

XXXIII.—*The Influence of Temperature on the Heat of Dissolution of Salts.*

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IN March last year, I brought before this Society the results of an investigation on the influence of temperature on the heat of chemical combination (Trans., 1886, 260), which tended to show that the heat evolved or absorbed when a salt is dissolved in water does not vary continuously with an alteration in temperature, but that irregularities

occur at intervals only a few degrees apart, indicative of alterations in the complexity of the molecular groupings present, and indicating at the same time variations of a less marked character in the heat of combination of the solid salt with its water of crystallisation. These results were subsequently criticised and disputed by Professor Tilden (Proc., No. 24, 198). The general fairness of this criticism I willingly admit, although I cannot agree with it in all its details. A worker is no doubt apt to be misled by having had for a long time too close and, perhaps, a one-sided view of his own work, but something must also be subtracted from the critic's opinion, from the fact that he has not followed the work in the whole of its progress, especially so when he himself has performed work of a similar nature, but under totally different conditions, and with different and comparatively imperfect instruments. So far, however, as his general conclusions went, I must admit that I believe Professor Tilden was right, and my thanks are therefore due to him for exposing my error. The peculiarities which I noticed in the lines representing the heat of dissolution, consisted of indentations occurring at various points, converting these lines into a series of curves: as to the existence of such indentations I now consider that I was quite wrong; they do not exist: but that changes more or less sudden do occur in these lines, and in the nature of the molecular aggregates of a salt in solution, the present work will, I trust, place beyond a doubt. I can scarcely attribute the errors into which I was led in the first instance to carelessness or insufficient work, the multiplicity of the experiments and of the different instruments used in them might have been reasonably taken as a safeguard against error, and from want of other adequate causes I can only attribute the error which did occur to peculiarities in these instruments, and in thermometers in general, although there are various reasons which render such an explanation unsatisfactory.

The objections which Professor Tilden raised against my work were three in number. First, that I trusted too much to mean results, independent of the value of the individual experiments constituting the mean. This, I hope, I have obviated in the present instance: all results which appeared exceptional were repeated, and such alterations in the lines as exist depend, as will be found, on series of experiments extending over many degrees, and not on experiments at one particular temperature only; moreover, no alterations are insisted on unless they are clearly shown by at least two whole series of experiments performed with different instruments.

The second objection raised was the difficulty of accurately ascertaining the correction for cooling (or heating) during the experiment. Here, I think, Professor Tilden has been misled by his own experience derived from experiments in which the correction for cooling attained very much

larger proportions than in the present work. After the salt has been introduced and dissolved the thermometer was read at intervals of two minutes in order to determine the rate of cooling, and from it the corrected final temperature. The average cooling during these two-minute intervals amounted to less than 0.01° , and, as the rate given by the first two observations did not differ generally by more than 0.001° , the error in applying this correction cannot be very large. If the variation was greater than 0.001° , a larger number of observations were made. Owing to the rate of cooling being so small, it remains quite constant throughout the whole experiment.

The last objection was a more subtle one. The rate of cooling may be determined with accuracy, Professor Tilden suggests, but while the salt is dissolving there is a period when the temperature is rising (or falling), and during this period the rate of cooling is uncertain; this period, moreover, will vary in length as the temperature is higher or lower, and any errors in the correction applied for it may attain much greater dimensions at lower than at higher temperatures. It may be pointed out in the first place that such errors would not cause any *sudden*, but only a *gradual* alteration in the results; Professor Tilden, however, greatly overestimates the difficulties of the case. It is true that the salts do take longer to dissolve at low temperatures than at high ones, but in the present instances this difference is quite inappreciable. The time thus occupied was ascertained in a few cases at widely different temperatures; the moment the thermometer was read, the moment when the salt first touched the water, and the moment when the thermometer attained its maximum (or within 0.1° of its final position), being noted with the help of an assistant. The results were as follows:—

Anhydrous Strontium Chloride.

	At 24° .		At 23° .	
	Sec.	Interval.	Sec.	Interval.
Temperature read	0		0	
Salt added	12	14	14	13
Maximum attained.	26		27	

Mean interval 13.5 sec.

	At 5° .		At 4° .	
	Sec.	Interval.	Sec.	Interval.
Temperature read	0		0	
Salt added	15	11	15	16
Maximum attained.	26		31	

Mean interval 13.5 sec.

Anhydrous Sodium Acetate.

	At 24°.		At 23°.	
	Sec.	Interval.	Sec.	Interval.
Temperature read	0		0	
Salt added	16		16	
Maximum attained	40	24	42	26

Mean interval 25 sec.

	At 5°.		At 4°.	
	Sec.	Interval.	Sec.	Interval.
Temperature read	0		0	
Salt added	17		15	
Maximum attained	40	23	40	25

Mean interval 24·5 sec.

Thus, although there is a difference of 20° between the two pairs of experiments in each case, the interval elapsing between the moment when the salt first touched the water and that when the thermometer reached its maximum is the same within one second. These two salts were selected owing to their being extreme cases in opposite directions; strontium chloride may be added to the water very quickly, whereas sodium acetate must be added more slowly, and floats some time on the surface of the water before sinking. The uncertain interval, therefore, during which the thermometer is rising may be taken to be on an average the mean of these two, namely, 19 seconds, while the average rate of cooling after the maximum is attained is, as mentioned above, 0·045° per minute. During the uncertain interval, the rate of cooling is somewhere between that of the initial temperature (the rate there is *nil*) and that of the final temperature; I assume that it is exactly intermediate between them; hence on an average the amount of cooling during this uncertain interval would be $\left(\frac{19}{60} \text{ of } \frac{0\cdot0045}{2} = \text{not much over}\right) 0\cdot0005^\circ$, a quantity almost negligible: where, therefore, the total correction is so small, the error which it may contain is surely not worth consideration.

Apparatus.

In the present series of experiments, the apparatus employed was far more perfect than in the previous work. The contents of the calorimeter were stirred by means of a platinum rod with three blades arranged like a screw at the lower end; this was rotated by means of an electromotor. The results with this stirrer were found to be

very satisfactory when the motor was worked by a battery of some constancy; if, however, the battery is not constant the rate of cooling will be irregular.

The thermometers were suspended immediately above the rotating arms, and were tapped on the upper end continuously by means of clockwork apparatus. They were read with a cathetometer, and hence, except to add the salt, the operator never approached the calorimeter. The salts were weighed out into test-tubes on feet, as in former experiments, and were left till they had attained the temperature of the air of the laboratory, an hour and a half being found requisite for this, and were protected from draughts meanwhile by being surrounded with a water-jacket, similar to that of the calorimeter itself, but covered at the top; in this vessel, a delicate thermometer was suspended. The air was kept constant within 0.1° of the initial temperature of the experiments. A very simple arrangement was adopted after a time for preventing salts from splashing when shaken out into the calorimeter, consisting of a small piece of platinum gauze hanging on the edge of the calorimeter, and immersed about $\frac{1}{8}$ -inch below the surface of the water.

Thermometers.

The thermometers employed in this work were two in number (Nos. 65108 and 65561, by Casella), both different from any used in the previous work. They were both made out of the same cane, and their bulbs contained 39 and 46 grams of mercury respectively. The value of 1 millimetre of the mercurial column was 0.0116° and 0.0097° , an estimation figure of 0.05 mm., corresponding, therefore, to about 0.0005° C.

The production of these instruments was the result of some years labour and repeated failures. The delicacy of a thermometer depends, of course, on the fineness of the bore of the tube and the size of the bulb; but many unexpected difficulties are met with when we push both these conditions to their extreme limits. Tubes of the requisite strength and of very fine bore can be obtained by chance only; from the glassblower's point of view, indeed, they are failures, and he tries to avoid producing them; moreover, such as are sometimes produced are generally too flat in the bore to be suitable for a really fine instrument. The bore should be flat, but at the same time well rounded at the edges, for if the edges be wedge-shaped the mercury will often not entirely fill the tube, and the instrument will be untrustworthy and useless.

The impossibility of obtaining a suitable tube forced me to reduce the delicacy of my present instruments to less than the delicacy which

I had obtained in some previous ones (0.0003°). The bulb of the instrument presents fewer difficulties, though long practice only can give the experience which is necessary to tell whether the mercury in it has been efficiently boiled. The pressure of the column of mercury in the tube of these delicate instruments produces an expansion of the bulb, which attains very considerable apparent dimension. Thus with one of my thermometers there would be as much as 20 or 30 mm. difference in the reading of the same temperature, according as the instrument was held in a vertical or horizontal position. The variations of pressure on the bulb produced by the alteration in the height of the column are not considered, however, to affect the accuracy of the measurements, provided the thermometer be always held in the same position, since the expansion of the bulb is directly proportional to the pressure (Egen, *Pogg. Ann.*, **11**, 283; Mills, *Proc. Roy. Soc. Edin.*, **29**, 285); but this, I find, is not entirely true: the expansion is directly proportional to the pressure, but it is apt to take place in an irregular manner, resembling the sudden alterations in shape which may often be noticed when increasing the pressure on a thin tinplate vessel. Serious errors may thus arise, and the only way in which they can be obviated is by increasing the strength, and thus diminishing the expansibility of the bulbs. This I effect by having the bulbs made out of carefully selected glass cylinders, and not blown before the lamp; much greater uniformity in substance and regularity of action is thus obtained. A further large increase of rigidity is obtained by having a double bulb instead of a single one. The walls of the tubing out of which the bulb is made may be of considerable thickness without diminishing the sensitiveness of the instrument to any appreciable extent, provided always the thermometer is to be employed in taking the temperatures of liquids, and that the agitation of the liquid be perfect. I use tubing as much as 0.7 mm. thick in the walls for bulbs containing 30—50 grams of mercury, and find that the temperature of the liquid is attained in about five seconds. The coefficient of expansion of the bulb of a thermometer of the delicacy of those here discussed should not be much more than 0.00000003 per mm. of mercury pressure; with a coefficient of 0.000000045 I have noticed considerable irregularities in the expansion.

One point which is of vital importance in the construction of a delicate thermometer is that the interior of the tube should be protected from contact with the air. The more delicate instruments which I employed formerly had the serious defect of giving a different reading according as the column had risen or fallen to the position of rest, and after much trouble this defect was traced to the fact that the instruments had been opened after they had been made up, a temporary bulb having been attached at first for the purposes

of calibration. It was found that such an operation entirely ruined the tube, and that it was only by observing the most minute precautions, and by never opening the tube till the moment the bulb was ready to be attached that a perfect instrument could be produced. By exposure to the air glass absorbs moisture and carbon dioxide as well as air (see some experiments of Bottomley, *Proc. Roy. Soc.*, **38**, 158), which form an elastic coating on its surface, and cannot be removed subsequently by any applicable process. The practice of calibrating the tube while open to the air, so generally adopted by the makers, and advocated even by many eminent physicists, will utterly ruin any tube for really delicate work.

I may be excused for drawing attention to one other detail in construction, the observance of which may save a good instrument from being spoilt at the last moment. The graduation of the stem should never be left to the workman's discretion, and should never be commenced without first having a trial made on a waste piece of glass. It is of the greatest importance that the lines should be very fine, regular, and clean cut; but in addition to this they should be very short, and well to the side of the front portion of the stem; the fifth and tenth lines should be only just perceptibly longer than the others, and the figures should be at some distance from the lines. In this way a good view of the mercurial column may be obtained to the side of the graduations, and it is never obstructed by the graduations themselves.

However good a thermometer tube may be, there are generally a few points in it past which the mercury will not move easily, and at which the column will even break off in some cases. These sticking points are caused by some contraction or imperfection in the bore of the tube, too minute to be noticed in the calibration of the instrument; and such points must be sought out, and, if possible, be avoided in any experiments, or, at any rate, the final and initial readings of the instrument should be adjusted so as to be clear of them.*

The calibration correction in the case of both instruments used in the present work was very small considering their length (graduated stem = 400 mm.), and the errors due to such corrections were almost entirely eliminated by the method described previously, of removing some of the mercury into the upper chamber, so that exactly the same portion of the stem should be used for all experiments with the same salt, whatever the actual temperature of the experiment might be. Instead of removing the mercury by heat, a simpler arrangement was after much trouble procured. On to the upper end of the tube, a wider tube was attached, and in this there was a small constriction, or knife-edge, as it is termed technically, sufficiently wide

* Further details respecting thermometers will be found in the *Phil. Mag.*, 1886, 180, 330, and 1887.

to allow the mercury to pass freely in either direction, but at which the column at once separates if the instrument be swung or jerked. After each adjustment the calorimetric thermometer is compared with the others used in the work (for the temperature of the salt, &c.), and with the standard which gives the value of the initial reading in degrees centigrade. The initial reading of the instrument in each experiment of a series was identical within less than 1 mm.

Methods of Experimenting.

In conducting an experiment, the rate of cooling before the salt is added was practically *nil*, owing to the temperature of the air being the same as that of the calorimeter. It is advisable, however, that it should not be absolutely *nil*: for the motion of the mercury past certain points in the stem not being regular, as mentioned above, more reliance can be placed on any reading where the column is moving slowly but steadily than when it is quite stationary. In each experiment, the thermometer was read once before the initial temperature was finally read, so as to make sure that no sticking of the column had taken place. The rate of cooling necessary is only about 0.001° per one or two minutes, a rate which, for the purposes of calculating the loss during the uncertain interval while the salt is dissolving, may safely be taken as *nil*.

As soon as the thermometer is read, the salt is removed from the water-jacket surrounding it and shaken into the calorimeter; this operation occupies an interval (which we may term A), which may be seen from the experiments quoted above to be very constant in duration (15 secs.); a second interval, B, then occurs, during which the salt is dissolving, the time is then noted, and a third interval, C, equal in duration to A, is allowed. If the initial temperature were read at 0' 0'', and the end of the interval C occurred at 1' 0'', the initial temperature was taken as having been read at 0' 30'', and, in order to obtain the final temperature, the thermometer was read at 2' 30'', 4' 30'', 6' 30'', &c., the rate of cooling thus determined being added on to the first of these readings. In this way the correction for cooling applied to the uncertain interval is half the rate at the final temperature, that is, intermediate between the initial (*nil*) and final rates; the interval C counterbalancing the interval A.

Salts examined.

The previous investigation was confined to metallic sulphates, and for the present one typical salts of other classes were sought. Very great difficulty was met with in procuring suitable substances. In order

to obtain great accuracy in the results, the salt must dissolve quickly and without much caking; it must be obtainable in the anhydrous state without decomposition, a circumstance which precludes the use of very many salts (*Chem. News*, **53**, 279). Moreover, in order to powder and sift them on a large scale, they must not be very deliquescent or efflorescent; and, finally, the salts sought were those which in their respective classes contained a considerable amount of water, and exhibited considerable differences in their heat of dissolution.

Thirteen salts were finally selected, and 2 or 3 kilos. of each were prepared: in helping me with which laborious work, and also with the calculation of a considerable part of the results, I have to thank Mr. P. G. Sanford. It is, for reasons pointed out elsewhere (*Chem. News*, **54**, 277), impossible to prepare most hydrated salts with the exact theoretical percentage of water, this was, therefore, not attempted, and the salts contained generally slightly less than the calculated amount. The preparations were as follows:—

Potassium Chloride.—This salt requires prolonged heating at a low red heat to drive off all the enclosed moisture. In order to ascertain whether the temperature of preparation had any effect on the calorimetric results, two samples were dehydrated: the one at the lowest possible temperature, the other at a temperature just below its melting point; these gave on dissolving in 200 H₂O—

No. 3663 lowest temp.	—	4672 cal. at 13.5°.
„ 3664 highest	„	— 4701 „ „
Thomsen found	„	— 4597 „ „*
Berthelot	„	— 4480 „ „

The two preparations were, therefore, identical. That used in the series of experiments (No. 3675) gave —4655 cal. at the same temperature.

Sodium Chloride.—Examined in the same way as the potassium salt, gave—

No. 3665 lowest temp.	—	1355 cal. at 13.6°.
„ 3664 highest	„	— 1361 „ „
Thomsen found	„	— 1321 „ „
Berthelot	„	— 1311 „ „

The sample used in the series of experiments (No. 3674) gave —1366 cal.

Potassium Nitrate.—As this salt melts at 360°, the sample which was prepared at the highest temperature was not heated above 300°.

* Deduced from results at 18° and 21.6° respectively; in some cases the temperatures at which Berthelot and Thomsen dissolved their salts are given approximately only.

that prepared at the lowest temperature was heated at 100—110°; they gave the following results:—

No. 3661 lowest temp.	— 8514*	cal. at 13·47°.
„ 3660 highest „	— 8600	„ „
Thomsen found	— 8672	„ „
Berthelot „	— 8352	„ „

Two samples were used in the series of experiments, Nos. 3659 and 3978; they gave —8596 and —8609 cal. respectively at this temperature.

Strontium Chloride, Anhydrous.—The last traces of moisture in this salt could be expelled only by protracted heating in a platinum dish over a rose burner. Two samples prepared at as low and as high a temperature as possible, gave—

No. 3652 lowest temp.	— 10874	cal. at 13·5°.
„ 3653 highest „	— 10927	„ „
Thomsen found	— 10770	„ „
Berthelot „	— 11300	„ „

The sample used in the series of experiments (No. 3667) gave 10915 cal.

Strontium Chloride, Hydrated, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$.—Some difficulty was experienced in preparing this salt, owing to its being deliquescent. After finely powdering, it was exposed in a vacuum for a few minutes, and then sifted very quickly. On analysis, the sample (No. 3672) gave—

- (1.) 40·512 per cent. water.
 (2.) 40·510 „ „

Mean.. 40·511

Theory.. 40·542 per cent.;

and hence it contained $5\cdot992\text{H}_2\text{O}$.

