325				
1.619	-10353	-10314	-9364	- 950	15.725
1.606	-10274				
1.6345	-10371				
1.6465	-10417				
1.650	-10515				
1.5755	(-10454)	-10452	-9328	-1124	15.00
1.611	-10511				
1.6225	-10554				
1.651	-10411				
1.6285	-10405				
1.727	-10601	-10542	-9227	-1315	13.05
1.6855	-10483				
1.6915	-10741	-10670	-9145	-1525	11.46
1.6475	-10600				
1.7355		-10917	-9076	-1841	10.12
1.816	-11059	-11067	-9019	-2048	9.00
1.795	-11076				
1.771	-11291	-11349	-8941	-2408	7.49
1.766	-11408				
1.8205	-11363				
1.834	-11422	-11411	-8867	-2544	6.06
1.8705	-11447				
1.870		-11476	-8854	-2705	4.06
1.896		-11845	-8726	-3149	2.45

TABLE VII.—*Heat of Dissolution of Anhydrous Potassium Copper Sulphate.*  $\text{CuSO}_4\cdot\text{K}_2\text{SO}_4 = 333\cdot02$ ;  
 $\frac{3}{80}$  mol. =  $12\cdot488$  grams.

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t' - t$ .	M.	T.
1. 2744, 2746, and 2717	12·518	614·271	81	33·60	33·814	35·414	1·600	10109	22° 90 C.
2. 2744, &c...	12·494	614·271	81	35·18	33·737	35·331	1·594	10091	
3. 2717 ....	12·392	614·12	81	18·62	21·456	22·988	1·532	9753	
4. 2717 ....	12·434	614·12	81	18·52	21·3845	22·8905	1·506	9577	
5. 2744 ....	12·588	614·12	81	20·35	21·397	22·948	1·551	9743	
6. 2744 ....	12·605	614·21	81	26·54	21·7795	23·3385	1·559	9762	18·25
7. 2746 ....	12·423	614·21	81	25·94	21·705	23·222	1·517	9657	
8. 2744, &c...	12·471	614·21	81	21·65	22·3735	23·910	1·5365	9744	
9. 2744 ....	12·570	614·02	83	34·32	32·163	33·636	1·473	9116	
10. 2746 ....	12·611	614·02	83	34·18	32·1275	33·602	1·4745	9096	13·25
11. 3426 ....	12·320	614·12	83	32·02	32·251	33·678	1·427	9070	
12. 2744, &c...	12·385	614·05	83	20·92	20·815 (8·94)	22·1095	1·2945	8132	
13. 3426 ....	12·141	614·03	83	18·99	18·9385 (8·21)	20·2135	1·275	8160	8·60
14. 3426 ....	12·043	614·00	83	13·25	13·275 (6·05)	14·4565	1·1815	7621	
15. 2744, &c...	12·473	614·00	83	14·31	13·109 (6·01)	14·336	1·227	7653	6·03
16. 3426 ....	12·788	614·07	83	9·02	8·1375	9·323	1·1855	7210	4·11
17. 2744, &c...	12·364	613·95	83	1·57	4·1195	5·199	1·0795	6789	2·59

TABLE VIII.—*Heat of Dissolution of Hexhydrated Potassium Copper Sulphate.*  $\text{CuSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O} = 440.78$ ;  
 $\frac{3}{80} \text{ mol.} = 16.529 \text{ grams.}$

Sample.	<i>w.</i>	W.	Therm.	$\tau$ .	<i>t.</i>	$t'.$	$t - t'.$	<i>m.</i>	$6/m.$	M.	T.
1. 2738	16.038	612.04	81	31.57	33.712	31.6295	2.0825	-13544}	-9733	-3858	22.91C.
2. 2738	15.687	611.96	81	32.68	33.9025	31.851	2.0515	-13639}	-9611	-4021	20.53
3. 2738	15.975	612.01	81	27.43	27.619	25.531	2.088	-13774}	-13632		
4. 2693	16.500	612.04	81	20.10	23.191	21.012	2.179	-13697}			
5. 2693	16.372	612.04	81	20.61	23.128	20.978	2.150	-13825}			
6. 2738	16.522	612.04	81	17.40	23.062	20.852	2.190	-13879}	-13728	-4212	18.71
7. 2738	16.454	612.04	81	17.92	23.353	21.1635	2.1895	-13463}			
8. 2738	16.044	611.99	81	23.31	21.7155	19.6445	2.071				
9. 2738	10.738	609.65	81	15.11	13.707	12.226	1.441		-13942	-4608	15.15
10. 2738	16.448	611.92	83	32.50	34.124	31.850	2.274	-14220}			
11. 2738	16.586	611.94	83	33.50	33.988	31.713	2.275	-14118}	-14154	-4880	13.965
12. 2738	15.889	611.96	83	34.36	33.949	21.762	2.187	-14125}			
13. 2738	15.697	611.82	83	31.05	30.561	28.4035	2.1575		-14102	-4897	12.63
14. 2738	16.261	611.88	83	23.05	20.943	18.6475	2.296	-14488}			
15. 2738	16.108	611.84	83	23.13	20.935	18.657	2.276	-14511}	-14499	-5480	9.00
16. 2738	16.336	611.85	83	16.52	13.084	10.724	2.360		-14796	-5942	5.99
17. 2738	16.029	611.73	83	1.16	3.0475	0.638	2.409		-15418	-6761	2.17

TABLE IX.—Heat of Dissolution of Anhydrous Sodium Sulphate.  $\text{Na}_2\text{SO}_4 = 141.81; \frac{3}{40} \text{ mol.} = 10.636 \text{ grams.}$ 