On dissolution at 18°, it gave —7545 cal., as against —7500 obtained by Thomsen with a sample containing $6\text{H}_2\text{O}$, and —7010 obtained by Berthelot.

Strontium Nitrate, Anhydrous.—Prepared in a similar manner to the chloride; two samples gave—

No. 3654 lowest temp.	— 5157	cal. at 13·51°.
„ 3655 highest „	— 5126	„ „
Thomsen found	— 4943	„ „
Berthelot „	— 5113	„ „

* These preliminary experiments were not performed with the delicate thermometers.

The sample used in the series of experiments (No. 3666) gave —5108 cal. at this temperature.

Strontium Nitrate, Hydrated, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.—The preparation of this salt (No. 3668) gave on analysis—

(1.)	25.330	per cent. water.	
	25.328	„	„
	25.338	„	„
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Mean..	25.333		Theory.. 25.394 per cent.;

hence it contains $3.987\text{H}_2\text{O}$.

On dissolution, it gave —12794 cal. at 18° , against Thomsen's preparation with $4.02\text{H}_2\text{O}$, which gave —12300.

Sodium Carbonate, Anhydrous.—Samples of this salt, prepared at temperatures between 60° and its fusing point, gave identical results, details of which will be found in this vol., p. 72.

Sodium Carbonate, Hydrated, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.—On analysis, the sample (No. 3683) gave—

(1.)	62.826	per cent. water.	
(2.)	62.826	„	„
			Theory.. 62.920 per cent.;

hence it contained $9.96\text{H}_2\text{O}$.

On dissolution, it gave —16185 cal. at 18° , against Thomsen's —16160 at the same temperature.

Sodium Acetate, Anhydrous.—Samples were prepared in a vacuum, at 100° and 200° ; they gave—

No. 3658	in vacuo,	3886	cal. at 13.58° .
„	3649 at 100° ,	3854	„
„	3650 at 200° ,	3922	„
Thomsen found		3825	„
Berthelot	„	4185	„

Two preparations were used in the series of experiments; No. 3679 gave 3913 cal., and No. 4552 gave 3910 cal. at this temperature.

Sodium Acetate, Hydrated, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$.—The sample of this salt (No. 3689) gave on analysis—

(1.)	39.829	per cent. water.	
(2.)	39.848	„	„
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Mean..	39.838	„	„
			Theory.. 39.704;

so it appeared to contain $3.017\text{H}_2\text{O}$. As this excess over $3\text{H}_2\text{O}$ is probably due to the presence of traces of enclosed water, or to a slight amount of decomposition having occurred during the dehydra-

tion, it was considered advisable to take the water as being exactly $3\text{H}_2\text{O}$ in the calculations.

On dissolution at 18° , it gave -4773 cal., against Thomsen's -4810 , and Berthelot's -4640 at the same temperature.

Rochelle Salt, Anhydrous.—The hydrated salt was heated at a temperature below 100° ; it fused, and after the greater portion of the water had been expelled, and the salt solidified, it was powdered and sifted, and then heated again at about 150° till constant in weight. As a lower temperature was found insufficient to dehydrate it, and a higher temperature induced decomposition, it is not possible to feel certain that the salt was perfectly anhydrous. On dissolution, the sample used in the experiments, No. 3914, gave -2975 cal. at 15° , against -1900 (?) found by Berthelot at the same temperature.

Rochelle Salt, Hydrated, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ (sample No. 3688).—For the reason first stated it is not possible to rely on the water determinations made with this salt; they were—

(1.)	23·475	per cent.	
*(2.)	23·488	„	
Mean..	23·482	„	= $3\cdot56\text{H}_2\text{O}$;

which, if right, show a considerable deficit, the theoretical percentage being $25\cdot520$. In the calculations, I have assumed that the salt contained the theoretical amount.

On dissolution at -15° , it gave -12520 cal., while Berthelot found -12300 .

The sulphates which were examined were prepared in the same manner as in the earlier work (p. 269).

The dehydrated salts were kept in a number of small bottles, each of which contained sufficient for two determinations. The large bottles containing the hydrated salts were kept continually shaken, it being important to avoid caking in the bottle, which is apt to render the contents unhomogeneous.

Series of Experiments.

All the series of experiments were started at 14° with thermometer 65108, the initial reading of the mercurial column being identical in all cases, and experiments were performed at each degree centigrade up to 25° . After this a similar series of experiments at the same temperatures were started at 13° , with thermometer 65561, and carried up to 25° . At temperatures below 13° , experiments were generally done at every other degree only with each instrument,

* A third analysis gave $24\cdot206$, but this may be a simple mistake.

using No. 65108 for the even degrees and 65561 for the uneven ones, and the experiments were thus carried down, as the atmospheric temperatures served, to 3° .

In cases where the series showed irregularities which required further investigation, other fresh series of experiments more or less complete were performed, using for them a totally different portion of the stem of the thermometer; this, I believe, to be in every way equivalent to using a different instrument. Provided the bulb of a thermometer be a good one, all the peculiarities of the instrument are attributable, I feel sure, to the stem. The series performed with different portions of the stem of the thermometers 65108 and 65561 may be conveniently designated as with '08A, '08B, '61C, &c.*

Any experiments which appeared to be exceptional or of doubtful accuracy were repeated, and if not confirmed, were rejected; these, however, amount in all to only 25 (of which 20 were known at the time of their performance to have come entirely to grief) out of a total of 730—a small percentage when it is remembered that work which is dependent on atmospheric temperatures must often be done against time, and that various small circumstances, such as an accidental splash or a sudden draught, &c., may invalidate the results.

As various experiments about 14° were being performed at intervals throughout the duration of the work, these would have afforded evidence in case the sample used had suffered any alterations since the commencement of the work at this temperature. No such alteration, however, was observed in any case.

Explanation of the Tables and Plates.

The proportion of salt to water taken was 1:200H₂O in the case of salts of the monobasic acids, and 1:400H₂O in the other cases; the actual proportions being $\frac{1}{8}$ and $\frac{1}{12}$ gram-molecule to 600 c.c. of water. An estimation figure (0.05 mm.) of the thermometer corresponds in the former cases to 2.1 and 1.8 cal. according as thermometer '08 or '61 was used, in the latter to 4.3 and 3.6 cal. respectively.

In the Tables A, B, &c., experimental details are given sufficient for the recalculation of any of the results, though in a more abbreviated form than in the previous communication. w is the weight of salt taken, corrected to weight in a vacuum. The water equivalent of the calorimeter and its contents is made up of 601.74 + 0.016 ($T^{\circ} - 4$) c.c. of water + any water contained in the salt, calcu-

* The actual positions of the mercury at the initial temperatures were '08A = 244 mm.; '08B = 147 mm.; '08D = 367 mm.; '61A = 258 mm.; '61B = 147 mm.; '61C = 58 mm.; '61D = 365 mm., the graduated stem being 400 mm. long.

lated according to the analytical results (except in the case of hydrated Rochelle salt and sodium acetate, where the theoretical amount was taken as being present) + the water equivalent of the thermometer, stirrer, &c., amounting to 8.099 grams when '08 was employed and 8.26 grams when '61 was employed. In the case of hydrated Rochelle salt and hydrated sodium carbonate, and in a few other less important cases, another 0.11 gram must be added for the wire gauze tray which was used. With anhydrous Rochelle salt and with anhydrous sodium carbonate, the total water equivalent is 0.21 and 0.44 gram less respectively, owing to the thermometers being immersed to a smaller depth in the liquid. The total water equivalent amounts roughly to 610 grams with the anhydrous salts, 616 grams with hydrated Rochelle salt and strontium nitrate, 619 grams with hydrated strontium chloride and sodium acetate, and 625 grams with hydrated sodium carbonate.

It has been thought unnecessary to give the temperature of the salt before its introduction into the calorimeter, as this rarely differed by more than 0.05° from that of the water, and its effect on the initial temperature scarcely ever amounted to one estimation figure of the thermometer. The initial temperature t is given in round numbers (to 0.005°) in degrees centigrade, and the rise or fall, $t' - t$ or $t - t'$, is given accurately in like degrees. M represents the molecular heat of dissolution given in one column at the initial temperature t , and in another, for the sake of comparison, at the nearest whole degree centigrade (deduced diagrammatically by joining all the results at t by straight lines). With hydrated salts, M is the corrected heat of dissolution, obtained by subtracting from the observed heat, m , the heat of fusion of the water contained in it, taking the amount given by the analyses (except in the case of Rochelle salt and sodium acetate) and using the numbers given in Plate VII of the former communication, in which paper will also be found further details as to the calculation.

Each series with a different instrument is given separately.

The mean results are collected and discussed in the Tables I, II, &c., given in the text, and are further illustrated in the diagrams. These contain the figure representing the heat of dissolution of the anhydrous salt, the figure representing the "corrected" heat of dissolution of the hydrated salt (called formerly the "true" heat of dissolution), a third figure representing the apparent heat of dissolution of the same, and, lastly, one representing the heat of combination of the solid salt with its water of crystallisation, obtained by deducting the corrected heat of dissolution of the hydrated salt from that of the anhydrous salt.

The method adopted in drawing the curves will be best explained

by taking an instance: thus, with potassium chloride (Plate I and Table I, p. 306) the 16 mean results from 10° to 25° inclusive evidently form a straight line; taking the mean of the first eight of these we get -4348 cal. at 21.5° , and of the last eight -4654 cal. at 13.5° ; these two points were then plotted down, and the straight line joining them was extended upwards to 25° and downwards till it met the straight line obtained in a similar manner from the experiments below 9° . The mean results taken for this purpose are given in the various cases at the foot of the Tables I, II, &c.

Each small division of the paper represents 25 cal. with salts of the monobasic acids and 50 cal. with those of the bibasic acids.

A higher position on the paper corresponds to a larger evolution of heat or a smaller absorption of heat.

The mean results are deduced from the lines representing the various series, and not from the individual results only; in this way no undue preponderance is given to any one series: for instance, the mean results with potassium chloride at 17° depends on the value given by the series '61A as well as those given by the other series, although no experiment with '61A was done at that temperature, but only at 16° and 18° . In four cases confirmatory experiments at 4° were performed with '08B (*e.g.*, KCl), and as these stood by themselves in their series, only half value has been assigned to them in calculating the mean result at this temperature; in one or two other cases, results of doubtful accuracy were allowed half value only, and this is indicated in the tables by placing such results within brackets.

The points given in the lines representing the heat of combination of the salt with its water of crystallisation are deduced from points in the *mean lines* representing the heat of dissolution of the salt, and not from the position of the actual experiments at those points.

Experimental Results.

Potassium Chloride.—The four series of experiments performed with this salt, together with the resultant mean series, are given in Plate I, and are marked '08A, '61A, &c., according to the thermometer used. The individual series are represented by dotted lines and are plotted for the sake of greater clearness 4, 8, 12, &c., divisions (100, 200, 400 cal.) above their proper position according to the numbers given in the margin; each one, however, is accompanied by a continuous line which represents the mean result in a similar position. The figures in the margin refer only to the curve marked "mean."

Now looking at the portions of the curves with '08A above 13° (those results obtained first), it will be noticed that, in ascending, the line is suddenly shifted up at a certain point. This alteration was at first thought to be real, and in order to investigate it further the two

other series '08B and '61B as well as '61A, were performed, but, as they failed to show any similar change, the shifting had to be attributed to some experimental error. This apparent shifting up of the line as the temperature rises is not so marked here as in some other cases to be noticed below, and a similar shifting (in one or two cases downwards) was noticed at some point with many of the salts. It often occurred persistently in the results with both the instruments '08A and '61A at nearly the same temperature, but in every case was found to be illusory when investigated more fully. It was experimental errors of this nature, combined with the comparative incompleteness of the various series, which deceived the author in his earlier work, and which led him to regard the curves or lines as a series of separate curves. For some satisfactory explanation of these sudden shiftings of the curves (generally indicating diminution of the heat absorbed or increase of the heat evolved) he has sought in vain. The height of the barometer, the small variations in the quantity of salt taken, the gases dissolved in the water used, are all possible causes which have been investigated, but found inadequate to afford any explanation. They must perforce be attributed to errors in the thermometers, although this is equally unsatisfactory: the starting point of the mercurial column is the same in each experiment of the whole series, the final point is not; in one case the mercury falls to t' , whereas at some higher temperature it will only fall to t'' ; one can only imagine that there exists some point between t' and t'' which tends to make the mercury stick, and that when below this point, at t' , it works normally, whereas above it, at t'' , it is prevented by the obstruction from falling as far as it should. Such sticking points certainly do exist, as has been already mentioned, but the explanation is not satisfactory, for the final temperature is not read when the column is stationary but when moving, and the rate of cooling determined in these cases should exhibit irregularities as the column approaches or recedes from the sticking point; moreover, the rise in the curves occurred in many very different cases (that is, when the final position of the mercury was in all parts of the tube), at nearly the same actual temperatures (at about 18°), although the two series of experiments were performed at very different times; and another objection to such an explanation is that, owing to the slight variation in the weight of salt taken, the column often falls as far as t' in the experiment at the *higher* temperature and only as far as t'' in that at the lower temperature. Whatever be the true cause of these irregularities, they may be obliterated by a sufficient number of experiments with different parts of the instruments, and in their nature are easily recognisable from such variations as, I take it, are really due to variations in the heat evolved on dissolution.

These variations consist, as will be seen at once, of a sudden and well-defined alteration in the inclination of the lines representing the heat of dissolution. A careful inspection of Table I, which contains

TABLE I.—*Potassium Chloride. Mean Results.*

T.°	M, found.	Differences.	M, calculated.	Difference.
25	—4218 cal.		—4210 cal.	+ 8
24	—4252 "	34	—4248 "	+ 4
23	—4285 "	33	—4287 "	—2
22	—4323 "	38	—4325 "	—2
21	—4365 "	42	—4364 "	+ 1
20	—4403 "	38	—4403 "	0
19	—4441 "	39	—4442 "	—1
18	—4477 "	36	—4480 "	—3
17	—4522 "	45	—4519 "	+ 3
16	—4555 "	33	—4558 "	—3
15	—4596 "	41	—4596 "	0
14	—4634 "	38	—4635 "	—1
13	—4674 "	40	—4673 "	+ 1
12	—4709 "	35	—4712 "	—3
11	—4750 "	41	—4750 "	0
10	—4791 "	41	—4789 "	+ 2
9	—4833 "	42	—4828 "	+ 5
8	—4883 "	50	—4884 "	—1
7	—4936 "	53	—4934 "	+ 2
6	—4985 "	49	—4984 "	+ 1
5	—5033 "	48	—5034 "	—1
4	—5085 "	52	—5084 "	+ 1
3	—5134 "	49	—5134 "	0

Average points for the highest portion, —4345.5 cal. at 21.5° and —4654 cal. at 13.5°, whence increase = 38.6 per degree; ditto for lowest portion, —4909 at 7.5° and 5059 at 4.5°, whence increase = 50 per degree.

the mean results with this salt cannot fail, I think, to carry conviction with it as to the reality of this alteration, and inspire confidence in the results generally. Columns 1 and 2 contain the temperatures and the experimental results. In column 3 the differences between the results at consecutive degrees are given; these arrange themselves into two groups. From 25° to 9°, the increase for a fall of one degree is 38.4 cal., the various numbers ranging from 33 to 42 cal., and as to the uniformity of this increase, and, consequently, the straightness of the line which represents it, there can be little doubt, the increase from 25° to 17° giving an average of 38 cal. per degree, and that from 17° to 9°, 38.8 cal. All these differences, however, depend on the comparison of the results at two points only, and a more accurate number for the rate of increase may be deduced from the average points given at the foot of the table, and inserted in column 3 in brackets.

Below 9° the rate of increase becomes suddenly augmented by 30 per cent., reaching 50 cal. per degree, and remains constant throughout an interval of six degrees, the total increase from 9° to 6° , and from 6° to 3° differing by 3 cal. only.

In column 4 are given the calculated values as deduced from the "average points" by drawing straight lines through them, and continuing them till they meet; and in the last column are given the differences between these calculated values and the observed values. The one result at the extreme point 25° is exceptionally high (only 8 cal., however), and, as a similar excess occurs in the case of sodium chloride, it is probable that the line undergoes another deflection at about 24° ; omitting this one result, therefore, it will be seen that the greatest errors amount to 5 cal. in one case, 4 cal. in one case also, and all the others 3 cal. or less; the average error of the 22 results being only 1.7 cal., a quantity which corresponds to somewhat *less than 0.05 mm. of the mercurial column, or the two-thousandth of a degree*. It is true that the results with potassium chloride are exceptionally concordant, but the general mean of the similar errors in the whole work amounts to only 3.5 cal. (calculated as for salts of monobasic acids),* or less than the one-thousandth of a degree. This does not, of course, represent the error of single experiments, as each of these points are the result of two or three experiments; but the average divergence of each single experiment from the calculated value is only 7.4 cal., and the average difference between any pair of experiments 11 cal. (both calculated to salts of monobasic acids); a result which cannot be regarded otherwise than satisfactory, especially when it is noted that the greater part of this error results from peculiarities which do not affect the conclusions here drawn, for on looking at Plate I it will be seen that the results obtained with one instrument are often uniformly above the average (*e.g.*, '08A and '61A), whereas those with the others are uniformly below it (*e.g.*, '08B and '61B). This does not affect the inclination of the lines, though it augments considerably the divergence between the actual experiments. A similar fact was observed in nearly all cases, but the higher results were obtained in some with one instrument, in others with the other, according to which salt happened to be under examination. It must be remembered also that all the duplicate experiments in this work were performed under conditions most unfavourable for producing concordance, namely, with different instruments, and at long intervals of time apart.†

* The same thermometric quantity represents double the number of calories with salts of bibasic acids.

† The average difference between experiments performed under like conditions in my former work would be 25 cal. See *Phil. Mag.*, 1886, 328.

I have indicated by a line across the tables which formula was used for obtaining the calculated value at the temperature where the change of rate occurs.

Sodium Chloride. Tables II and B, Plate I.—The lines representing the results with sodium chloride are very similar to those with

TABLE II.—*Sodium Chloride. Mean Results.*

T.°	M, found.	Differences.	M, calculated.	Difference.
25	−1024 cal.	22	−1040 cal.	+6
24	−1046 "	29	−1072 "	+3
23	−1075 "	29	−1103 "	+1
22	−1104 "	31	−1134 "	+1
21	−1135 "	29	−1166 "	−2
20	−1164 "	29	−1197 "	−4
19	−1193 "	30	−1228 "	−5
18	−1223 "	31	−1260 "	−6
17	−1254 "	36	−1291 "	−1
16	−1290 "	37	−1322 "	+5
15	−1327 "	31	−1353 "	+5
14	−1358 "	28	−1385 "	+1
13	−1386 "	27	−1416 "	−3
12	−1413 "	32	−1447 "	−2
11	−1445 "			
10	−1483 "	38	−1478 "	+5
9	−1521 "	38	−1520 "	+1
8	−1556 "	36	−1563 "	−7
7	−1597 "	41	−1605 "	−8
6	−1648 "	51	−1648 "	0
5	−1693 "	45	−1690 "	+3
4	−1736 "	43	−1732 "	+4
3	−1775 "	39	−1775 "	0

Average points for the highest portion, −1134.3 cal. at 21° and −1353.3 at 14°, whence increase = 31.3 per degree; ditto for lowest portion, −1520.4 at 9° and −1690 at 5°, whence increase = 42.4 per degree.

potassium chloride. The result at 25° is considerably below (larger heat absorption) the calculated value, and is probably the beginning of a fresh rate of alteration. The rate of increase with falling temperature, which is rather less than with the potassium salt, alters suddenly at the same temperature (10°) within experimental error, becoming 39 per cent. larger. The average error here is 3.2 cal.

Potassium Nitrate. Tables III and C, Plate I.—The results with this salt closely resemble those with potassium chloride, except that the break occurs at a higher temperature, 12°, and that there is no indication of any other break at 25°. At the break, the rate of alteration is increased by 32 per cent. The average error is 4.3 cal.

TABLE III.—*Potassium Nitrate. Mean Results.*

T.°	M, found.	Differences.	M, calculated.	Difference.
25	—8220 cal.	39	—8219 cal.	+ 1
24	—8259 "	35	—8253 "	+ 6
23	—8294 "	26	—8286 "	+ 8
22	—8320 "	27	—8319 "	+ 1
21	—8347 "	29	—8353 "	— 6
20	—8376 "	43	—8386 "	—10
19	—8419 "	40	—8419 "	0
18	—8459 "	27	—8453 "	+ 6
17	—8486 "	27	—8486 "	0
16	—8513 "	37	—8519 "	— 6
15	—8550 "	42	—8552 "	— 2
14	—8592 "	23	—8586 "	— 6
13	—8615 "		—8619 "	— 4
<hr/>				
12	—8655 "	40	—8649 "	+ 6
11	—8696 "	41	—8693 "	+ 3
10	—8738 "	42	—8737 "	+ 1
9	—8777 "	39	—8781 "	— 4
8	—8819 "	42	—8825 "	— 6
7	—8868 "	49	—8869 "	— 1
6	—8915 "	47	—8913 "	+ 2
5	—8961 "	46	—8957 "	+ 4
4	—9007 "	46	—9001 "	+ 6
3	—9033 "	26	—9045 "	—12

Average points for the highest portion, — 8319.3 cal. at 22° and — 8519 at 16°, whence increase = 33.3 per degree; ditto for the lowest portion, — 8737 at 10° and — 8956.8 at 5°, whence increase = 44 per degree.

Strontium Chloride. Tables IV, V, D, and E, Plate II.—The results with the anhydrous salt were not very concordant, and show an average divergence from the calculated values of 7.7 cal. (corresponding to 3.8 cal. in the salts previously discussed). The experiments at 3° give abnormally high results, but there can be little doubt but that there is an increase in the rate of change at 8°, amounting to 19 per cent.; the hydrated salt shows a similar increase at the same point, amounting to 21 per cent. With the anhydrous salt, another change of 20 per cent. appears to take place at 13°, above which temperature the rate of increase remains constant up to 25°. I do not feel at all certain as to this break at 13°, not only because the individual experiments with this salt were not very concordant, but also because there is no well-defined break at the same point with the hydrated salt; at a somewhat higher temperature, it is true, 15—16°, a slight change in this direction does occur, the rate

altering from 91.8 to 87.5 cal., but this alteration is so small that if it stood by itself, it would not be worth consideration.

The average error for the hydrated salt is 5.8 cal.

TABLE IV.—*Anhydrous Strontium Chloride. Mean Results.*

T. °	M, found.	Differences.	M, calculated.	Difference.
25	11818 cal.	$\left. \begin{array}{l} 52 \\ 71 \\ 87 \\ 91 \\ 87 \\ 85 \\ 88 \\ 82 \\ 71 \\ 76 \\ 61 \end{array} \right\} \begin{array}{l} 76.8 \\ \\ 76.1 (80.4) \\ 75.5 \end{array}$	11842 cal.	-24
24	11766 "		11762 "	+ 4
23	11695 "		11681 "	+14
22	11612 "		11601 "	+11
21	11521 "		11520 "	+ 1
20	11434 "		11440 "	- 6
19	11349 "		11360 "	-11
18	11271 "		11279 "	- 8
17	11189 "		11199 "	-10
16	11118 "		11118 "	0
15	11042 "		11138 "	+ 4
14	10981 "	$\left. \begin{array}{l} 105 \\ 93 \\ 100 \\ 92 \\ 97 \\ 93 \end{array} \right\} 96.8 (96.5)$	10977 "	+ 4
13	10876 "		10880 "	+ 4
12	10783 "		10785 "	- 2
11	10683 "		10688 "	- 5
10	10591 "		10591 "	0
9	10494 "		10494 "	0
8	10401 "	$\left. \begin{array}{l} 112 \\ 123 \\ 121 \\ 122 \\ 69 \end{array} \right\} 110.0 (115.3)$	10399 "	+ 2
7	10289 "		10284 "	+ 5
6	10163 "		10169 "	+ 6
5	10042 "		10053 "	-11
4	9920 "		9938 "	-18
3	9851 "		9823 "	+28

Average points for the highest portion, 11641 cal. at 22.5° and 11158.4 cal. at 16.5°, whence decrease = 80.4 per degree; ditto for the middle portion, 10880 cal. at 13° and 10542.3 cal. at 9.5°, whence decrease = 96.5 per degree; ditto for the lowest portion, 10284 at 7° and 9938 at 4°, whence decrease = 115.3 per degree.

TABLE V.—*Hydrated Strontium Chloride. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
25	2527 cal.	76	2535 cal.	- 8
24	2451 "	95	2448 "	+ 3
23	2356 "	88	2360 "	- 4
22	2268 "	69	2272 "	+ 4
21	2199 "	104	2185 "	+ 14
20	2095 "	87	2098 "	- 3
19	2008 "	84	2010 "	- 2
18	1924 "	93	1923 "	+ 1
17	1831 "	89	1835 "	+ 4
16	1742 "	72	1747 "	- 5
15	1670 "		1660 "	+ 10
14	1560 "	110	1569 "	- 9
13	1476 "	84	1477 "	- 1
12	1387 "	89	1385 "	+ 2
11	1293 "	94	1294 "	- 1
10	1202 "	91	1202 "	0
9	1114 "	88	1110 "	+ 4
8	1016 "	98	1018 "	- 2
7	910 "	106	913 "	- 3
6	822 "	88	802 "	+ 20
5	685 "	137	690 "	- 5
4	575 "	110	579 "	- 4
3	476 "	99	468 "	+ 8

Average points for highest portion, 2316 cal. at 22·5° and 1835 at 17°, whence decrease = 87·5 per degree; ditto for middle portion, 1523 at 13·5° and 1156 at 9·5°, whence decrease = 91·8 per degree; ditto for lowest portion, 913 at 7° and 578·7 at 4°, whence decrease = 111·4 per degree. For *m* these points are - 7384 at 22·5°, - 7583 at 17°, - 7715 at 13·5°, - 7874 at 9·5°, - 7985 at 7° and - 8164 at 4°.

Strontium Nitrate. Tables VI, VII, F, and G, Plate III.—With the anhydrous salt there appears to be a break at 21°, when the rate increases by 16 per cent. of its value, and a similar break of 16 per cent. also occurs at the same temperature with the hydrated salt. Another increase of 30 per cent. then takes place at 8·5° with the anhydrous salt, and an increase of 28 per cent. at 9° with the hydrated salt.* As far as the differences given in Table VI are concerned, the break with the anhydrous salt would appear to take place at 7°, but

* The experiment at 4° with '08B has been omitted in this case in calculating the mean result at this temperature, on account of its being considerably below the results in the other series, and of there being no other experiments with the same instrument at contiguous temperatures. It entirely confirms, however, the increased rate of alteration at low temperatures.

the diagram shows that the junction of the two lines really occurs at a temperature practically identical with that in the case of the hydrated salt.

The average error here is 6 cal. for the anhydrous salt, 5.8 cal. for the hydrated salt.

TABLE VI.—*Anhydrous Strontium Nitrate. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
25	—4348 cal.	49	—4341 cal.	+ 7
24	—4397 "	65	—4402 "	— 5
23	—4462 "	55	—4463 "	— 1
22	—4517 "	73	—4523 "	— 6
		60.3 (60.5)		
21	—4590 "	65	—4583 "	+ 7
20	—4655 "	69	—4648 "	+ 7
19	—4724 "	57	—4718 "	+ 6
18	—4781 "	79	—4789 "	— 8
17	—4860 "	68	—4859 "	+ 1
16	—4928 "	54	—4930 "	— 2
15	—4982 "	98	—5000 "	— 8
14	—5080 "	57	—5071 "	— 9
13	—5137 "	58	—5141 "	— 4
12	—5195 "	75	—5212 "	—17
11	—5270 "	85	—5282 "	—12
10	—5355 "	73	—5353 "	+ 2
9	—5428 "	80	—5423 "	+ 3
		70.8 (70.5)		
8	—5508 "	81	—5503 "	— 5
7	—5589 "	98	—5595 "	— 6
6	—5687 "	98	—5687 "	0
5	—5785 "	91	—5779 "	+ 6
4	—5876 "	75	—5871 "	+ 5
3	—5951 "		—5963 "	—12
		88.6 (92)		

Average points for the highest portion, — 4402 at 24° and — 4523 at 22°, whence increase = 60.5 per degree; ditto for middle portion, — 4788.6 at 18° and — 5282 at 11°, whence increase = 70.5 per degree; ditto for the lowest portion, — 5595 at 7° and — 5871 at 4°, whence increase = 92 per degree.

TABLE VII.—*Hydrated Strontium Nitrate. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
25	—6005 cal.		—6013 cal.	— 7
24	—6083 "	78	—6078 "	+ 5
23	—6147 "	64	—6143 "	+ 4
22	—6208 "	61	—6207 "	+ 1
21	—6267 "	59	—6268 "	— 1
20	—6344 "	77	—6339 "	+ 5
19	—6427 "	73	—6414 "	+13
18	—6489 "	62	—6488 "	+ 1
17	—6565 "	76	—6563 "	+ 2
16	—6627 "	62	—6637 "	—10
15	—6698 "	71	—6711 "	—13
14	—6786 "	88	—6786 "	0
13	—6866 "	80	—6851 "	+15
12	—6927 "	61	—6925 "	+ 2
11	—6992 "	65	—7009 "	—17
10	—7083 "	91	—7083 "	0
9	—7166 "	83	—7158 "	+ 8
		80		
8	—7246 "	95	—7245 "	+ 1
7	—7341 "	95	—7341 "	0
6	—7436 "	94	—7437 "	— 1
5	—7530 "	95	—7532 "	— 2
4	—7625 "	105	—7628 "	— 3
3	—7730 "		—7724 "	+ 6

Average points for the highest portion, — 6078 cal. at 24° and — 6207 at 22°, whence increase = 64·5 cal. per degree; ditto for middle portion, — 6488 at 18° and — 7009 at 11°, whence increase = 74·5 per degree; ditto for lowest portion, — 7341 at 7° and — 7628 at 4°, whence increase = 95·7 per degree.

These points for *m* are, — 12579 at 24°, — 12643 at 22°, — 12790 at 18°, — 13067 at 11°, — 13260 at 7° and — 13443 at 4°.

Sodium Carbonate. Tables VIII, IX, H, and I, Plate III.—Owing to the excessive degree in which the anhydrous salt cakes, and, as a consequence, the length of time required for its dissolution, it was not originally intended to examine this salt; a few experiments (two at every third degree) were subsequently performed, chiefly with a view to the heat of its combination with its water of crystallisation. In spite of the difficulties of dealing with it, the average error is not large (8·2 cal.), and the general results are well borne out by their agreement with those obtained with the hydrated salt. At 19° an increase of 26 per cent. occurs in the rate of alteration, and at 7° there is another much larger increase, amounting to 92 per cent. The experiments are, however, not sufficiently numerous to settle with certainty the exact temperature at which these changes occur. Taking the hydrated salt, the first increase occurs at about 18°, and

TABLE VIII.—*Anhydrous Sodium Carbonate. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
25	5852 cal.	$\left. \begin{array}{l} 3 \times 52 \\ 3 \times 54 \\ 3 \times 72 \end{array} \right\} 53 \cdot 0$	—	—
22	5695 "		5693 cal.	+ 2
19	5533 "		—	—
16	5316 "	$\left. \begin{array}{l} 3 \times 77 \\ 3 \times 57 \\ 3 \times 70 \end{array} \right\} 69 \cdot 3 (67 \cdot 2)$	5311 "	+ 5
13	5084 "		5109 "	- 25
10	4912 "		4908 "	+ 4
7	4701 "	3×129	4706 "	- 5
4	4315 "		—	—

Average points for the middle portion 5311 cal. at 16° and 4807 at 8·5°, whence decrease = 67·2 per degree; decrease for the highest portion = 53 per degree.

TABLE IX.—*Hydrated Sodium Carbonate. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
25	+ 5 cal.	$\left. \begin{array}{l} 54 \\ 53 \\ 73 \\ 61 \\ 53 \\ 57 \end{array} \right\} 60 \cdot 1 (62 \cdot 9)$	+ 14 cal.	+ 9
24	- 49 "		- 49 "	0
23	- 102 "		- 112 "	- 10
22	- 175 "		- 175 "	0
21	- 236 "		- 237 "	- 1
20	- 299 "		- 300 "	- 1
19	- 356 "	$\left. \begin{array}{l} 72 \\ 96 \\ 49 \\ 87 \\ 112 \\ 90 \\ 99 \\ 79 \\ 82 \\ 82 \\ 88 \end{array} \right\} 85 \cdot 1 (88 \cdot 0)$	- 363 "	- 7
18	- 428 "		- 420 "	+ 8
17	- 524 "		- 508 "	+ 16
16	- 573 "		- 596 "	+ 23
15	- 660 "		- 684 "	- 24
14	- 772 "		- 772 "	0
13	- 862 "		- 860 "	+ 2
12	- 961 "		- 948 "	+ 13
11	- 1040 "		- 1036 "	+ 4
10	- 1122 "		- 1124 "	- 2
9	- 1204 "		- 1212 "	- 8
8	- 1292 "	$\left. \begin{array}{l} 108 \\ 111 \\ 113 \\ 107 \\ 77 \end{array} \right\} 103 \cdot 2 (106 \cdot 7)$	- 1294 "	- 2
7	- 1400 "		- 1401 "	- 1
6	- 1511 "		- 1507 "	+ 4
5	- 1624 "		- 1614 "	+ 10
4	- 1731 "		- 1721 "	+ 10
3	- 1808 "		- 1828 "	- 20

Average points for the highest portion, - 80·3 at 23·5° and - 300·3 at 20°, whence increase = 62·9 per degree; ditto for the middle portion, - 552·2 at 16·5° and - 1080·2 at 10·5°, whence increase = 88 per degree; ditto for the lowest portion, - 1401 at 7° and - 1721 at 4°, whence increase = 106·7 per degree. For *m* these points are - 16286·3 at 23·5°, - 16210·3 at 20°, - 16162·2 at 16·5°, - 16172·2 at 10·5°, - 16189 at 7° and 16245 at 4°.

amounts to 40 per cent., the second one at 7.5° , amounting to 21 per cent. With the *observed* heat of dissolution it will be seen that it decreases from 25° to 18° , remains constant for the next 12 degrees, and then decreases again.

The average error here is somewhat large (7.5 cal.), as is generally the case with salts containing a considerable amount of water, various sources of error being thereby increased.