Sample.	w.	W.	Therm.	$\tau$ .	t.	t'.	$t' - t \text{ or } t - t'$ .	M.	T.
1. 2775	10.668	614.32	81	38.41	38.396	38.4795	0.0835	264	24.66C.
2. 2775	10.601	614.32	81	39.79	38.252	38.3435	0.0905	287	
3. 3604	10.603	608.39	39	36.13	38.634	38.976	0.342	169	22.13
4. 3604	10.659	608.39	39	39.37	39.3625	39.732	0.3635	180	
5. 2775	10.550	614.25	81	25.3	27.626	27.647	0.021	68	
6. 3036	10.653	614.25	81	27.14	27.658	27.674	0.016	47	
7. 3052	10.627	614.25	81	27.51	27.325	27.342	0.017	50	20.55
8. 3081	10.481	614.25	81	31.33	27.670	27.689	0.019	61	
9. 3604	10.617	608.33	39	52.73	51.900	51.708	0.192	94	
10. 3604	10.605	608.33	39	51.65	52.230	52.12	0.170	83	18.617
11. 3604	10.641	608.33	39	37.64	42.750	42.679	0.071	35	
12. 3604	10.591	608.32	39	42.87	44.395	44.225	0.170	83	
13. 3604	10.611	608.32	39	41.44	44.106	43.915	0.191	93	17.76
14. 3604	10.574	608.32	39	39.50	38.866	38.3845	0.4815	237	
15. 3604	10.611	608.32	39	43.77	41.420	40.958	0.462	226	16.307
16. 2775	10.550	614.16	83	35.75	36.9915	36.909	0.0825	259	
17. 3052	10.685	614.16	83	36.06	36.871	36.775	0.096	298	15.07
18. 3604	10.537	608.27	39	44.08	43.0315	42.3965	0.635	313	
19. 3604	10.613	608.27	39	54.24	55.666	55.023	0.643	315	14.34
20. 3604	10.558	608.24	39	29.25	49.0775	48.0555	1.022	501	
21. 3604	10.555	608.24	39	29.41	49.705	48.885	1.020	502	12.215
22. 3604	10.616	608.24	39	48.84	50.168	49.176	0.992	486	
23. 3604	10.460	608.20	39	34.21	34.841	32.525	1.316	654	
24. 3604	10.309	608.20	39	36.09	35.0975	33.7965	1.301	656	
25. 3052	10.658	614.08	83	21.62	23.456	23.240	0.216	671	10.00
26. 3052	10.524	614.08	83	23.46	23.421	23.193	0.222	684	
27. 3407	10.451	614.08	83	24.27	23.485	23.270	0.215	682	
28. 3098	10.503	614.07	83	22.63	22.295	22.071	0.224	707	

TABLE IX—(continued.)

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t - t'$ .	M.	T.
29. 3604	10·670	608·18	39	43·21	42·154	(8·70)	1·704	-830	8° 437 C.
30. 3604	10·619	608·18	39	51·04	51·379	(8·32)	1·764	-863	
31. 3604	10·582	608·18	39	51·98	51·539	(5·95)	1·734	-851	
32. 3407	10·483	614·00	83	8·20	12·828	(5·92)	0·323	-1021	
33. 3407	10·588	614·00	83	9·87	12·803	(5·665)	0·323	-1011	
34. 3604	10·554	608·14	39	58·64	50·672	(3·03)	2·122	-1016	
35. 3604	10·651	608·14	39	59·60	46·673	(2·33)	2·207	-1045	5·871
36. 3604	10·696	608·11	39	55·30	53·612		51·152	-1077	
37. 3407	10·443	613·95	83	5·47	5·325		2·4602	-1254	4·07
38. 3407	10·100	613·95	83	1·42	3·467		0·3955	-1324	2·68

TABLE X.—Heat of Dissolution of Decahydrated Sodium Sulphate.  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 321·41$ ;  $\frac{3}{40} \text{ mol.} = 24·106 \text{ grams.}$ 

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t - t'$ .	m.	10/m.	M.	T.
1. 3095	23·974	623·53	81	38·76	39·191	33·264	5·927	-19156	-16400	-2756	25° 015 C.
2. 3418	23·967	621·59	81	36·86	37·400	31·459	5·941	-19147	-16345	-2802	24·31
3. 3095	24·087	623·47	81	34·76	34·306	28·3385	5·9725	-19211			
4. 3095	23·899	623·24	81	34·57	34·349	28·474	5·875	-19039			
5. 3418	23·816	621·46	81	34·56	34·191	28·291	5·900	-19132			
6. 3418	24·121	621·53	81	34·30	34·247	28·264	5·983	-19158			
7. 3095	23·908	623·21	81	28·38	28·113	22·188	5·925	-19193			
8. 3095	24·052	623·50	81	28·48	28·205	22·3445	5·946	-19154			
9. 3418	23·698	623·05	81	28·27	28·015	22·180	5·865	-19194			
10. 3418	24·057	623·28	16	28·47	28·290	32·410	5·880	-19190			
			81	28·082	28·082	22·1545	5·9275	-19116			
			16	38·3555	38·3555	32·401	5·9345	-19086			

TABLE X—(continued.)

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t - t'$ .	m.	$10/m$ .	M.	T.
11. 3418	24·002	623·44	81	24·62	24·698	18·788	5·910	{ -19077 -19130	{ -19104 -19160	{ -3184 -3318	{ 19°41 C. 18·515
12. 3095	24·365	621·72	16	—	34·944	29·010	5·944				
13. 3418	23·855	623·16	81	21·30	21·266	16·314	6·0425	{ -19156 -19153	{ -19158 -19160	{ -3351 -3407	{ 18·08 17·11
14. 3418	23·922	623·19	16	—	31·4885	15·375	5·891				
15. 3418	23·965	623·19	81	21·37	21·300	25·532	5·9065	{ -19164 -19160	{ -19158 -19160	{ -3351 -3407	{ 18·08 17·11
16. 3418	24·061	623·26	16	—	31·524	15·390	5·910				
17. 3418	23·795	623·10	81	18·80	18·895	25·599	5·925	{ -19182 -19182	{ -19182 -19182	{ -3351 -3407	{ 18·08 17·11
18. 3418	24·377	623·43	16	—	18·695	12·769	5·926				
19. 3418	24·090	623·31	81	17·15	28·899	22·9885	5·9105	{ -19079 -19126	{ -19131 -19187	{ -3351 -3518	{ 18·08 16·50
20. 3418	24·055	623·22	16	—	18·7575	12·8195	5·938				
21. 3418	24·239	623·29	81	17·06	28·9575	23·0065	5·951	{ -19150 -19192	{ -19187 -19137	{ -3351 -3518	{ 18·08 16·50
22. 3418	24·359	623·35	16	—	17·147	11·272	5·875				
23. 3095	24·236	623·28	81	17·15	27·366	21·462	5·904	{ -19191 -19126	{ -19187 -19137	{ -3351 -3518	{ 18·08 16·50
24. 3095	23·778	623·35	16	—	27·4035	11·163	6·0285				
25. 3418	24·150	623·21	81	15·98	15·6445	9·706	5·9385	{ -19126 -19162	{ -19137 -19187	{ -3351 -3518	{ 18·08 16·50
26. 3418	24·269	623·29	16	—	25·857	19·891	5·966				
			81	15·65	15·742	9·8195	5·9225	{ -19153 -19178	{ -19137 -19187	{ -3351 -3518	{ 18·08 16·50
			16	—	25·961	20·0055	5·9555				
			83	36·09	35·185	30·099	6·087	{ -19170 -19170	{ -19137 -19187	{ -3351 -3518	{ 18·08 16·50
			16	—	22·950	16·9435	6·0065				
			83	36·32	36·111	30·025	6·086	{ -19076 -19076	{ -19121 -19121	{ -3351 -3518	{ 18·08 16·50
			16	—	22·874	16·871	6·003				
			83	32·58	32·418	26·345	6·073	{ -19098 -19053	{ -19113 -19113	{ -3351 -3518	{ 18·08 16·50
			16	—	32·624	26·6805	5·9435				
			83	32·70	32·465	26·3865	6·060	{ -19164 -19102	{ -19113 -19125	{ -3351 -3518	{ 18·08 16·50
			16	—	19·250	13·287	5·963				
			83	33·43	32·548	26·4715	6·0765	{ -19124 -19112	{ -19113 -19125	{ -3351 -3518	{ 18·08 16·50
			16	—	19·340	13·365	5·965				

TABLE X.—(continued.)