Sodium Acetate. Tables X, XI, J and K, Plate V.—No less than five nearly complete series of experiments were performed with this salt, on account of the irregularities exhibited. They are given in full in the Plate, and illustrate well the nature of the errors by which I was misled in my former work. (N.B. the general concordance of the irregularities in the series '08A and '61A between 3° and 17° .) The differences which occur between the experiments are very considerable, and much weight could not be attached even to the mean result

TABLE X.—*Anhydrous Sodium Acetate. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
25	3971 cal.	$\left. \begin{array}{l} - 2 \\ - 4 \\ 2 \\ 3775 \\ 1 \end{array} \right\} - 0.8 (-0.8)$	3973	- 2
24	3973 "		3974	- 1
23	3977 "		3975	- 2
22	3775 "		3975	0
21	3974 "		3976	- 2
20	3960 "	$\left. \begin{array}{l} 14 \\ 12 \\ 0 \\ 3948 \\ 10 \\ 2 \\ 5 \\ 11 \\ 7 \\ 16 \\ 14 \end{array} \right\} \begin{array}{l} 7.7 \\ \\ \\ 10.6 (10.1) \\ 13.3 \end{array}$	3968	- 8
19	3948 "		3958	-10
18	3948 "		3948	0
17	3938 "		3938	0
16	3936 "		3928	+ 8
15	3931 "		3917	+14
14	3920 "		3907	+13
13	3903 "		3897	+ 6
12	3887 "		3887	0
11	3873 "		3877	- 4
10	3862 "	$\left. \begin{array}{l} 11 \\ 8 \\ 14 \end{array} \right\} 13.3$	3867	- 5
9	3854 "		3857	- 3
8	3840 "		3845	- 5
7	3826 "		3825	+ 1
6	3809 "		3805	+ 4
6	3785 "	$\left. \begin{array}{l} 24 \\ 17 \\ 25 \end{array} \right\} 20.5 (19.9)$	3795	-10
4	3768 "		3765	+ 3
3	3743 "		3745	- 2

Average points for the highest portion, 3973.7 at 24° 3975.3 at 22° , whence increase = 0.8 per degree; ditto for the middle portion, 3948 at 18° and 3877 at 11° , whence decrease = 10.1 per degree; ditto for the lowest portion, 3825 at 7° and 3765.3 at 4° , whence decrease = 19.9 per degree.

TABLE XI.—*Hydrated Sodium Acetate. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
25	+ 7 cal.	-12	+ 15 cal.	+ 8
24	+ 19 "	18	+ 9 "	-10
23	+ 1 "	6	+ 3 "	+ 2
22	- 5 "	- 2	- 2 "	+ 3
21	- 3 "	4	- 3 "	0
20	- 7 "	19	- 9 "	- 2
19	- 26 "	- 1	- 20 "	+ 6
18	- 25 "	21	- 31 "	- 6
17	- 46 "	2	- 41 "	+ 5
16	- 48 "	14	- 52 "	- 4
15	- 62 "	20	- 62 "	0
14	- 82 "	1	- 73 "	+ 9
13	- 83 "	6	- 84 "	- 1
12	- 89 "	9	- 94 "	- 5
11	- 98 "	14	- 105 "	- 7
10	- 112 "	10	- 115 "	- 3
9	- 122 "	7	- 126 "	- 4
8	- 129 "	18	- 130 "	- 1
7	- 147 "	24	- 149 "	- 2
6	- 171 "	33	- 175 "	+ 4
5	- 204 "	20	- 200 "	- 4
4	- 224 "	26	- 226 "	- 2
3	- 250 "		- 252 "	- 2

Average points for the highest portion, + 9 cal. at 24° and - 2·3 at 22°; whence increase = 5·7 per degree; ditto for the middle portion = - 30·6 at 18° and - 104·7 at 11°, whence increase = 10·6 per degree; ditto for the lowest portion - 149 at 7° and - 226 at 4°, whence increase = 25·7 per degree. For *m* these points are - 4887 at 24°, - 4847·3 at 22°, - 4771·6 at 18°, - 4666·7 at 11°, - 4606 at 7° and - 4604 at 4°.

were it not that it is well supported by the experiments with the hydrated salt.

The influence of temperature on the heat of dissolution of this salt is much smaller than in any other case examined; from 25—21° it is practically constant, *increasing* even at the small rate of 0·8 cal. per degree with fall of temperature. All the five series are so far concordant that they show no increase from 21° upwards, the rate then alters, a decrease of 10·1 cal. per degree occurring till 8°, when this decrease becomes nearly double, 19·9 cal. With the hydrated salt, we have a similar series of changes, an increase of 85 per cent. (not a large quantity in actual quantities; from 5·7 to 10·6 cal.) occurring at 19·5°, and another increase of 142 per cent. at 7°. The apparent heat of dissolution presents the anomaly (noticed also with sodium carbonate over a shorter range) of an *increase* of heat absorbed with *increase* of temperature.

The average error is 4.5 and 3.9 cal. with the anhydrous and hydrated salts respectively.

Rochelle Salt. Tables XII, XIII, L, and M, Plate VI.—In the series of '61A with the anhydrous salt, which was in this case performed first, the rate of change appeared to be considerably less between 20° and 21°, and also between 16° and 18°, than in the rest of the line extending between 13° and 25°. The experiments with '08A were then performed and confirmed these peculiarities in a marked manner. This, however, was not considered as sufficient proof, and two other short series with '08D and '61D were performed, and they showed perfect regularity between 16° and 21°, while experiments with '08E and '61C gave even a higher rate than the normal between 20° and 21°, reducing the mean results to a straight line within experimental error. This instance serves to illustrate what errors may be made by trusting to an insufficient number of series of experiments. This salt cakes considerably, and at low temperatures dissolves very slowly, the results below 8° are consequently not very

TABLE XII.—*Anhydrous Rochelle Salt. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
25	-2480 cal.	52	-2473 cal.	+ 7
24	-2532 "	51	-2525 "	+ 7
23	-2583 "	53	-2578 "	+ 5
22	-2630 "	56	-2631 "	- 1
21	-2683 "	49	-2683 "	0
20	-2732 "	53	-2736 "	- 4
19	-2785 "	56	-2788 "	- 3
18	-2841 "	42	-2841 "	0
17	-2883 "	45	-2893 "	-10
16	-2928 "	48	-2946 "	-18
15	-2976 "	57	-2999 "	-23
14	-3035 "	60	-3052 "	-17
13	-3095 "	54	-3104 "	- 9
12	-3149 "	58	-3157 "	- 9
11	-3207 "	70	-3210 "	- 3
10	-3277 "	68	-3262 "	+15
9	-3345 "		-3315 "	+30
8	-3398 "	43	-3397 "	+ 1
7	-3484 "	86	-3486 "	- 2
6	-3576 "	92	-3575 "	+ 1
5	-3685 "	109	-3664 "	+21
4	-3769 "	84	-3753 "	+17
3	-3806 "	37	-3843 "	-37

Average points for the higher portion, - 2683.2 cal. at 21° and - 3157 at 12°, whence increase = 52.6 per degree; ditto for the lower portion, - 3486 at 7° and - 3753 at 4°, whence increase = 89.1 per degree.

TABLE XIII.—*Hydrated Rochelle Salt. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
25	-5778 cal.	$\left. \begin{array}{l} 43 \\ 38 \\ 51 \\ 42 \\ 46 \end{array} \right\} \begin{array}{l} 44 \cdot 0 \\ 44 \text{ (44.7)} \\ 46 \cdot 3 \end{array}$	-5775 cal.	+ 3
24	-5821 "		-5819 "	+ 2
23	-5859 "		-5864 "	- 5
22	-5910 "		-5909 "	+ 1
21	-5952 "		-5953 "	- 1
20	-5998 "		-5998 "	0
19	-6071 "	$\left. \begin{array}{l} 73 \\ 67 \\ 67 \\ 41 \\ 61 \\ 86 \\ 52 \\ 49 \\ 67 \\ 79 \\ 58 \\ 66 \end{array} \right\} \begin{array}{l} 65 \cdot 8 \\ 63 \cdot 8 \text{ (63.1)} \\ 61 \cdot 8 \end{array}$	-6066 "	+ 5
18	-6138 "		-6129 "	+ 9
17	-6205 "		-6192 "	+13
16	-6246 "		-6255 "	- 9
15	-6307 "		-6318 "	-11
14	-6393 "		-6382 "	+11
13	-6445 "		-6445 "	0
12	-6494 "		-6508 "	-14
11	-6561 "		-6571 "	-10
10	-6640 "		-6634 "	+ 6
9	-6698 "		-6697 "	+ 1
			-6760 "	+ 4
8	-6764 "	$\left. \begin{array}{l} 87 \\ 80 \\ 86 \\ 93 \\ 59 \end{array} \right\} 87 \text{ (93.3)}$	-6849 "	+ 2
7	-6851 "		-6942 "	-11
6	-6931 "		-7035 "	+12
5	-7047 "		-7129 "	+11
4	-7140 "		-7222 "	-23
3	-7199 "			

Average points for the highest portion, 5819.8 at 24° and -5953.3 at 21°, whence increase = 44.7 per degree; ditto for the middle portion, -6160.8 at 17.5° and -6570.7 at 11°, whence increase = 63.1 per degree; ditto for the lowest portion, -6848.7 at 7° and -7128.7 at 4°, whence increase = 93.3 per degree. For *m* these points are -12347.3 at 24°, -12377.3 at 21°, -12465.3 at 17.5°, -12652.7 at 11°, -12792.9 at 7° and -12965.7 at 4°.

trustworthy, but I think they show an unmistakeable increase of about 70 per cent. in the rate of change, agreeing well with that observed with the hydrated salt. The average divergence from the calculated values is 10 cal.

Besides the increase of 48 per cent. in the rate at 7.5° observed with the hydrated salt, there is also another change at 20° of a similar nature. As some of the results here were not very concordant I have given them in full. They may be summarised thus:—

	25°.	20°.	Increase per degree, 25—20°.	17°.	Increase per degree, 20—17°.
'08A.....	—5746	—5995	50	—6223	76
'61A.....	—5782	—6018	47	—6216	66
'08D ... {	—5844 } 5829*	—5984	29	—6222	79
	—5814 }				
'61D	—5753	—5978	45	—6142 } 6150*	57
'61E.....	—5778	—6012	47	—6159 }	67
				—6214 }	
	—5778	—5997	44	—6205	70

In every case, the rate between 25° and 20° is less than between 20° and 17°, but series '61D shows the change but very slightly, while '08D shows it in an exaggerated form. If we take the mean of the whole number of experiments we get 44 and 70 cal. as the two rates, or, if we take the most concordant results only (*i.e.*, omitting the results marked with an asterisk), we get the almost identical numbers 45 and 74 cal. There cannot, I think, be much doubt that there is a change at 20°. The average error here is 7.1 cal.

Having thus found that in all the cases investigated any waviness which appeared at first in the lines representing the results was due to error, but little doubt remained but that this appearance observed in my former work on the sulphates was in like manner erroneous. Two cases, however, were selected for investigation, potassium sulphate and hydrated magnesium sulphate: subsequently a few experiments with anhydrous magnesium sulphate and with both the copper sulphates were added, to settle certain points with reference to the heat of combination with the water of crystallisation.

Potassium Sulphate.† Tables XIV and N, Plate I.—The original results are represented in the Plate by the discontinuous line; this consists of two straight lines‡ inclined to each other at an angle, with a considerable depression at their juncture. The fresh experiments are depicted in the continuous lines and show that this depression was illusory; in another respect, however, they entirely confirm the

† With this, and the other sulphates, I have used the same proportions of water as in my previous work, $\frac{3}{10}$ instead of $\frac{1}{12}$ th of a gram-molecule of salt to 600 c.c. water.

‡ The lower portion I have drawn straighter than in my first communication. An inspection of the original experiments will show that this is justifiable: both series form straight lines below 11°, but the mean becomes somewhat curved, owing to their not being coincident, and to the preponderance of experiments in one series over those in the other at certain points.

TABLE XIV.—*Potassium Sulphate. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
20	—6401 cal.	$\left. \begin{array}{l} 3 \times 85 \cdot 0 \\ 2 \times 86 \cdot 5 \\ 81 \cdot 0 \end{array} \right\} 84 \cdot 7 \text{ (85)}$	—6401 cal.	0
17	—6655 "		—6656 "	— 1
15	—6828 "		—6826 "	+ 2
14	—6909 "	$\left. \begin{array}{l} 2 \times 90 \cdot 5 \\ 2 \times 105 \cdot 5 \\ 3 \times 95 \cdot 0 \\ 3 \times 103 \cdot 0 \\ 101 \cdot 0 \end{array} \right\} \begin{array}{l} 98 \\ 98 \\ 99 \end{array} \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} 98 \cdot 9 \text{ (98.9)}$	—6910 "	— 1
12	—7090 "		—7100 "	—10
10	—7301 "		—7298 "	+ 3
7	—7587 "		—7594 "	— 7
4	—7896 "		—7891 "	+ 5
3	—7997 "		—7990 "	+ 7

Average points for the highest portion, —6528 cal. at $18 \cdot 5^\circ$ and —6868 at $14 \cdot 5^\circ$, whence increase = 85 cal. per degree; ditto for the lowest portion, —7100 at 12° and —7792 at 5° , whence increase = $98 \cdot 9$ per degree.

previous results. They form two straight lines showing rates of increase of 85 and $98 \cdot 9$ cal. respectively, meeting at 14° ; while the earlier experiments, for such portions as conform to straightness, the rates of increase are $82 \cdot 3$ cal. from 27° to 17° , and $105 \cdot 3$ cal. (from 12° to 3°) respectively; or, taking the results obtained with thermometer '83 only (given by a fine continuous line in the Plate), which was used in 23 of the 28 experiments below 12° , the rate for the lower portion is $97 \cdot 2$ cal., a number agreeing more fully still with my present determinations.

Magnesium Sulphate. Tables XV, XVI, O, and P. Plate VII.—The curved nature of the line obtained in the first experiments (the dotted line in the Plate) is proved to be incorrect in this case also. The present experiments, represented by the continuous line, show, in the case of the anhydrous salts, no break from 3° to 17° , the rate of

TABLE XV.—*Anhydrous Magnesium Sulphate. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
20.0	20540 cal.	$\left. \begin{array}{l} 3 \cdot 0 \times 59 \\ 3 \cdot 5 \times 87 \\ 3 \cdot 5 \times 87 \\ 3 \cdot 0 \times 90 \\ 4 \cdot 0 \times 89 \end{array} \right\} \begin{array}{l} 87 \cdot 0 \\ 88 \cdot 3 \text{ (88.7)} \\ 89 \cdot 6 \end{array}$	—	—
17.0	20327 "		20333 cal.	—6
13.5	20024 "		20023 "	+1
10.0	19718 "		19713 "	+5
7.0	19447 "		19446 "	+1
3.0	19091 "		19092 "	—1

Average points for the lowest portion, 20023 cal. at $13 \cdot 5^\circ$ and 19269 at 5° , whence decrease = $88 \cdot 7$ cal. per degree.

TABLE XVI.—*Hydrated Magnesium Sulphate. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
20	7298 cal.	$\left. \begin{array}{l} 3 \times 73 \\ 2 \times 72 \\ 80 \end{array} \right\} 74 (73.5)$	7298 cal.	0
17	7078 "		7078 "	0
15	6934 "		6931 "	+ 3
14	6854 "		6857 "	- 3
12	6705 "	$\left. \begin{array}{l} 2 \times 75 \\ 2 \times 89 \\ 3 \times 84 \\ 3 \times 93 \\ 93 \end{array} \right\} 89 (86.5)$	6695 "	+ 10
10	6527 "		6522 "	+ 5
7	6275 "		6263 "	+ 12
4	5997 "		6003 "	- 6
3	5904 "		5916 "	- 12

Average points for the highest portion, 7188 cal. at 18.5° and 6894 at 14.5°, whence decrease = 73.5 cal. per degree; ditto for the lowest portion, 6695.3 at 12° and 6089.5 at 5°, whence decrease = 86.5 cal. per degree. For *m* these points are -3900 at 18.5°, -3956 at 14.5°, -4006 at 12° and -4190 at 5°.

increase being 88.7 cal. per degree, the experiments at 20° show that this rate then diminishes to 59 cal. The results with the hydrated salt are more numerous, and are best represented by two straight lines meeting at 12°, the rate of change above this point being 73.5 cal. and below it 86.5 cal. The experiments, however, are not sufficiently numerous in this case to settle with certainty the exact temperatures at which the change occurs, especially so with the anhydrous salt.

Copper Sulphate. Tables XVII, XVIII, Q, and R. Plate VIII.—The old and new experiments are given in the Plate in the same manner as with magnesium sulphate. The determinations are not numerous, but with both the hydrated and anhydrous salt there appears to be an alteration in the rate, of the same nature as in other cases, at 10—11°. It will be seen that the present results with the anhydrous salt are entirely at variance with those originally obtained

TABLE XVII.—*Anhydrous Copper Sulphate.*

T°.	M, found.	Differences.	M, calculated.	Difference.
20	16095 cal.	$\left. \begin{array}{l} 3.0 \times 58.0 \\ 3.5 \times 58.6 \\ 6.5 \times 74 \\ 3.0 \times 84 \end{array} \right\} 58.2$	15921 cal.*	0
17	15921 "			
13.5	15716 "			
7	15235 "			
4	14982 "			

* Calculated value if in the same straight line with results at 20° and 13.5°.