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t - t'$ .	m.	$10l_m$ .	M.	T.
27. 3418	24·160	623·09	83	28·79	29·573	23·545	6·028	—19001	—15309	—3789	12·25 C.
			16	—	16·4355	6·010	6·010	—19198			
28. 3418	24·475	623·37	83	26·81	26·3845	20·260	6·1245	—19115	—15206	—3844	11·03
			16	—	13·2615	7·228	6·0335	—19076			
29. 3418	23·861	623·02	83	26·76	26·3345	20·4275	5·907	—18900			
			16	—	13·2210	7·3535	5·8675	—19018			
30. 3418	24·012	623·03	83	26·61	24·676	18·700	5·976	—19003	—15150	—3853	10·40
			16	—	11·584	5·6685	5·899	—19002			
31. 3418	23·937	623·04	83	23·23	23·2865	17·2855	6·001	—19170	—15108	—4026	9·88
			16	—	10·189	4·252	5·937	—19182			
32. 3418	24·349	623·27	83	23·18	23·3765	17·2825	6·094	—19116			
			16	—	10·279	4·2785	6·0005	—19067			
33. 3095	24·017	623·21	83	22·45	22·002	15·986	6·016	—19140	—15076	—4039	9·54
34. 3095	23·910	623·16	83	22·70	22·740	16·734	6·006	—19090			
35. 3418	24·249	623·20	83	20·34	20·597	14·5045	6·0925	—19185	—15025	—4116	8·85
			16	—	7·5245	1·5185	6·006	—19157			
36. 3418	24·502	623·34	83	20·78	20·582	14·467	6·115	—19064			
			16	—	7·5155	1·449	6·0665	—19159			
37. 3418	24·495	623·33	83	17·30	18·9745	12·814	6·1605	—19211			
			16	—	5·944	—0·141	6·088	—19231			
38. 3418	24·565	623·37	83	17·37	19·1585	13·0025	6·156	—19143	—14966	—4238	8·25
			16	—	6·1295	0·024	6·1055	—19232			
39. 3095	24·269	621·44	83	11·1	11·322	5·2885	6·0337	—18892	—18902		
40. 3095	23·829	623·15	83	11·45	11·8805	5·9665	5·914	—18912			
41. 3418	24·127	621·48	83	14·99	15·2545	9·2035	6·050	—19056	—14736	—4190	5·55
42. 3418	23·842	621·19	83	11·99	12·065	6·123	5·942	—18930	—18938		
43. 3418	24·227	621·41	83	12·54	12·1865	6·1455	6·041	—18947			
44. 3418	22·802	620·61	83	9·26	9·372	3·683	5·689	—18934			
45. 3418	24·637	621·62	83	6·43	6·580	0·445	6·135	—18928	—14553	—4375	3·53
46. 3418	24·417	621·49	83	6·81	6·735	0·654	6·081	—18927			



TABLE XI.—Heat of Dissolution of Potassium Sulphate.  $K_2SO_4 = 173.88; \frac{3}{40} \text{ mol.} = 13.041 \text{ grams.}$ 

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t - t'$ .	M.	Correc- tion.	M corrected.	T.
1. 3603	13.097	610.14	80*	—	30.935	29.117	1.818	—	—	—5851	26° 50C.
			84*	29.77	29.813	28.795	1.018	—	—	—5831	
2. 3603	13.108	610.08	80	39.48	39.309	33.426	1.883	—	—	—6055	
			84	—	34.545	33.517	1.028	—	—	—5889	
3. 3613	13.525	608.45	39	52.94	52.565	39.835	12.730	—6010	—63	—5947	
4. 3428	12.950	608.45	39	52.56	52.565	40.421	12.1455	—5989	—38	—5951	
5. 3428	13.126	608.45	39	52.14	52.3125	39.977	12.3155	—5991	—38	—5953	25.21
6. 3603	13.182	610.07	80	38.24	38.3215	36.4715	1.850	—	—	—5915	
			84	—	34.018	32.975	1.043	—	—	—5941	
7. 3603	13.027	610.07	80	38.34	38.3265	36.5005	1.826	—	—	—5908	
			84	—	34.023	32.987	1.036	—	—	—5971	
8. 3603	13.194	610.09	80	36.65	36.142	34.267	1.875	—	—	—5990	
			84	—	32.784	31.741	1.043	—	—	—5936	
9. 3603	13.123	610.09	80	36.80	36.145	34.289	1.856	—	—	—5961	
			84	—	34.289	31.752	1.037	—	—	—5933	
10. 3603	13.162	610.09	80*	—	25.640	23.760	1.880	—	—	—6020	24.2
			84*	26.81	26.848	25.778	1.070	—	—	—6104	
			80*	25.85	25.454	23.5545	1.8995	—	—	—6101	
11. 3603	13.123	610.09	84	—	32.829	31.773	1.056	—	—	—6042	
12. 3603	13.088	608.40	39	52.64	51.8955	39.244	12.6415	—	—	—6163	
13. 3428	13.435	608.40	39	53.42	52.7225	39.810	12.9125	—6139	—38	—6131	
14. 3613	13.049	608.40	39	52.40	52.012	39.442	12.570	—6150	—63	—6087	
			80	32.93	32.677	30.742	1.935	—	—	—6191	
15. 3603	13.172	610.04	84	—	30.818	29.733	1.085	—	—	—6184	
			80	32.90	32.735	30.864	1.871	—	—	—6126	22.865
16. 3603	12.873	610.04	84	—	30.853	29.798	1.055	—	—	—6153	

\* Some of the mercury having been removed into the upper chamber.

TABLE XI—(continued).