TABLE XVIII.—*Hydrated Copper Sulphate. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
20	5270 cal.	$\left. \begin{array}{l} 3.0 \times 73 \\ 3.5 \times 60 \\ 6.5 \times 75 \\ 3.3 \times 77 \end{array} \right\} \begin{array}{l} 66.0 \\ 75.6 \end{array}$	5072 cal.*	-22
17	5050 "			
13.5	4841 "			
7	4355 "			
4	4123 "		4350 ", *	+ 5

* Calculated values if in the same straight line with the results at 20° and 13.5° and at 13.5° and 4° respectively.

above 10°, the difference at 20° amounting to 300 cal., a quantity which cannot be accounted for by experimental error. In order to examine the cause of this difference, a fresh sample of the sulphate was prepared and dissolved at 20°, but it gave the same results as the first sample did; they were—

No. 4565	16112 } 16095 cal.
	16078 }
No. 4586	16089 } 16095 cal.
	16102 }

and showed that the error must have been in the former results. I can only account for it on the grounds that the two samples used now had been desiccated at a higher temperature (360°) than in my previous work (200—250°), and that in driving off the water a certain amount of decomposition occurs, resulting in the liberation of free sulphuric acid, which would not have been expelled at these lower temperatures. These traces of acid might not affect the determinations appreciably at low temperatures, although they did at higher temperatures, owing to the rate of alteration in the heat of dissolution of the acid being very different from that of the salt.

It will be noticed that in every case my later determinations with the sulphates give lower results than were obtained in the earlier work, although these "lower" results imply sometimes a larger thermometric change in the calorimeter, sometimes a smaller one, and it is very difficult to conceive any source of error which should have acted in that direction.

The general nature of the lines given by my former experiments consisted of a curve rising from low temperatures, falling at about 14°, and then another curve starting from this point and falling at about 25°. The majority of these experiments were performed with two thermometers, one used from 3—14° and the other from 14° to 25°, and from this fact it is probable that the peculiarities observed were

due to the thermometers, the middle portions of the stems of these instruments giving higher results than either of their extremities. There are many difficulties in the way of accepting such an explanation, but at any rate it argues strongly in favour of the necessity of employing the same portion of the thermometer stem in all series of experiments where great accuracy is required.

One general conclusion may be drawn from a study of the results originally obtained with those sulphates which have not been re-examined here, namely, that the rate of alteration in the heat of dissolution is greater at low temperatures than at high ones (except in the case of the lithium sulphate), a fact which is entirely in accordance with all the present results. Thus dividing the curves into two halves at about 14° we get—

	Rate below 14° .	Rate above 14° .
$\text{MgK}_2(\text{SO}_4)_2$	192 cal.	167 cal.
$\text{MgK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} - 6l_m$..	161 „	151 „
$\text{CuK}_2(\text{SO}_4)_2$	209 „	96 „
$\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} - 6l_m$..	176 „	98 „
Na_2SO_4	85 „	56 „
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - 10l_m$	—	82 „
Li_2SO_4	79 „	81 „

In calculating the numbers, I have omitted the deep indentation with hydrated potassium copper sulphate, and I have taken the anhydrous sodium sulphate results to consist of two perfectly straight lines meeting at about 15° , with which view they agree very well. With hydrated sodium sulphate, the experiments at low temperatures are too irregular to be of any value.

Discussion of the General Results.

Without insisting on the correctness of all the details mentioned above, there can, I think, be little doubt but that the heat of dissolution of salts does undergo sudden changes as the temperature rises, the rate at which heat is developed being lessened at each successive change. The results are far too concordant in themselves to permit of imagining these changes to be merely the result of experimental error, especially when no source of error can be conceived which would come into play so suddenly at certain temperatures and introduce errors exhibiting such regularity. It may be noted also that neither the character of the changes nor the actual temperatures at which they occur, bear any relationship to the heat development in the calorimeter, this varying between the limits of $+12000$ and -16000 cal.

One point which affords strong confirmation as to the reality of

these alterations in the rates is that in nearly every case the alteration is observed at the same temperature with both the anhydrous and hydrated salts, although the actual changes of temperature observed in the calorimeter are so different in the two cases. Sometimes, it is true, there may be a difference of a degree in the temperatures at which the break occurs, but it is very easy to see how such a difference may arise from causes other than mere experimental errors: the actual weight of salt taken in the individual experiments varies, of necessity, within certain limits, and hence the proportion of salt to water is not always the same, moreover $\frac{1}{1\frac{1}{2}}$ (or $\frac{1}{6}$) of a gram-molecule of both salts were always taken and dissolved in the *same* volume of water, whereas, in order to obtain solutions of exactly the same strength, the volume of water used for the hydrated salts should have been less by the amount of water of crystallisation in the salt itself. This source of error was not perceived till too late.

In a few cases, such as hydrated sodium carbonate, anhydrous sodium acetate, and anhydrous Rochelle salt, the results are not incompatible with their being represented by a series of very slight curves, but in the large majority the rectilinear nature of the lines is so unmistakable that such is in all probability the nature of them all.

The first break which occurs in ascending from low temperatures takes place between the somewhat wide limits of 7° and 14° according to the salt examined. The annexed table gives the actual temperatures at which both it and the second break occur, and the thermometric interval between them.

TABLE XIX.

Salt.	1st change.	2nd change.	Interval.
Potassium sulphate..	14·0°	Higher than 27°	> 13·0°
„ nitrate ...	12·0	„ 25	> 13·0
Sodium chloride....	10·0	24 ?	14·0 ?
Potassium „	9·5	24 ?	14·5 ?
Strontium nitrate ...	9·0	21	12·0
„ chloride ..	8·0	13 ?	5·0 ?
Rochelle salt.....	8·0	20	12·0
Sodium acetate.....	7·5	21 (? 19·5°)	13·5 (? 12·5°)
„ carbonate ...	7·0	18	11·0

Where the temperature of the change with the anhydrous and hydrated salts was different, I have adopted that one which was most in accord with the change in the heat of combination of the salt with its water of crystallisation, as given in the diagram at the foot of the Plates. One point of relationship between the temperatures of

the two breaks becomes at once apparent, and it is a relationship which increases one's confidence in the trustworthiness of the results, namely, that the higher the temperature at which the first break occurs, the higher also that at which the second occurs. There is but one marked exception to this rule—that of strontium chloride, where, for reasons given above, the second break must be accepted with considerable reservation. The interval between the two breaks varies but little from 11° to 14.5° , and in no case, be it remarked, have more than two breaks been observed in the range of 22° over which the experiments extended.

A further examination of the table shows an unmistakeable connection between the temperature at which the change occurs and the nature of the salt. In the case of all the four salts which exist normally without water of crystallisation, the change takes place at higher temperatures than with any hydrated salt, and the salt where the change occurs at the lowest observed temperature is the one which contains the greatest amount of water of crystallisation—sodium carbonate. Looking at the intervals between the two breaks, it is found that this is greater in the case of the anhydrous salts, and least in the case of sodium carbonate; beyond this, however, any relationship does not appear, except that strontium nitrate, Rochelle salt, and sodium acetate—which contain nearly the same amount of water of crystallisation—show the same interval between two consecutive changes. To the fact that the chlorides of the two alkali metals, the two strontium salts, and the two organic salts come next to each other respectively in the order of temperatures at which the breaks occur, no weight can, I think, be attached. Potassium sulphate is included with the other salts in this table, but the other sulphates do not seem to accord with the general order observed. The only break which each of them exhibited being—

Sodium sulphate at 15° ,
 Magnesium sulphate at 12° (? 17°),
 Copper sulphate at 10.5° ;

little weight, however, can be attached to these temperatures.

In Table XX (p. 326) the various salts are arranged according to the increase (in calories) in the rate which occurs at the lowest break, the percentage increase, as well as the increase at the higher break (where there is one) is also given. Another column contains the actual rate of change at 15° , and after that comes the corrected heat of dissolution of the salt* and its heat of combination with 1 mol. of water of crystallisa-

* The true heat of dissolution of the hydrated salt would be this "corrected" heat plus the heat of fusion of the anhydrous salt, at present an unknown quantity.

TABLE XX.

Salt.	Increase in rate at lowest change.		Increase at highest change. Cal.	Rate at 15°.	Corrected heat of dissolution at 15°.	Heat of combination with each H ₂ O.
	Percentage.	Cal.				
Potassium copper sulphate.....	98	23.8	—	24.3 cal.	-1150 cal.	2330 cal.
Sodium acetate.....	142	15.1	4.9	10.6 "	— 62 "	1330 "
Rochelle salt.....	48	15.1	9.2	31.6 "	-3659 "	830 "
Sodium sulphate.....	54	*14.5	—	*28.0 "	*-1785 "	330 "
Potassium sulphate.....	28	12.0	—	42.5 "	-3410 "	—
" chloride.....	39	11.4	—	38.6 "	-4596 "	—
Sodium chloride.....	39	11.1	—	31.3 "	-1322 "	—
Potassium nitrate.....	32	10.7	—	33.3 "	-8552 "	—
Strontium ".....	28	10.6	5.0	37.3 "	-3256 "	430 "
" chloride.....	21	9.8	(2.2)	45.9 "	+ 830 "	1570 "
Sodium carbonate.....	21	9.4	12.6	44.0 "	- 342 "	600 "
Magnesium sulphate.....	16	6.0	—	36.8 "	+3415 "	1800 "
Copper sulphate.....	14	4.7	—	33.0 "	+2465 "	1810 "
Potassium magnesium sulphate.....	11	4.5	—	39.8 "	- 275 "	2020 "

* The actual values are halved in the case of salts of bibasic acids in order to make them comparable with salts of monobasic acids. Similarly with the double sulphates the values are divided by 4.

tion. Between these last two quantities and the rate of change with temperature, or the increase of this rate, there appears to be no connection. In examining the increases in the rates at the two points where alterations occur, it will be seen that the alteration is greater at the lower break than at the higher one; the only exception being sodium carbonate.*

Taking the increase in calories at the lowest break (which is more trustworthy than the higher break), it will be observed that it is the same in both the organic salts, and greater with them than in any case, except the doubtful instance of potassium copper sulphate. The four anhydrous salts also come next to each other in the series, potassium and sodium chloride being very near together. The two nitrates of potassium and strontium exhibit an identical increase, while the two most highly hydrated salts show the smallest increase of any. The actual rate of change does not appear to influence the extent to which the rate is altered, though it may be noted that in the two salts other than sulphates, where the alteration is least, the rate attains the highest proportions.

Here, again, little value can be attached to the results with the sulphates, but it is noticeable that those two hydrated ones which were most thoroughly examined, as well as potassium magnesium sulphate, exhibit an increase in rate far less than in any other case.

To sum up: the chief factors influencing the extent of the changes in the heat of dissolution of a salt, the temperature at which they occur, and the frequency of their occurrence, would appear to be the nature of the non-metallic portion of the salt, and the extent to which the salt combines with water; a much larger number of instances, however, would be requisite to establish this relationship with any degree of precision.

In my previous communication, I interpreted the irregularities which I imagined occurred in the heat of dissolution of a salt by the development of additional heat as the temperature rises, due to the formation of higher hydrates. The present results may be interpreted in a similar manner, but it is equally possible to explain the changes in a diametrically opposite manner. A prolongation of the circumstances existing, say in the case of potassium chloride, between 3° and 8° , would give a larger heat of dissolution for the salt at temperatures above 8° than that which is observed, that is, at these *higher* temperatures some alteration has occurred *absorbing* heat. But, on the other

* For these numbers I take the heat of dissolution of the *hydrated* salt, as that of the anhydrous salt may be complicated by alterations in the heat of combination of this salt with water of crystallisation. Taking *anhydrous* sodium carbonate, the increase of the lower break is greater than that at the higher break, the numbers being 10.9 and 7.1 cal. respectively.

hand, prolonging the conditions existing between 25° and 8° downwards to lower temperatures, we find that the heat of dissolution should be greater than it is, that is, as the temperature *falls* changes involving *absorption* of heat occur. The rectilineal nature of the lines permits, however, of settling between these opposite explanations.

The increase in the heat of dissolution of a salt with rise of temperature is an inevitable consequence of the specific heat of the solution being less than the sum of the specific heats of its components, the anhydrous salt and water, and the greater this difference is the greater will be the increase in the heat of dissolution of a salt produced by rise of temperature. In every case the change which occurs consists in the sudden lowering of this rate of increase as certain higher temperatures are reached, that is, the difference between the specific heat of the solution and the sum of those of its components becomes suddenly diminished; such a diminution implies *decomposition* and not *combination*; the sudden alterations are, therefore, due to successive simplification of the particles constituting the solution.

The bearing of these observations on the nature of dissolution is of considerable importance. If dissolution be but the result of a purely physical attraction of the salt for water, involving no combination of a chemical nature, that is, in which a certain definite number of molecules are concerned, it is obvious, I think, that a rise of temperature could produce alterations of a uniform nature only. Sudden alterations are characteristic of changes in the component particles of a complex structure, exemplified by the re-arrangement of atoms in molecules (ordinary chemical change), or the re-arrangement or aggregation of a large number of molecules themselves (changes in state from liquid to solid, &c.). The changes here may consist either of the diminution of the degree of hydration of the dissolved salt, or in a reduction of the number of the molecules which are united to form those complex aggregates, which are probably the acting units of which liquids are composed (comp. *Chem. News*, 54, 215).

Between those ranges of temperature where the heat of dissolution of a salt is represented by a straight line, the specific heat of the solution will of necessity remain constant. At the points where the rate of increase of the heat of dissolution is lowered, the specific heat of the solution will be increased.* No experiments have yet been made which would show that the specific heat is constant through certain small ranges of temperature, but the well-established fact that for considerable ranges it is higher at high than at low temperatures, agrees well with the present observations; these observations, indeed, affording an explanation of the fact.

* The specific heat of water and of the salt being practically constant within these small ranges, that of the solution only need be considered.

Tilden's experiments on this same subject (*Proc. Roy. Soc.*, **38**, 401) would appear to bear out the conclusion that the rate at which the heat of dissolution of a salt is influenced by the temperature, is diminished as the temperature rises, and, if correct, would tend to show that further changes occur at temperatures higher than those reached in my work. Thus:—

		Pickering.	Tilden.
Rate with sod. sulphate ..	{ 2—15°	15—25°	32—64°
	{ 85 cal.	56 cal.	25 cal.
			(sample C)
,, pot. sulphate ..	{ 3—14°	14—27°	15—45°
	{ 99 cal.	85 cal.	17 cal.
,, pot. nitrate....	{ 3—12°	12—25°	15—53°
	{ 44 cal.	33 cal.	11 cal.
,, sod. carbonate..	{ 4—19°	19—25°	22—52°
	{ 67 cal.	53 cal.	22 cal.

Tilden's result, however, must, I venture to think, be accepted with considerable reservation for the following reason:—The principle connecting the heat developed in any chemical reaction with the specific heats of the reagents and product was first enunciated by Person in the equation $Q_T = Q_t + (U - V)(T - t)$ (Q being the heat evolved at T and t , and U and V the specific heat of the reagents and compound respectively), and is accepted on all hands as necessarily true, and as one of the fundamental principles on which thermochemistry depends; indeed if it were not true, if $Q_T < Q_t + U - V$, we should have a creation of energy, and by continually repeating a series of operations (in this case, for instance, dissolving the salt at t , heating the solution to T , crystallising out the salt, and cooling it and the water again to t), perpetual motion would be produced. Now Tilden certainly recognises the obvious truth of Person's principle, and indeed (p. 406) accepts it as applied to the question of dissolution itself; yet the whole object and the chief result of his paper is to prove that it is not applicable. In the case of each salt examined, he arrives at the conclusion that $Q_T < Q_t + U - V$. This result is impossible: either the values he obtains for Q_T and Q_t (heat of dissolution) are incorrect, or the values taken for U and V (the specific heat of salts and solutions given by Kopp and Marignac) are incorrect. Q_T must be equal to $Q_t + U - V$.*

* The only case in which the observed value for Q_T could differ from that calculated from Q_t and the specific heats, would be if the solution obtained by dissolving the salt at the higher temperature T was not identical with that obtained by

As both Marignac's and Kopp's determinations of the various specific heats are too concordant to permit us to imagine that they contain an error of a magnitude sufficient to account for the difference in the values calculated and found for Q_T , we must necessarily suppose that the error occurs in Tilden's experimental numbers, a supposition which will appear more probable on a closer examination of his results. When his determinations with potassium sulphate, for instance, are compared with those of other physicists, we find—

Heat of dissolution at 15°.	Increase per degree from 15—24°.
† — 6956* cal. (Favre)	—
— 6826 „ (Pickering)	85 cal.
— 6636 „ (Thomsen) }	73 „
— 6580 „ (Berthelot) }	
— 5338 „ (Tilden)	18 „

indicating an error amounting to 1200 or 1300 cal. In like manner, his results with potassium nitrate, judged by comparison with the mean deduced from those of Thomsen, Berthelot, Favre, and myself, is roughly 500 cal. too low, with hydrated sodium carbonate 500 cal. too low, and with hydrated sodium sulphate 900 cal. too low. Where errors of such magnitude occur in his experiments at the ordinary atmospheric temperature, 15°, it would be useless to attach any value to the conclusions drawn from experiments at higher temperatures, where the difficulties are increased tenfold, especially as these conclusions depend on differences not greater (94 to 1200 cal.) than the errors observed in those determinations which should be most accurate.

Setting aside, then, Tilden's direct determination of the heat of dissolution of salts at temperatures above 25°, our only means of obtaining any light on the subject will be from the specific heats of their solutions at these temperatures.

heating a colder solution up to T . Such a view, however, can hardly be suggested, and is not even hinted at by Tilden.

† There is some uncertainty about the temperature and degree of dilution in Favre's experiment. Berthelot quotes a determination by Chodin as identical with his own and Thomsen's, and also one by Graham giving —6600 cal.