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t - t'$ .	M.	Correc- tion.	M corrected.	T.
17. 3428	12·976	609·88	16	39·44	39·189	37·1965	1·9925	—6288	—38	—6250	21° 10 C.
			80	—	28·1635	26·227	1·9425	—6322	—38	—6284	
18. 3603	13·132	610·00	80	27·02	26·213	24·242	1·971	—	—	—6325	20·31
			84	—	27·204	26·094	1·110	—	—	—6346	
19. 2725	13·016	607·99	81	22·4	33·811	21·7555	2·0555	—6466	+18	—6484	
			16	—	33·846	31·789	2·057	—6477	—38	—6439	
20. 3428	13·005	609·85	80	23·51	22·9785	20·959	2·0195	—6542	—38	—6504	
			16	33·68	33·8825	31·806	2·0765	—	—	—6449	
21. 3603	13·134	609·82	84	—	25·410	24·287	1·123	—	—	—6393	18·912
			84	—	25·420	24·318	1·102	—	—	—6403	
22. 3603	12·920	609·82	80	22·97	23·045	21·059	1·986	—6516	+18	—6478	
			81	19·62	23·154	21·086	2·068	—	—	—6534	
23. 2725	13·127	607·99	39	31·39	52·0635	38·7885	13·295	—	—	—6518	
24. 3603	13·021	608·33	16	29·19	29·0835	27·003	2·0805	—6599	—38	—6561	
25. 3428	12·909	609·82	80	—	18·349	16·326	2·023	—6600	—38	—6562	16·915
			16	27·24	27·635	25·542	2·093	—6700	—38	—6662	
26. 3428	12·791	609·81	80	—	16·940	14·916	2·024	—6682	—38	—6644	
			80	14·88	13·789	11·695	2·094	—	—	—6767	
27. 3603	13·038	609·92	84	—	20·230	19·036	1·194	—	—	—6874	15·42
			80	14·7	813·855	11·783	2·072	—	—	—6711	
28. 3603	13·009	609·92	84	—	20·269	19·088	1·181	—	—	—6816	
			89	51·9	352·290	38·450	13·840	—	—	—6820	
29. 3603	12·955	608·28	39	22·6	722·890	20·7275	2·1625	—6822	+18	—6840	14·895
30. 2725	12·908	607·90	16	22·8	123·0425	20·8615	2·181	—6861	+18	—6879	
31. 2725	13·015	609·78	80	—	12·497	10·405	2·092	—6771	+18	—6789	

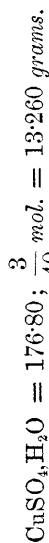
TABLE XI—(continued.)

Sample.	w.	W.	Therm.	$\tau$ .	$t$ .	$t'$ .	$t - t'$ .	M.	Correc- tion.	M corrected.	T.
32. 3603	13.071	608.26	39	53.42	52.457 (13.96)	38.2945	14.1625	—	—	—	—
33. 3603	13.135	608.26	39	52.10	52.3035 (13.95)	38.0825	14.270	—	—	—	—
34. 3428	13.160	608.26	39	49.95	52.0265	37.6645	14.362	—6966	—38	—6928 —6928 —6941	—6952
35. 2725	13.104	608.26	39	52.78	52.088 (13.96)	37.823	14.265	—6949	+18	—6967	—6941
36. 2725	13.106	607.89	83	34.36	33.825	31.536	2.289	—7032	+18	—6979	—6952
37. 2725	13.213	607.89	83	35.18	34.1375 (13.935)	31.8775	2.260	—6890	+18	—6908	—6952
38. 2725	13.052	607.89	83	35.67	33.9725	31.7155	2.257	—6967	+18	—6985	—6952
39. 2725	13.158	607.89	83	34.15	33.9815	31.7225	2.259	—6918	+18	—6936	—6952
40. 3603	13.035	608.24	39	51.55	52.476	38.135	14.341	—	—	—	—
41. 2725	13.107	607.90	83	25.39	25.377 (10.75)	23.082	2.315	—7115	+18	—7133	12.36
42. 3603	12.889	608.20	39	52.18	52.380 (10.455)	37.820	14.50	—	—	—7210	10.434
43. 3428	12.98	607.92	83	24.34	24.530	22.193	2.337	—7253	—38	—7215	—7180
44. 3428	13.032	607.92	83	24.42	24.491 (10.35)	22.145	2.346	—7219	—38	—7181	—7184
45. 3428	12.978	607.92	83	24.35	24.515	22.197	2.318	—7195	—38	—7157	—7157
46. 3428	13.062	607.92	83	24.37	24.515	22.173	2.342	—7223	—38	—7185	—7185
47. 2725	13.014	607.91	83	23.05	23.034	20.694	2.340	—7243	+18	—7261	—7261
48. 2725	13.163	607.91	83	23.06	23.212	20.8635	2.3485	—7187	+18	—7205	—7205
49. 3603	12.987	608.18	39	52.02	52.905	37.770	15.135	—	—	—	—
50. 2725	13.193	607.87	83	14.98	14.791 (6.63)	12.3185	2.4725	—7549	+18	—7567	—7567
51. 2725	13.038	607.87	83	15.12	14.726 (6.45)	12.268	2.458	—7568	+18	—7586	—7586
52. 3613	13.048	608.15	39	52.01	52.447 (5.965)	36.682	15.756	—7711	—63	—7648	—7648
53. 3603	13.051	608.14	39	60.90	51.438 (5.80)	35.708	15.730	—	—	—7692	—7692
54. 3428	12.823	607.85	83	11.52	11.495 (5.80)	9.0085	2.4505	—7698	—38	—7660	—7660
55. 3428	12.995	607.85	83	11.79	11.6125 (3.99)	9.1375	2.485	—7703	—63	—7665	—7665
56. 3613	13.046	608.11	39	51.44	52.3445 (3.01)	36.0445	16.300	—7974	+18	—7911	—7911
57. 2725	13.068	607.81	83	6.63	5.2205 (2.42)	2.6595	2.5610	—7894	+18	—7912	—7912
58. 2725	12.992	607.81	83	2.50	3.706 (2.42)	1.1465	2.5595	—7945	+18	—7953	—7953