My own results in the case of all the normally anhydrous salts give somewhat higher numbers than those of Berthelot and Thomsen, due partly to my having generally employed a larger proportion of water than they did, and partly to the special precautions which I took to deprive the specimens of all traces of enclosed water.

The actual proportion of water used by Tilden was 100 H_2O , whereas the other physicists used 200 or 400 H_2O ; the smaller proportion of water would entail a smaller absorption of heat on dissolving the salt, though the reduction could scarcely amount to the 1200 or 1300 cal. which Tilden's results indicate. An experiment,

The quantity $U - V$ gives the difference between the heat of dissolution at temperatures 1° apart, that is, the rate of increase in the heat of dissolution. In Table XXI (p. 332), values for this quantity are given for various degrees of dilution, and for two ranges of temperature, as calculated from the results of Marignac (*Ann. Chim. Phys.* [5], 8, 416). My own direct determinations of the rate are also inserted in the table, and are distinguished by (P). Unfortunately, Marignac did not extend his observations to solutions as dilute as those employed by myself (except in the case of sodium chloride), so that our results are not strictly comparable, but it may be inferred from an examination of his results with stronger solutions, that the rate which he would have found for solutions of same strength as those used by myself would have been 5 or 10 cal. larger (with salts of mono- and bi-basic acids respectively) than the rates with the strongest solutions which he used; these probable values I have inserted in the table in brackets, and it will be seen that they confirm in a very marked degree my own direct determinations.

In drawing any conclusions as to the rates at higher temperatures given by Marignac's determinations, we must, as he expressly states (p. 420), take the general bearing of the results only, and not attach much importance to the values obtained in each individual case; on the whole, however, it seems certain that the rate of increase is lower between 20° and 50° than at lower temperatures, indicating that further changes do occur beyond those here noticed; that the magnitude

however, was performed at 15° in which the proportion of water taken was $100 \text{ H}_2\text{O}$, and the value obtained for the heat of dissolution was -6183 cal. This, however, did not represent the whole absorption, for it was found that some of the salt had remained undissolved in spite of the experiment having lasted as long as 23 minutes, the stirrer having been worked rapidly throughout, and notwithstanding that the salt had been previously sifted through the finest silk. In the experiment, the temperature of the liquid fell to 11.7° , and according to Kopp's determination, a saturated solution at this temperature contains 10.4 parts of salt to 100 of water, whereas a solution of K_2SO_4 in $100 \text{ H}_2\text{O}$ would contain 9.7 of the salt, that is, it would be very nearly saturated: it is difficult to understand how Tilden could have obtained such a solution of such a difficultly soluble salt, unless he had allowed a length of time for the operation quite inconsistent with obtaining results having the least pretensions to accuracy; it would be legitimate to suggest that he may have omitted to notice that some of the salt remained undissolved in this case, were it not that his results at higher temperatures, when the solubility is considerably greater, show a still larger error when compared with those of Berthelot, Thomsen, and myself.

A second attempt to determine the heat of dissolution in $100 \text{ H}_2\text{O}$ gave the same results, but, by determining the amount of salt which had been dissolved, as well as the rate of cooling by a blank experiment performed immediately afterwards, a fairly trustworthy value was obtained: it was -6316 cal., a number smaller than those obtained with the weaker solutions, but still showing an excess of 1000 cal. over that given by Tilden.

TABLE XXI.—*Rate of Increase of the Heat of Dissolution with Rise of Temperature.*

Salt.	Proportion of water.					Tempera- ture.
	25H ₂ O.	50H ₂ O.	100H ₂ O.	200H ₂ O.	400H ₂ O.	
KCl	{ 27 25	{ 31 30	{ 36 34	{ (41), 39 (P) —	{ — —	{ 17—22° 20—51
NaCl	{ 17 16	{ 23 21	{ 30 24	{ (35), 31 (P) —	{ — —	{ 16—20 22—52
SrCl ₂	{ — —	{ 57 55	{ 68 66	{ 75 77	{ (85), 81 (P) —	{ 21—26 19—51
Sr(NO ₃) ₂	{ — —	{ — 30	{ 47 47	{ 55 58	{ (65), 61 (P) —	{ 21—26 19—51
KNO ₃	{ 15 14	{ 22 19	{ 30 21	{ (35), 33 (P) —	{ — —	{ 18—23 22—52
Na ₂ CO ₃	{ — —	{ 17 13	{ 36 28	{ 42 33	{ (52), 53 (P) —	{ 21—26 21—52
NaC ₂ H ₃ O ₂ ..	{ -13 -15	{ - 8 -10	{ + 2 - 7	{ (7), 1 (P) —	{ — —	{ 20—25 19—52
K ₂ SO ₄	{ — —	{ — —	{ 65 54	{ 75 63	{ (85), 85 (P) —	{ 18—23 22—52
MgSO ₄	{ — —	{ 44 40	{ 55 54	{ 75 74	{ (85), 59 (P) —	{ 19—24 22—52
CuSO ₄	{ — —	{ 37 26	{ 48 36	{ 56 46	{ (66), 58 (P) —	{ 18—23 22—53

of these changes, however, is probably less at the higher temperatures, for the greatest decrease in the rates observed does not exceed 12 cal. in this interval of 30°. That the change should be less marked as the temperature is higher, is strictly in accordance with my own observations in those cases where two changes were noticed.

Water of Crystallisation.

The heat of combination of the solid salt with its water of crystallisation (solid) is the difference between the heat of dissolution of anhydrous and hydrated (corr.) salt. The result is given diagrammatically at the foot of each Plate, the marked points showing the values deduced at various temperatures from the straight lines given by the heat of dissolution, and not from the mere experimental results at those temperatures.

In drawing any conclusion as to the variation of the heat of combination of the salt with its water, it must be remembered that its value is given by the combination of two independent quantities, and that the errors made may be considerable unless these conclusions be of a general nature only.

Although any sudden change which occurs in this value can occur only at the temperature where the rate of increase of the heat of dissolution alters, an alteration in this latter rate is by no means always accompanied by a change in the solid crystallised salt. In about one-half of the cases here investigated, the change in the conditions of the salt when dissolved is not accompanied by any change in the solid hydrated salt. Thus although the rate of increase of the heat of solution of the nitrates of strontium is twice lowered between 3° and 25° , the heat of combination of $\text{Sr}(\text{NO}_3)_2 + 4\text{H}_2\text{O}$ is represented by a straight line throughout. Nearly every table exhibits instances of a similar character.

Between the limits of 3° and 25° there is certainly a general tendency for the heat of combination to decrease; although the decrease is not large. The total decrease in the various cases is—

Sodium carbonate.....	165 cal.
Rochelle salt.....	100 „
Strontium chloride	95 „
„ nitrate	95 „
Sodium acetate	30 „

With strontium nitrate, and possibly with sodium acetate, this decrease is continuous throughout the whole 22° range, but in the other cases it is more or less confined to the higher temperatures, the rate of decrease per degree is consequently greater in these cases than would be given by dividing the above total decrements by 22° . The rates are—

$\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$	14.7 cal. per degree	$7-25^{\circ}$
$\text{SrCl}_2, 6\text{H}_2\text{O}$	9.5 „ „	$10-25$
$\text{NaKC}_4\text{H}_4\text{O}_6, 4\text{H}_2\text{O}$	8.5 „ „	$8-20$
$\text{Sr}(\text{NO}_3)_2, 4\text{H}_2\text{O}$	4.3 „ „	$3-25$
$\text{NaC}_2\text{H}_3\text{O}_2, 3\text{H}_2\text{O}$	4.5 „ „	$21-25$

The general order of the rate of decrease is according to the amount of water contained in the salt, and this affords some confirmation of the correctness of the observed values, but they must still be accepted with considerable reservation. With sodium carbonate, the decrease is less above 17° than it is between 17° and 7° , but the difficulties attending the examination of the anhydrous salt render it impossible to attach much value to this apparent change at 17° . Again, with sodium acetate, an increase of the rate of diminution above 21° is very doubtful, and the whole line between 3° and 25° may well be perfectly straight; if we take the exact course indicated by the plotting in this case, the heat of combination from 21° to 8° is absolutely constant, while from

8° to 3° there is a slight rise. With Rochelle salt, the rise at the higher temperatures, 20—25°, is altogether exceptional, and from the paucity of experiments with the anhydrous salt in this region, cannot be regarded as well authenticated.

In two cases, there is a marked diminution in the heat of combination as the lower temperatures are attained, thus with—

Sodium carbonate, decrease from 7—4° = 70 cal., or 23 cal. per degree;

Strontium chloride, decrease from 13—3° = 50 cal., or 5 cal. per degree;

while with Rochelle salt, the increase, which was 8.5 cal. per degree down to 8°, becomes reduced at that temperature to 3 cal. per degree; the actual plottings, also, with strontium nitrate indicate a change in the same direction below 7°, but it is too small to be relied on. Here again the sharpness of the decrease at low temperatures follows the order of the degree of hydration of the salt. It is not difficult to understand how a diminution in the heat of combination of the salt with its water may occur at temperatures which are not far removed from those at which the water molecules present would, if free, aggregate together, and assume a crystalline form peculiar to themselves. This tendency to unite with each other would, as soon as it began to be appreciable, loosen the energy with which they were attached to the salt, and the greater the number of water molecules present the greater would be the effect thus produced, as is indicated in the present results.

The general tendency above 7° or 8°, however, is towards a diminution in the heat of combination as the temperature rises, and as precisely the opposite conclusions were deduced from my previous work on the sulphates, the cases of the copper and magnesium salts were re-examined. The rapid rise in the case of the copper salt was found to be entirely erroneous, owing to the wrong values obtained for the heat of dissolution of the anhydrous salt. The present results indicate a resemblance to the conditions found with the other salts, there being an increase from 4° up to 10°, followed by a decrease as the temperature rises to 20°. This alteration, however, must be looked upon as very uncertain, the actual experiments, shown here by crosses, indicate no appreciable change between 7° and 17°. The increase previously observed in the case of magnesium sulphate is confirmed to a certain extent by the more recent results. The heat of combination increases by 80 cal. from 3° to 17° (the highest temperature noticed in any case at which the heat of combination is increasing), but above that point it begins to decrease rapidly, instead of showing a small further increase, as this decrease, however, depends on determina-

tions at 20° only, it must not be insisted on; similarly with the change at 12° . My former results on this point with other salts cannot, of course, be accepted as being of any appreciable value; it may be observed, however, that the results with potassium copper sulphate are in accordance with my present work, there being an increase in the heat of combination from low temperatures up to $13-15^{\circ}$, after which there is no further increase; and so also with sodium sulphate, the rapid decrease noticed between 16° and 25° is analogous to that noticed in the case of the other highly hydrated salt, sodium carbonate.

Conclusion.

The main results arrived at in the present work may be briefly summarised as follow:—

1. The heat of dissolution of a salt increases uniformly with the temperature up to a certain point, when the rate of increase is suddenly lowered, and this fresh rate continues uniform till lowered again at some higher temperature.

2. These sudden alterations in the rate indicate the occurrence of some fresh heat-absorbing action, as the temperature rises; this action may be the decomposition of some hydrate in solution, or the simplification of the aggregates constituting the true molecules of the solution.

3. As far as the present experiments extend, it would appear that the temperature at which the first alteration in the rate occurs is lower, and the successive alterations are more frequent, according as the salt is more highly hydrated in the normal solid condition.

4. The alterations at higher temperatures are of smaller magnitude than those at lower temperatures.

5. The rate at which the heat of dissolution is found to increase with the temperature is confirmed by the results deduced for the specific heats of the solutions, and these indicate that further alterations in the rates occur at temperatures between 25° and 50° . Tilden's direct determination of the rates in certain cases at these higher temperatures must be regarded as doubtful, since they are entirely at variance with the specific heats.

6. The heat of combination of a solid salt with its water of crystallisation would appear to be diminished by a rise of temperature, the diminution being more marked as the amount of water present is greater. At low temperatures, the reverse is the case, the effect of temperature being, probably, more than counterbalanced by the tendency of the water molecules to leave the salt in order to combine with each other. In the most highly hydrated salts, this diminution with fall of temperature is most apparent.

It has been objected that it is improbable that the molecules of solids and liquids should undergo changes in their constitution at every few degrees, as is shown by the present work; but we certainly have very little grounds on which we can consistently maintain such a view. Of the constitution and complexity of solid and liquid molecules we know nothing, their percentage composition alone is known to us; and till we have some knowledge, however slight, of what these unknown units may be, I venture to think we should be content to investigate, without entering into any useless discussion of probabilities.

Additional Note.—In the discussion which followed the reading of this paper Dr. Wright suggested that the lines representing the heat of dissolution of the salts might in reality be curves represented by formulæ such as $1 + \alpha t + \beta t^2$, instead of being combinations of straight lines. I have consequently examined some of my results in accordance with this suggestion. With potassium chloride, two curves were calculated, taking the experiments at 3° and 6° as origins, and deducing the values of α and β from four and three other pairs of experiments in the series; these two curves were then combined into one, and all the values given by it altered to the extent necessary to render the sum of the negative and positive errors of the observed values equal. The equation for this curve was:—

$$M = -5123 + 48.05(t - 3) - 0.315(t - 3)^2,$$

and the differences between the values calculated from it and the observed values at each successive degree were as follows:—

25°.	24°.	23°.	22°.	21°.	20°.	19°.	18°.	17°.
— 4	— 2	— 3	— 1	+ 5	+ 6	+ 7	+ 3	+ 10
	16°.	15°.	14°.	13°.	12°.	11°.	10°.	
	— 5	+ 6	+ 3	0	— 8	— 6	— 12	
	9°.	8°.	7°.	6°.	5°.	4°.	3°.	
	— 14	— 9	— 2	+ 1	+ 3	+ 6	+ 11 cal.	

Now the average of these differences is 5.1 cal., a quantity three times larger than that given on the supposition that the results are represented by two straight lines (Table I); but that which tells far more strongly against the curvilinear nature of the results, than the mere increase of the average error which it would entail, is the arrangement of the errors according to their signs; instead of the positive and negative errors occurring indiscriminately, as they do in Table I, they are here arranged in groups, the observed results being uniformly above the curve throughout certain intervals, and uniformly

below throughout others, the arrangement, in fact, is exactly what would follow from the observed results being made up of two straight lines meeting at 9° or 10° ; and that such, and not a curve, is their nature, is, I think, thus proved beyond question.

Taking the results at 15 points in the case of hydrated strontium nitrate, the equation obtained was $M = -7724 + 95.8(t - 3) - 0.83(t - 3)^2$, and the differences between the values given by this equation and the observed results from 25° downwards were—

$$\begin{aligned} & -14, +4, +2, +4, +1, +8, +21, +14, +21, +10, +4, \\ & +16, +11, 0, -16, -10, -13, -20, -14, -9, -7, \\ & -8, +6, \end{aligned}$$

the distribution of the signs of these differences showing clearly that the curve is inapplicable, while an attempt to apply it raises the average error from 5.8 to 10.1 cal.

With sodium chloride, the application of a curve represented by $M = -1772 + 42.1(t - 3) - 0.36(t - 3)^2$ raises the average differences from 3.2 to 5.4 cal., the signs of the differences being arranged in a manner closely resembling those with strontium nitrate. With potassium nitrate, the formula $M = -9047 + 46.3(t - 3) - 0.41(t - 3)^2$ increases the grouping together of differences of like signs, but does not increase the average difference much, namely, from 4.3 to 5.8 cal. only.

With hydrated sodium acetate, where the differences given in Table XI are higher than the average, the curve equation obtained was $M = -234 + 18.35(t - 3) - 0.315(t - 3)^2$, which gave the differences from 25° downwards as being—

$$\begin{aligned} & +11, -6, +6, +6, \\ & -3, -6, +5, -4, +8, 0, +2, +12, +1, -5, -8, -7, -12, \\ & -19, -17, -10, +7, +9, +16. \end{aligned}$$

Here the results obtained at the higher temperatures might be expressed by the curve, but those at lower temperatures are clearly not expressible in such a manner, indeed from 21° downwards the sign of the differences follows exactly the order which would be produced by two straight lines meeting at about 8° and cutting the curve at three points. The application of this curve would double the average error of the observed results from 3.9 to 7.8 cal.

With hydrated sodium carbonate, the equation obtained was $M = -1827 + 109.85(t - 3) - 1.195(t - 3)^2$, which gave the differences from 25° downwards to be—

$$\begin{aligned} & +3, +1, -6, +4, -5, \\ & -14, -19, +7, -26, -18, +11, +14, +28, +19, +7, -6, \\ & -16, -9, +2, +11, +10, -19, \end{aligned}$$

the average of which is 11.7 cal. instead of the 7.5 cal. given by representing the results by three straight lines, while the arrangement of the positive and negative differences is on the whole such as would be produced by three straight lines cutting the curve.

Thus, in every case which has been investigated it is found impossible to express the experimental results by means of a curve with anything like the same degree of accuracy as they can be by two or three straight lines; the latter, then, is evidently their nature.

TABLE A.—*Heat of Dissolution of Potassium Chloride.* KCl = 74.40;

$$\frac{1}{12} \text{ mol.} = 12.600 \text{ grams.}$$

<i>w.</i>	<i>t</i> °.	(<i>t</i> − <i>t'</i>)°.	M at <i>t</i> .	M at T. Whole degrees C.
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Series with Thermometer '08 A.

1. 12.644	24.96	1.1701	−4201 cal.	−4200 cal. at 25°
2. 12.657	23.92	1.1828	−4242 „	−4240 „ 24
3. 12.678	22.85	1.1940	−4275 „	−4273 „ 23
4. 12.594	21.985	1.1955	−4309 „	−4308 „ 22
5. 12.601	20.895	1.2074	−4349 „	−4346 „ 21
6. 12.650	20.05	1.2224	−4386 „	−4388 „ 20
7. 12.620	18.82	1.2315	−4429 „	−4422 „ 19
8. 12.650	17.93	1.2423	−4457 „	−4454 „ 18
9. 12.682	17.07	1.2623	−4522 „	−4524 „ 17
10. 12.627	16.005	1.2676	−4556 „	−4556 „ 16
11. 12.671	15.005	1.2809	−4588 „	−4588 „ 15
12. 12.610	14.03	1.2864	−4630 „	−4630 „ 14
13. 12.603	12.01	1.3054	−4697 „	−4697 } −4707 „ 12
14. 12.538	12.05	1.3024	−4714 „	
15. 12.620	10.01	1.3318	−4789 „	−4789 „ 10
16. 12.611	8.00	1.3565	−4881 „	−4881 „ 8
17. 12.593	5.965	1.3835	−4985 „	−4984 „ 6
18. 12.651	3.925	1.4175	−5084 „	−5080 „ 4
19. 12.631	3.08	1.4270	−5126 „	−5129 „ 3

Series with Thermometer '61 A.

20. 12.621	23.89	1.1835	−4258 cal.	−4254 cal. at 24°
21. 12.648	21.895	1.2064	−4325 „	−4320 „ 22
22. 12.639	19.98	1.2251	−4401 „	−4401 „ 20
23. 12.622	18.02	1.2437	−4473 „	−4474 „ 18
24. 12.622	16.93	1.2559	−4517 „	−4514 „ 17
25. 12.671	15.935	1.2688	−4546 „	−4544 „ 16
26. 12.675	15.00	1.2831	−4596 „	−4596 „ 15
27. 12.700	14.00	1.2945	−4628 „	−4628 „ 14
28. 12.613	13.04	1.2966	−4667 „	−4669 „ 13
29. 12.622	10.98	1.3221	−4755 „	−4755 „ 11
30. 12.610	9.055	1.3413	−4828 „	−4830 „ 9
31. 12.620	6.91	1.3744	−4943 „	−4939 „ 7
32. 12.588	4.98	1.3960	−5033 „	−5033 „ 5
33. 12.503	2.99	1.4155	−5138 „	−5138 „ 3

<i>w.</i>	<i>t</i> °.	<i>t</i> - <i>t'</i> .	M at <i>t</i> .	M at T. Whole degrees C.
Series with Thermometer '08 B.				
34. 12·543	24·905	1·1666	-4222 cal.	-4218 cal. at 25°
35. 12·608	23·015	1·1913	-4289 „	-4290 „ 23
36. 12·519	21·09	1·2059	-4372 „	-4374 „ 21
37. 12·542	19·045	1·2292	-4448 „	-4450 „ 19
38. 12·538	16·87	1·2519	-4532 „	-4527 „ 17
39. 12·591	14·94	1·2779	-4606 „	-4604 „ 15
40. 12·562	13·005	1·2954	-4680 „	-4680 „ 13
41. 12·555	4·02	1·4094	-5093 „	-5092 „ 4
Series with Thermometer '61 B.				
42. 12·603	25·00	1·1750	-4233 cal.	-4232 cal. at 25°
43. 12·564	22·94	1·1875	-4292 „	-4289 „ 23
44. 12·604	20·975	1·2142	-4374 „	-4374 „ 21
45. 12·576	18·955	1·2317	-4447 „	-4451 „ 19
46. 12·620	16·885	1·2586	-4528 „	-4522 „ 17
47. 12·596	14·96	1·2762	-4599 „	-4596 „ 15
48. 12·582	13·01	1·2978	-4682 „	-4681 „ 13

TABLE B.—*Heat of Dissolution of Sodium Chloride.* NaCl = 58·365;
 $\frac{1}{6}$ mol. = 9·727 grams.

Series with Thermometer '08 A.				
1. 9·935	24·96	0·2847	-1029 cal.	-1028 cal. at 25°
2. 9·906	23·905	0·2965	-1066 „	-1065 „
3. 9·785	23·885	0·2848	-1037 „	-1035 „
4. 9·922	22·84	0·3004	-1078 „	-1076 „
5. 9·744	22·795	0·2986	-1088 „	-1086 „
6. 9·718	21·98	0·2973	-1090 „	-1090 „
7. 9·806	22·035	0·3031	-1110 „	-1113 „
8. 9·804	20·895	0·3143	-1141 „	-1138 „
9. 9·852	20·05	0·3241	-1172 „	-1174 „
10. 9·715	18·81	0·3293	-1207 „	-1202 „
11. 9·865	17·93	0·3445	-1243 „	-1239 „
12. 9·754	17·05	0·3467	-1266 „	-1268 „
13. 9·724	16·03	0·3560	-1304 „	-1304 „
14. 9·628	15·00	0·3612	-1336 „	-1336 „
15. 9·618	14·03	0·3696	-1368 „	-1369 „
16. 9·534	13·43	0·3671	-1371 „	-1371 „
17. 9·872	12·01	0·3916	-1411 „	-1411 „
18. 9·794	10·01	0·4074	-1481 „	-1481 „
19. 9·979	7·995	0·4345	-1550 „	-1550 „
20. 9·874	5·97	0·4574	-1649 „	-1649 „
21. 9·887	3·925	0·4831	-1739 „	-1736 „
22. 9·839	3·08	0·4893	-1770 „	-1774 „

<i>w.</i>	<i>t</i> °.	$(t-t')^{\circ}$.	M at <i>t</i> .	M at T. Whole degrees C.
Series with Thermometer '61 A.				
23. 9·934	24·93	0·2847	—1024 cal.	—1020 cal. at 25°
24. 9·850	23·89	0·2873	—1039 „	—1037 „ 24
25. 9·928	22·955	0·2998	—1075 „	—1073 „ 23
26. 9·842	21·90	0·3053	—1105 „	—1102 „ 22
27. 9·907	20·905	0·3148	—1132 „	—1130 „ 21
28. 9·841	19·995	0·3208	—1161 „	—1162 „ 20
29. 10·828	18·955	0·3616	—1189 „	—1188 „ 19
30. 9·900	16·905	0·3486	—1254 „	—1252 „ 17
31. 9·860	15·005	0·3454	—1320 „	—1320 „ 15
32. 9·850	13·03	0·3823	—1382 „	—1382 „ 13
33. 9·909	10·985	0·4025	—1446 „	—1444 „ 11
34. 10·000	9·055	0·4282	—1525 „	—1527 „ 9
35. 9·899	6·905	0·4446	—1599 „	—1595 „ 7
36. 9·923	4·98	0·4723	—1695 „	—1695 „ 5
37. 9·779	2·99	0·4876	—1775 „	—1775 „ 3
Series with Thermometer '08 B.				
38. 9·913	24·905	0·2844	—1022 cal.	—1021 cal. at 25°
39. 9·930	23·01	0·2974	—1071 „	—1072 „ 23
40. 9·814	21·09	0·3134	—1137 „	—1138 „ 21
41. 9·796	19·045	0·3259	—1185 „	—1190 „ 19
42. 9·867	16·865	0·3481	—1259 „	—1254 „ 17
43. 9·812	14·94	0·3698	—1342 „	—1336 „ 15
44. 9·831	13·005	0·3838	—1390 „	—1390 „ 13
45. 9·837	4·02	0·4785	—1731 „	—1732 „ 4
Series with Thermometer '61 B.				
46. 9·845	25·00	0·2833	—1025 cal.	—1025 cal. at 25°
47. 9·946	22·945	0·2974	—1075 „	—1071 „ 23
48. 9·880	20·97	0·3153	—1136 „	—1134 „ 21
49. 9·746	18·965	0·3267	—1194 „	—1192 „ 19
50. 9·982	16·88	0·3516	—1254 „	—1241 „ 17
51. 9·889	14·955	0·3664	—1319 „	—1315 „ 15
52. 9·806	13·01	0·3804	—1381 „	—1382 „ 13

TABLE C.—*Heat of Dissolution of Potassium Nitrate.* $\text{KNO}_3 = 100.92$;
 $\frac{1}{6}$ mol. = 16.82 grams.

<i>w.</i>	<i>t</i> °.	(<i>t</i> − <i>t'</i>)°.	M at <i>t</i> .	M at T.	Whole degrees C.
Series with Thermometer '08 A.					
1. 16.942	24.95	2.2622	−8223 cal.		−8220 cal. at 25°
2. 16.886	23.905	2.2673	−8268 "		−8262 " 24
3. 17.015	22.85	2.2886	−8282 "		−8281 " 23
4. 16.906	21.985	2.2803	−8305 "		−8305 " 22
5. 16.871	20.895	2.2849	−8339 "		−8336 " 21
6. 16.882	20.05	2.2946	−8369 "		−8372 " 20
7. 16.853	18.805	2.3046	−8420 "		−8412 " 19
8. 16.885	17.94	2.3156	−8443 "	−8442	} −8452 " 18
9. 16.688	17.91	2.2942	−8464 "	−8461	
10. 16.605	17.06	2.2915	−8496 "	−(8497)	} −8488 " 17
11. 16.792	16.91	2.3149	−8487 "	−8483	
12. 16.635	16.025	2.2965	−8500 "		−8502 " 16
13. 16.927	15.02	2.3474	−8542 "	−8543	} −8546 " 15
14. 16.926	14.98	2.3501	−8549 "	−8548	
15. 16.890	14.03	2.3555	−8587 "	−8590	} −8580 " 14
16. 18.715	13.92	2.6061	−8574 "	−8579	
17. 16.913	13.535	2.3654	−8590 "		
18. 16.777	13.515	2.3419	−8593 "		
19. 16.936	12.01	2.3838	−8666 "		−8666 " 12
20. 16.400	10.09	2.3305	−8749 "		−8754 " 10
21. 16.917	8.00	2.4249	−8823 "		−8823 " 8
22. 16.729	5.97	2.4253	−8924 "		−8924 " 6
23. 16.910	3.93	2.4774	−9016 "		−9013 " 4
24. 16.774	3.08	2.4596	−9026 "		−9031 " 3
Series with Thermometer '61 A.					
25. 15.522	23.88	2.2602	−8264 cal.		−8256 cal. at 24°
26. 16.886	22.96	2.2786	−8307 "		−8306 " 23
27. 16.910	21.90	2.2897	−8339 "		−8335 " 22
28. 16.909	19.95	2.2891	−8374 "	−8372	} −8381 " 20
29. 16.825	19.775	2.2946	−8399 "	−8390	
30. 16.758	18.955	2.2933	−8428 "		−8425 " 19
31. 16.834	18.005	2.3131	−8462 "	−8462	} −8465 " 18
32. 16.683	17.92	2.2921	−8464 "	−8459	
33. 16.764	17.86	2.3075	−8479 "	−8473	} −8484 " 17
34. 16.851	16.93	2.3226	−8488 "		−8524 " 16
35. 16.914	15.935	2.3421	−8527 "		−8554 " 15
36. 16.885	15.005	2.3451	−8554 "		−8604 " 14
37. 16.938	13.99	2.3665	−8604 "		
38. 16.937	12.925	2.3610	−8585 "	−8581	} −8606 " 13
39. 16.949	13.05	2.3752	−8629 "	−8630	
40. 16.867	10.98	2.3613	−8681 "		−8681 " 11
41. 16.889	9.05	2.4035	−8762 "		−8764 " 9
42. 16.858	6.92	2.4277	−8866 "		−8862 " 7
43. 16.909	4.97	2.4586	−8953 "		−8953 " 5
44. 16.810	2.99	2.4666	−9035 "		−9035 " 3

TABLE D.—*Heat of Dissolution of Anhydrous Strontium Chloride,*
 $\text{SrCl}_2 = 158.04$; $\frac{1}{12}$ mol. = 13.17 grams.

<i>w.</i>	<i>t</i> °.	(<i>t</i> ' - <i>t</i>)°.	M at <i>t</i> °.	M. at T. Whole degrees C.
Series with Thermometer '08 A.				
1. 13.125	24.84	1.6095	11826 cal.	11832 cal. at 25°
2. 13.198	23.78	1.6099	11771 "	11782 " 24
3. 13.215	22.72	1.6043	11706 "	11724 " 23
4. 13.181	21.855	1.5878	11615 "	11633 " 22
5. 13.231	20.765	1.5835	11540 "	11562 } 11554 " 21
6. 13.186	20.635	1.5743	11515 "	
7. 13.255	19.93	1.5753	11459 "	11463 " 20
8. 13.312	18.69	1.5704	11375 "	11398 " 19
9. 13.210	17.80	1.5495	11309 "	11325 " 18
10. 13.250	16.845	1.5385	11195 "	11214 " 17
11. 13.274	15.82	1.5312	11122 "	11132 " 16
12. 13.275	14.815	1.5234	11065 "	11073 " 15
13. 13.321	13.74	1.5160	10973 "	10992 " 14
14. 13.143	11.87	1.4676	10756 "	10773 " 12
15. 13.163	9.93	1.4469	10596 "	10600 " 10
16. 13.208	7.86	1.4246	10396 "	10412 " 8
17. 13.174	3.805	1.3515	9888 "	9912 " 4
18. 13.176	2.945	1.3360	9817 "	9822 " 3
Series with Thermometer '61 A.				
19. 13.178	23.64	1.6087	11788 cal.	11800 cal. at 24°
20. 13.215	22.715	1.6009	11685 "	11717 " 23
21. 13.201	21.65	1.5911	11632 "	11650 " 22
22. 13.237	19.74	1.5658	11414 "	11440 " 20
23. 13.210	18.71	1.5486	11306 "	11321 " 19
24. 13.227	17.745	1.5410	11236 "	11250 " 18
25. 13.252	16.685	1.5337	11162 "	11185 " 17
26. 13.267	15.67	1.5319	11135 "	11146 " 16
27. 13.232	14.80	1.5177	11062 "	11080 " 15
28. 13.139	13.775	1.4982	10997 "	11018 " 14
29. 13.234	12.805	1.4937	10885 "	10908 " 13
30. 13.168	10.765	1.4584	10655 "	10683 " 11
31. 13.150	8.845	1.4282	10482 "	10483 " 9
32. 13.153	6.73	1.4012	10271 "	10294 " 7
33. 13.219	3.76	1.3596	9915 "	9928 " 4
34. 13.215	2.81	1.3517	9862 "	9880 " 3
Series with Thermometer '08 B.				
35. 13.196	24.90	1.6182	11825 cal.	11830 cal. at 25°
36. 13.222	23.01	1.6020	11693 "	11682 " 23
37. 13.123	21.09	1.5694	11531 "	11523 " 21
38. 13.175	19.045	1.5522	11364 "	11360 " 19
39. 13.161	16.875	1.5245	11168 "	11180 " 17
40. 13.196	14.945	1.5061	11003 "	11007 " 15
41. 13.146	14.045	1.4916	10938 "	10933 " 14
42. 13.215	12.955	1.4849	10832 "	10836 " 13

<i>w.</i>	<i>t</i> °	(<i>t'</i> - <i>t</i>)°	M at <i>t</i> °	M. at T. Whole degrees C.
Series with Thermometer '61 B.				
43. 13·213	25·00	1·6149	11789 cal.	11789 cal. at 25°
44. 13·206	22·94	1·5961	11657 „	11658 „ 23
45. 13·188	20·975	1·5668	11458 „	11458 „ 21
46. 13·205	18·955	1·5495	11317 „	11318 „ 19
47. 13·208	16·88	1·5290	11163 „	11176 „ 17
48. 13·208	14·965	1·5070	11003 „	11007 „ 15

TABLE E.—*Heat of Dissolution of Hydrated Strontium Chloride*,
 $\text{SrCl}_2 \cdot 5 \cdot 992 \text{H}_2\text{O} = 265 \cdot 66$; $\frac{1}{12} \text{ mol.} = 22 \cdot 138 \text{ grams.}$