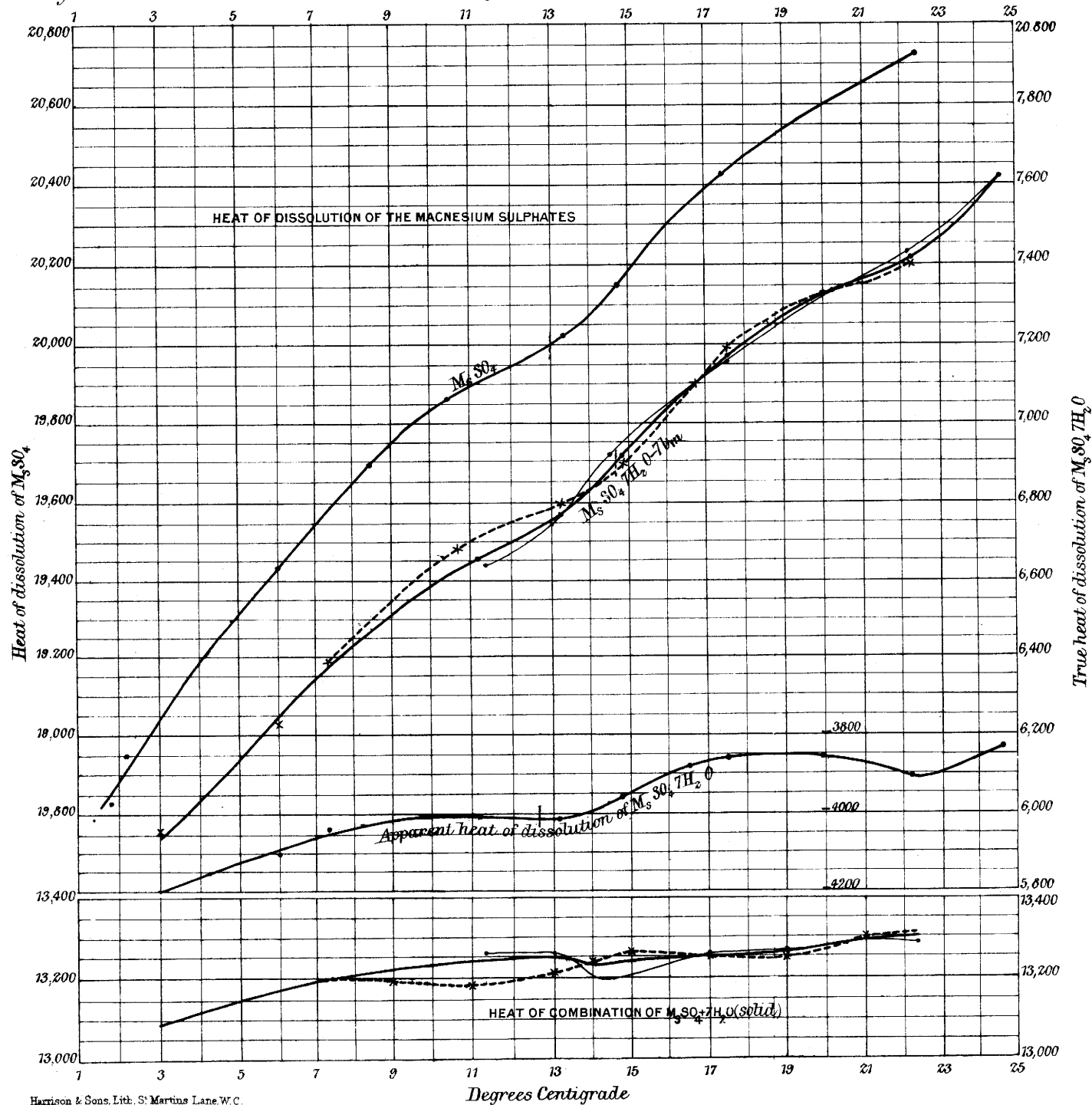
TABLE XII.—*Heat of Dissolution of Anhydrous Lithium Sulphate.*  $\text{Li}_2\text{SO}_4 = 109.84; \frac{3}{40} \text{ mol.} = 8.238 \text{ grams.}$

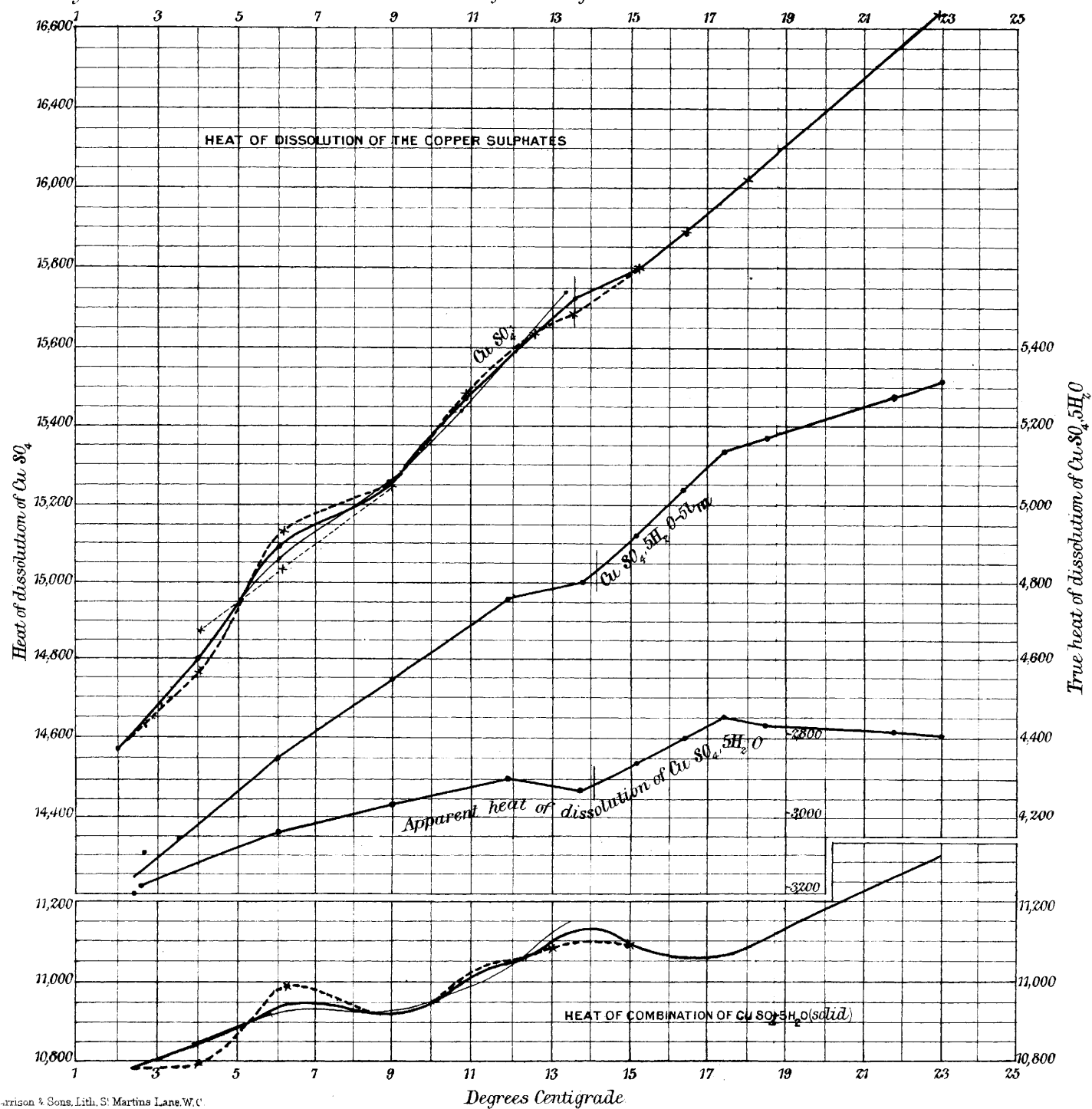
Sample.	w.	W.	Therm.	$\tau$ .	t.	t'.	t' - t.	M.	Correc- tion.	M corrected.	T.
1. 3074	8.205	614.27	81	32.92	33.688	35.746	2.058	—	—	6541	22° 86C.
2. 3406	8.396	614.26	81	30.54	30.477	32.593	2.116	—	—	6574	21.64
3. 3093	8.230	614.21	81	22.36	21.752	23.782	2.030	6434	-81	6353	18.27
4. 3406	8.165	614.20	81	20.29	20.220	22.190	1.970	—	—	6293	17.68
5. 3086	8.294	614.11	83	32.09	31.576 (13.02)	33.557	1.981	—	—	6130 } 6117	13.43
6. 3406	8.146	614.11	83	33.61	33.732 (13.85)	35.670	1.938	—	—	6105 }	
7. 3086	8.145	614.05	83	21.38	22.342	24.161	1.819	—	—	5731 } 5726	9.50
8. 3406	8.304	614.05	83	23.60	22.252	24.105	1.853	—	—	5726 }	
9. 3086	8.197	614.00	83	14.19	13.551	15.312	1.761	—	—	5512 }	
10. 3093	8.274	614.00	83	13.94	13.454	15.255	1.801	5585	-81	5504 } 5506	6.14
11. 3406	8.207	614.00	83	13.22	13.467	15.227	1.760	—	—	5503 }	
12. 3406	8.328	613.95	83	1.87	2.359	4.006	1.647	—	—	5074	1.91

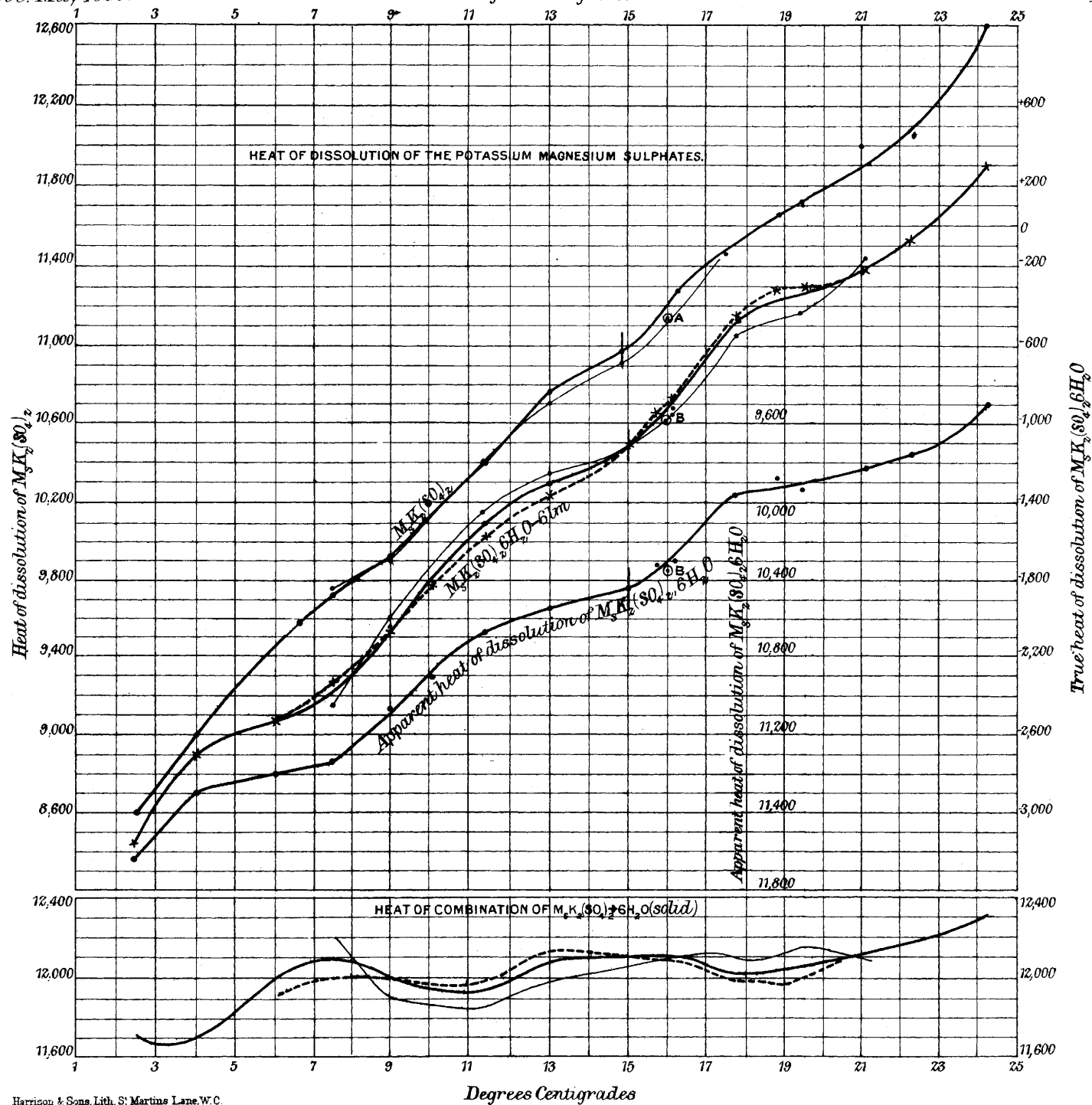
TABLE XIII.—Heat of Dissolution of the Monohydrated Sulphates of Copper, Magnesium, and Lithium.



Sample.	w.	W.	Therm.	$\tau$ .	t.	t'.	t' - t.	m.	$l_m$ .	M.	T.
<b>CuSO<sub>4</sub>·H<sub>2</sub>O.</b>											
1. 2734....	13.305	614.27	81	34.74	33.739	36.621	2.882	9115	1622	10711	22° 88C.
2. 2734....	13.428	614.27	81	34.74	33.739	36.631	2.892	9063			
3. 2734....	13.272	614.47	81	19.26	20.625	23.440	2.815	8295		10470	17.83
4. 2734....	13.387	614.47	81	19.75	20.714	23.533	2.819	8859			
5. 2734....	13.297	615.37	83	34.85	31.589	34.384	2.795	8701		10247	13.00
6. 2734....	13.480	615.39	83	34.54	31.484	34.323	2.839	8718			
<b>MgSO<sub>4</sub>·H<sub>2</sub>O.</b>											
7-15. 2755, 2758, 3032, and 3025...	} For details see <i>Chem. Soc. J.</i> , Trans., 1885, 100.										
						—	—	12091	1617	13708	22.30
<b>Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O.</b>											
16. 3215....	9.708	608.34	83	33.49	33.6195	34.6495	1.03	3138	1548	4686	13.80
17. 3353....	10.926	610.66	83	32.82	31.4625	32.586	1.1235	2911	1537	4448	12.97

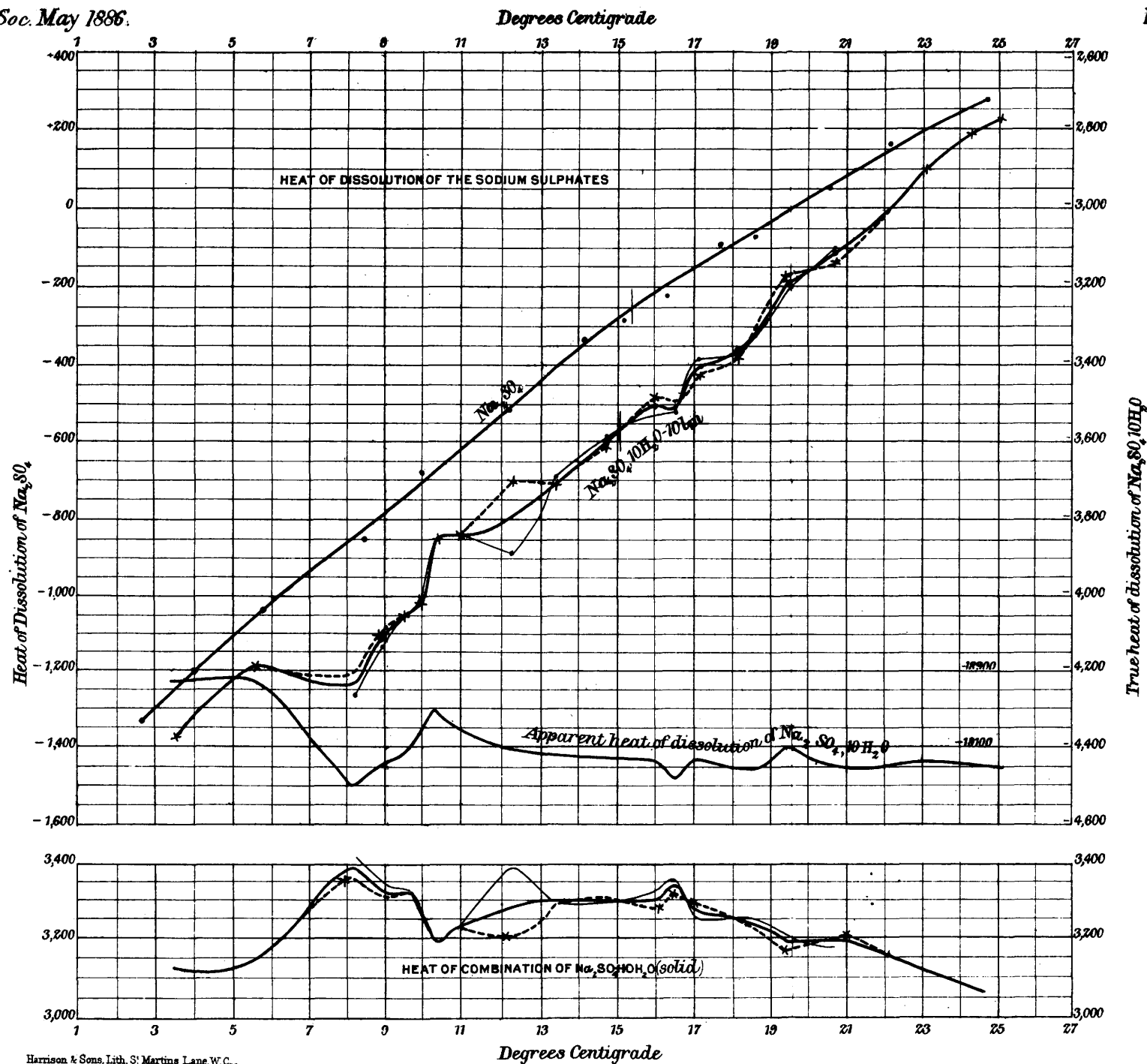


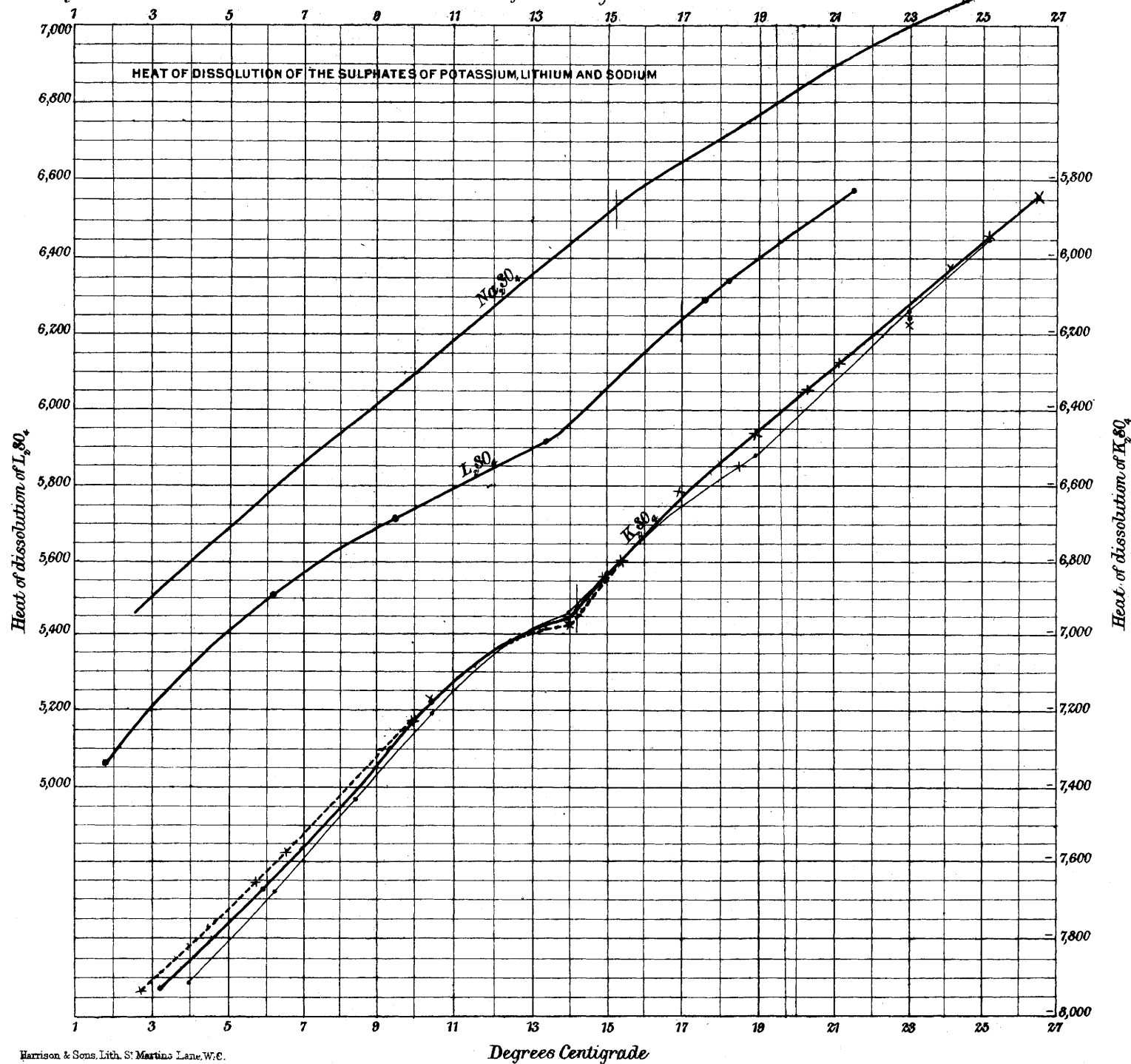












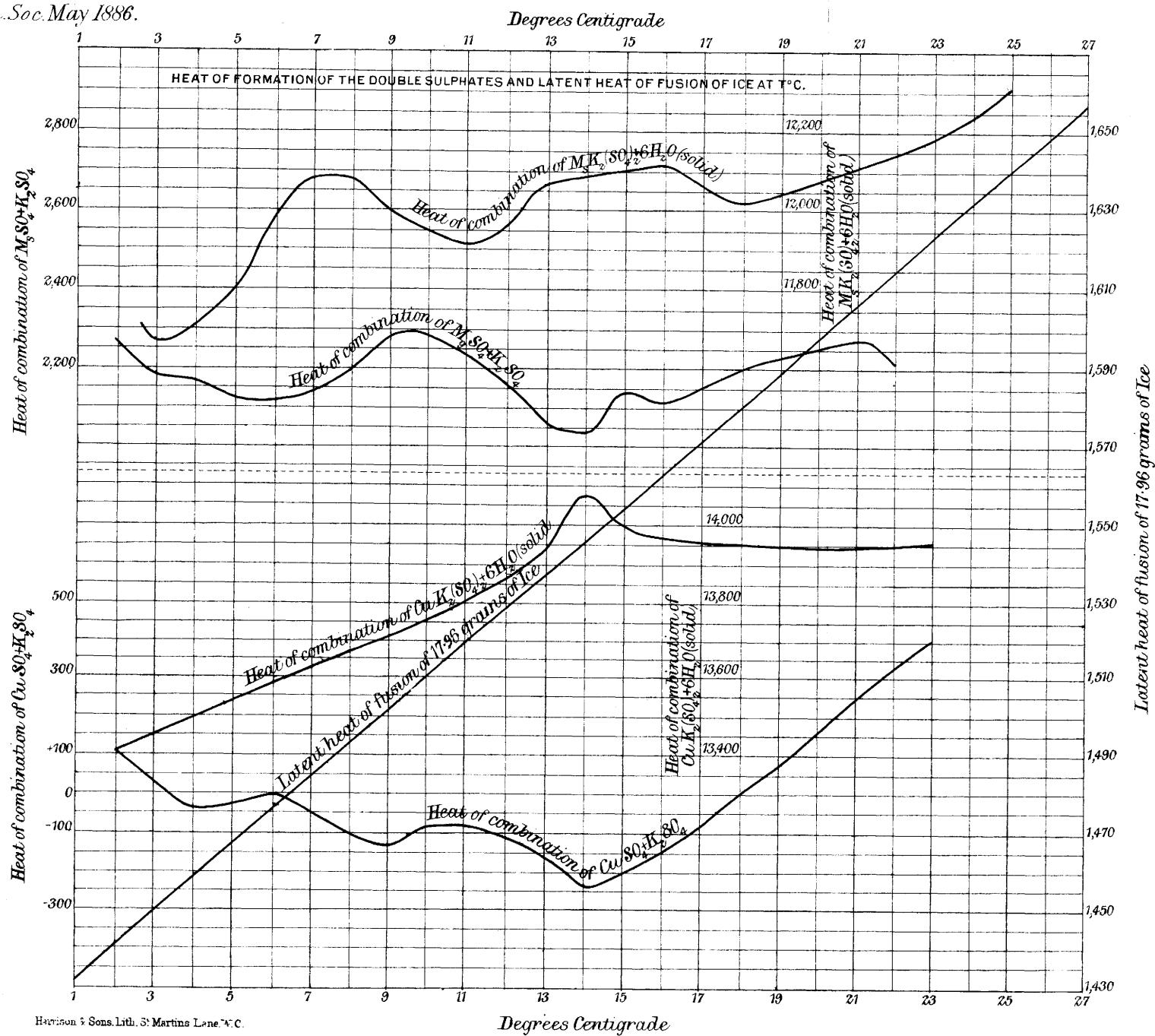


TABLE XIV.—*Heat developed on Mixing Solutions of Magnesium Sulphate or Copper Sulphate with a Solution of Potassium Sulphate.*Strength of each solution = 1 molecule to 400 H<sub>2</sub>O.

Quantity taken 307 c.c. of each.

Thermometers employed, 81 and 83.

*A.—Magnesium and Potassium Sulphates Mixed.*

Observed heat development.		Heat developed in blank experiments.	Corrected heat development.	Mean temperature.
1. + 56 cal.	} + 40 cal.	+ 63 cal.	- 23 cal.	7° 07 C.
2. + 24 „				
3. + 72 „	} + 55 „	+ 88 cal. + 38 „	- 8 „	13° 32 „
4. + 38 „				
5. - 6 „	} - 14 „	- 35 „ 0 „	+ 3 „	23° 0 „
6. - 22 „				

*B.—Copper and Potassium Sulphates mixed.*

1. + 104 cal.	} + 111 cal.	+ 102 cal. + 112 „	+ 4 cal.	10° 6° C.
2. + 118 „				
3. + 22 „	} + 36 „	+ 38 „	- 2 „	13° 22 „
4. + 51 „				
5. - 19 „	} - 13 „	- 16 „ 54 „	+ 22 „	22° 89 „
6. - 6 „				