<i>w.</i>	<i>t</i> °.	(<i>t</i> - <i>t'</i>)°.	<i>m</i> at <i>t</i> °.	<i>m</i> at T.	Whole degrees C.	M at T.
Series with Thermometer '08 A.						
1. 22·255	24·96	0·9866	-7292 cal.		-7291 cal. at 25°	2534 cal.
2. 22·145	23·91	0·9872	-7332 „		-7326 „ 24	2449 „
3. 22·125	22·85	0·9912	-7370 „		-7364 „ 23	2361 „
4. 22·192	21·98	0·9970	-7393 „		-7393 „ 22	2283 „
5. 22·086	20·885	0·9968	-7423 „		-7421 „ 21	2204 „
6. 22·308	20·05	1·0141	-7482 „		-7484 „ 20	2090 „
7. 23·384	18·815	1·0692	-7525 „		-7522 „ 19	1999 „
8. 22·264	17·935	1·0201	-7536 „		-7534 „ 18	1938 „
9. 22·237	17·05	1·0258	-7588 „		-7590 „ 17	1828 „
10. 21·776	16·01	1·0128	-7648 „		-7648 „ 16	1718 „
11. 21·940	15·015	1·0214	-7656 „	-7656 } -7634 }	-7645 „ 15	1670 „
12. 22·210	14·98	1·0310	-7634 „			
13. 22·187	14·02	1·0404	-7713 „		-7713 „ 14	1551 „
15. 22·155	13·475	1·0413	-7730 „			
14. 22·257	12·01	1·0509	-7777 „		-7777 „ 12	1382 „
16. 22·243	10·005	1·0629	-7758 „		-7758 „ 10	1298 „
17. 22·238	8·00	1·0700	-7911 „		-7911 „ 8	1040 „
18. 22·238	4·935	1·0985	-8122 „		-8119 „ 5	675 „
19. 22·232	3·93	1·1055	-8177 „		-8173 „ 4	570 „
20. 22·262	3·085	1·1115	-8209 „		-8204 „ 3	485 „
Series with Thermometer '61 A.						
21. 22·262	24·925	0·9886	-7366 cal.		-7364 cal. at 25°	2521 cal.
22. 22·188	23·885	0·9881	-7329 „		-7324 „ 24	2451 „
23. 22·247	22·95	0·9975	-7377 „		-7374 „ 23	2351 „
24. 22·220	21·90	1·0033	-7429 „		-7422 „ 22	2254 „
25. 22·247	20·895	1·0049	-7431 „		-7430 „ 21	2195 „
26. 22·216	19·99	1·0096	-7474 „		-7474 „ 20	2100 „
27. 22·178	18·96	1·0121	-7506 „		-7504 „ 19	2014 „
28. 22·238	17·92	1·3128	-7567 „		-7561 „ 18	1911 „
29. 22·243	16·905	1·0258	-7586 „		-7583 „ 17	1935 „
30. 22·192	15·93	1·0261	-7605 „		-7601 „ 16	1765 „
31. 22·228	14·83	1·0338	-7652 „		-7645 „ 15	1670 „
32. 22·252	13·98	1·0404	-7697 „		-7696 „ 14	1568 „
33. 22·310	13·05	1·0481	-7727 „		-7729 „ 13	1483 „
34. 22·263	10·98	1·0567	-7807 „		-7807 „ 11	1300 „
35. 22·228	9·05	1·0664	-7890 „		-7894 „ 9	1110 „
36. 22·236	6·905	1·0856	-8030 „		-8023 „ 7	875 „
37. 22·210	4·98	1·0932	-8095 „	-8095 } -8102 }	-8099 „ 5	746 „
38. 22·249	4·905	1·0964	-8106 „			
39. 22·225	2·99	1·1111	-8221 „		-8221 „ 3	468 „

TABLE F.—*Heat of Dissolution of Anhydrous Strontium Nitrate.*

$$\text{Sr}(\text{NO}_3)_2 = 211.08; \frac{1}{12} \text{ mol.} = 17.59 \text{ grams.}$$

<i>w.</i>	<i>t</i> °.	(<i>t</i> - <i>t'</i>)°.	M at <i>t</i> .	M at T. Whole degrees C.
Series with Thermometer '08 A.				
1. 17.808	24.96	0.6023	-4356 cal.	-4355 cal. at 25°
2. 17.841	23.91	0.6116	-4415 "	-4408 " 24
3. 17.946	22.85	0.6216	-4461 "	-4460 " 23
4. 17.810	21.98	0.6262	-4528 "	-4528 " 22
5. 17.801	20.95	0.6350	-4594 "	-4587 " 21
6. 17.682	20.05	0.6390	-4654 "	-4657 " 20
7. 17.631	18.81	0.6477	-4731 "	-4720 " 19
8. 17.698	18.00	0.7108	-4760 "	-4760 } -4762 " 18
9. 18.751	17.94	0.6964	-4767 "	
10. 17.808	17.07	0.6742	-4875 "	-4880 " 17
11. 17.725	16.00	0.6822	-4957 "	-4957 " 16
12. 17.641	15.015	0.6829	-4986 "	-4986 " 15
13. 17.487	14.03	0.6928	-5102 "	-5103 " 14
14. 17.487	13.43	0.6946	-5114 "	
15. 17.764	12.01	0.7174	-5195 "	-5195 " 12
16. 17.723	10.01	0.7248	-5351 "	-5351 " 10
17. 17.758	7.995	0.7582	-5496 "	-5496 " 8
18. 17.693	4.935	0.7948	-5783 "	-5776 " 5
19. 17.776	3.925	0.8132	-5889 "	-5880 " 4
20. 17.748	3.08	0.8195	-5943 "	-5947 " 3
Series with Thermometer '61 A.				
21. 17.784	24.595	0.6019	-4360 cal.	-4340 cal. at 25°
22. 17.880	23.89	0.6099	-4390 "	-4385 " 24
23. 17.888	22.955	0.6204	-4466 "	-4463 " 23
24. 17.899	21.90	0.6274	-4513 "	-4506 " 22
25. 17.859	19.985	0.6424	-4632 "	-4632 " 20
26. 17.882	18.95	0.6555	-4720 "	-4715 " 19
27. 17.905	18.005	0.6652	-4784 "	-4784 " 18
28. 17.869	16.905	0.6730	-4851 "	-4844 " 17
29. 17.840	15.935	0.6791	-4904 "	-4900 " 16
30. 17.803	15.03	0.6878	-4976 "	-4978 " 15
31. 17.892	13.975	0.7027	-5058 "	-5056 " 14
32. 17.864	13.035	0.7058	-5120 "	-5122 " 13
33. 17.736	10.98	0.7253	-5267 "	-5267 " 11
34. 17.881	9.05	0.7537	-5428 "	-5432 " 9
35. 17.820	6.94	0.7736	-5590 "	-5586 " 7
36. 17.763	4.91	0.7989	-5791 "	-5785 " 5
37. 17.782	3.96	0.8125	-5883 "	-5879 " 4
38. 17.791	2.995	0.8247	-5955 "	-5955 " 3
Series with Thermometer '08 A.				
39. 17.744	20.955	0.6360	-4616 cal.	-4610 cal. at 21°
40. 17.733	20.01	0.6418	-4661 "	-4662 " 20
41. 17.718	18.98	0.6519	-4738 "	-4737 " 19
42. 17.681	17.92	0.6617	-4815 "	-4808 " 18
43. 17.839	16.98	0.6733	-4860 "	-4860 " 17
44. 17.699	16.00	0.6790	-4940 "	-4940 " 16
45. 17.683	4.04	0.8049	-5860 "	-5863 " 4

w.	t°.	(t-t')°.	M at t°.	M at T.	Whole degrees C.
Series with Thermometer '61 A.					
46. 17·750	20·88	0·6345	-4605 cal.		-4597 cal. at 21°
47. 17·791	19·96	0·6449	-4673 "		-4670 " 20
48. 17·724	19·06	0·6498	-4723 "		-4726 " 19
49. 17·862	17·925	0·6612	-4768 "		-4763 " 18
50. 17·710	16·935	0·6680	-4858 "		-4854 " 17
51. 17·733	16·04	0·6761	-4911 "		-4912 " 16

TABLE G.—*Heat of Dissolution of Hydrated Strontium Nitrate.*

$\text{Sr}(\text{NO}_3)_2 \cdot 3 \cdot 987 \text{H}_2\text{O} = 282 \cdot 846; \frac{1}{12} \text{ mol.} = 23 \cdot 571 \text{ grams.}$

w.	t°.	(t-t')°.	m at t°.	m at T.	Whole degrees C.	M at T°.
Series with Thermometer '08 A.						
1. 23·317	24·96	1·6766	-12531 cal.		-12525 cal. at 25°	-5981 cal.
2. 23·617	23·92	1·7046	-12579 "		-12575 " 24	-6073 "
3. 23·405	22·85	1·6936	-12610 "		-12603 " 23	-6135 "
4. 23·510	21·985	1·7038	-12630 "		-12630 " 22	-6194 "
5. 23·635	20·89	1·7162	-12654 "		-12651 " 21	-6249 "
6. 23·361	19·845	1·7028	-12701 "		-12694 " 20	-6324 "
7. 23·248	18·81	1·7015	-12753 "		-12743 " 19	-6409 "
8. 23·706	17·945	1·7381	-12775 "		-12773 " 18	-6471 "
9. 23·742	17·06	1·7478	-12828 "		-12830 " 17	-6563 "
10. 23·487	16·045	1·7329	-12857 "		-12859 " 16	-6626 "
11. 23·366	15·03	1·7288	-12893 "		-12894 " 15	-6696 "
12. 23·609	14·03	1·7520	-12932 "		-12933 " 14	-6770 "
13. 23·652	12·01	1·7668	-13014 "		-13014 " 12	-6921 "
14. 23·763	10·005	1·7880	-13110 "		-13110 " 10	-7086 "
15. 23·735	8·00	1·7953	-13178 "		-13178 " 8	-7224 "
16. 23·872	3·93	1·8416	-13439 "		-13436 " 4	-7621 "
17. 23·792	3·08	1·8462	-13517 "		-13521 " 3	-7740 "

With Thermometer '08 B.

18. 23·718	4·31	1·8339	-13470 cal.	(-13490) cal. at 4	-7675 cal.
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Series with Thermometer '61 A.

19. 23·441	24·935	1·6926	-12588 cal.	-12585 }	-12572 cal. at 25°	-6028 cal.
20. 23·473	24·915	1·6952	-12562 "	-12559 }		
21. 23·441	22·95	1·6983	-12628 "		-12626 " 23	-6158 "
22. 23·740	20·905	1·7284	-12691 "		-12686 " 21	-6284 "
23. 23·610	18·96	1·7312	-12781 "		-12779 " 19	-6445 "
24. 23·841	17·995	1·7518	-12809 "		-12809 " 18	-6507 "
25. 23·654	16·905	1·7419	-12835 "		-12833 " 17	-6566 "
26. 23·519	15·915	1·7356	-12861 "		-12860 " 16	-6627 "
27. 23·582	15·02	1·7447	-12896 "		-12897 " 15	-6699 "
28. 23·830	13·985	1·7724	-12965 "		-12964 " 14	-6801 "
29. 23·748	13·04	1·7725	-13011 "		-13013 " 13	-6885 "
30. 23·763	10·98	1·7779	-13040 "		-13040 " 11	-6982 "
31. 23·702	9·05	1·7902	-13162 "		-13164 " 9	-7176 "
32. 23·716	6·91	1·8088	-13283 "		-13277 " 7	-7358 "
33. 23·887	4·985	1·8350	-13387 "		-13387 " 5	-7538 "
34. 23·820	2·99	1·8456	-13500 "		-13500 " 3	-7719 "

TABLE H.—*Heat of Dissolution of Anhydrous Sodium Carbonate.*

$$\text{Na}_2\text{CO}_3 = 105.84; \frac{1}{12} \text{ mol.} = 8.82 \text{ grams.}$$

<i>w.</i>	<i>t</i> °.	(<i>t</i> ' - <i>t</i>)°.	<i>M</i> at <i>t</i> °.	<i>M</i> at <i>T</i> . Whole degrees C.
Series with Thermometer '61 A.				
1. 8.825	24.605	0.7980	5839 cal.	} 5852 cal. at 25°
2. 8.825	24.600	0.7957	5822 "	
3. 8.826	21.775	0.7787	5695 "	
4. 8.854	21.775	0.7784	5675 "	
5—12. See Trans., 1887, 73.	} 18.815	—	5521 "	} 5533 " 19
13. 8.838		0.7246	5292 "	
14. 8.829	15.80	0.7275	5317 "	} 5316 " 16
15. 8.867	12.85	0.6969	5072 "	
16. 8.796	12.855	0.6926	5081 "	} 5084 " 13
17. 8.887	12.86	0.6987	5074 "	
18. 8.871	9.955	0.6760	4917 "	} 4912 " 10
19. 8.778	9.95	0.6674	4906 "	
20. 8.819	6.925	0.6420	4697 "	} 4701 " 70
21. 8.763	6.93	0.6382	4699 "	
22. 8.740	3.94	0.5811	4290 "	} 4315 " 4
23. 8.743	3.935	0.5864	4327 "	

TABLE I.—*Heat of Dissolution of Hydrated Sodium Carbonate.*

$$\text{Na}_2\text{CO}_3 \cdot 9.96\text{H}_2\text{O} = 284.722; \frac{1}{12} \text{ mol.} = 23.719 \text{ grams.}$$

<i>w.</i>	<i>t</i> °.	(<i>t</i> ' - <i>t</i>)°.	<i>m</i> at <i>t</i> °.	<i>m</i> at <i>T</i> . Whole degrees C.	<i>M</i> at <i>T</i> °.
Series with Thermometer '08 A.					
1. 23.766	24.95	2.1745	-16285 cal.	-16286 cal. at 25°	+ 44 cal.
2. 23.870	23.905	2.1802	-16258 "	-16262 " 24	- 15 "
3. 23.597	22.845	2.1476	-16202 "	-16211 " 23	- 47 "
4. 23.488	21.985	2.1394	-16211 "	-16207 " 22	- 127 "
5. 23.754	20.90	2.1604	-16186 "	-16189 " 21	- 196 "
6. 23.955	20.05	2.1782	-16184 "	-16184 " 20	- 274 "
7. 23.695	18.785	2.1525	-16165 "	-16168 " 19	- 343 "
8. 23.891	17.94	2.1708	-16172 "	-16169 " 18	- 432 "
9. 23.551	17.06	2.1441	-16204 "	-16201 " 17	- 549 "
10. 23.636	16.025	2.1422	-16127 "	-16127 " 16	- 559 "
11. 23.768	15.02	2.1549	-16135 "	-16136 " 15	- 656 "
12. 23.677	14.02	2.1490	-16149 "	-16149 " 14	- 756 "
13. 23.966	13.41	2.1735	-16140 "	} -16147	} -16166 " 13 - 856 "
14. 23.877	12.93	2.1719	-16189 "		
15. 23.871	12.015	2.1742	-16210 "		
16. 24.019	12.04	2.1833	-16179 "	} -16179	} -16195 " 12 - 972 "
17. 23.856	10.01	2.1673	-16168 "		
18. 24.000	8.00	2.1784	-16195 "	-16169 " 10	- 1121 "
19. 24.012	5.965	2.1853	-16204 "	-16195 " 8	- 1278 "
20. 24.059	3.93	2.1982	-16261 "	-16204 " 6	- 1504 "
21. 23.756	3.08	2.1656	-16218 "	-16260 " 4	- 1736 "
				(-16218) " 3	- 1781 "

$w.$	t°	$(t-t')^{\circ}$	m at t°	m at T.	Whole degrees C.	M at T° .
Series with Thermometer '61 A.						
22.	23·766	24·93	2·1882	-16329 cal.	-16332 cal. at 25°	- 2 cal.
23.	23·833	23·895	2·1808	-16296 „	-16298 „ 24	- 51 „
24.	23·817	22·965	2·1763	-16270 „	-16269 „ 23	- 105 „
25.	23·536	21·90	2·1516	-16277 „	-16276 „ 22	- 196 „
26.	23·393	20·905	2·1342	-16235 „	-16239 „ 21	- 246 „
27.	23·642	19·82	2·1606	-16274 „	-16277 } -16217 „ 20	- 307 „
28.	23·701	19·95	2·1508	-16157 „		
29.	23·759	18·955	2·1569	-16159 „	-16159 „ 19	- 334 „
30.	23·727	18·005	2·1507	-16134 „	-16134 „ 18	- 309 „
31.	23·524	16·905	2·1397	-16186 „	-16182 „ 17	- 445 „
32.	23·485	15·93	2·1319	-16153 „	-16153 „ 16	- 587 „
33.	23·788	15·005	2·1572	-16143 „	-16143 „ 15	- 663 „
34.	23·453	13·985	2·1384	-16225 „	(-16225) } -16178 „ 14	- 785 „
35.	23·474	13·99	2·1304	-16154 „		
36.	23·562	13·03	2·1413	-16179 „	-16179 „ 13	- 869 „
37.	23·060	10·97	2·1845	-16167 „	-16167 „ 11	-1032 „
38.	23·952	9·05	2·1759	-16171 „	-16172 „ 9	-1207 „
39.	23·960	6·965	2·1777	-16179 „	-16180 } -16196 „ 7	-1408 „
40.	23·909	6·955	2·1773	-16211 „		
41.	23·911	4·91	2·1808	-16238 „	-16240 „ 5	-1628 „
42.	23·891	2·985	2·1835	-16259 „	-16259 „ 3	-1822 „
Series with Thermometer '08 D.						
43.	23·827	24·945	2·1900	-16364 cal.	-16365 cal. at 25°	- 35 cal.
44.	23·895	19·98	2·1770	-16223 „	-16221 „ 20	- 311 „
45.	22·827	16·98	2·1933	-16161 „	-16161 } -16175 „ 17	- 523 „
46.	23·937	16·96	2·1768	-16188 „		
Series with Thermometer '61 D.						
47.	23·420	24·835	2·1458	-16313 cal.	-16317 cal. at 25°	+ 13 cal.
48.	23·866	19·96	2·1734	-16215 „	-16216 „ 20	- 306 „
49.	23·784	17·00	2·1536	-16121 „	-16121 } -16145 „ 17	- 493 „
50.	23·769	16·93	2·1583	-16166 „		

TABLE J.—*Heat of Dissolution of Anhydrous Sodium Acetate.*

$$\text{NaC}_2\text{H}_3\text{O}_2 = 81.855; \frac{1}{6} \text{ mol.} = 13.643 \text{ grams.}$$

<i>w.</i>	<i>t</i> °.	(<i>t</i> ' - <i>t</i>)°.	M at <i>t</i> °.	M at T. Whole degrees C.
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Series with Thermometer '08 A.

1. 13.652	24.95	1.0870	3977 cal.	3977 cal. at 25°
2. 13.676	23.915	1.0826	3972 "	3972 " 24
3. 13.678	22.845	1.0887	3976 "	3976 " 23
4. 13.713	21.98	1.0935	3982 "	3982 " 22
5. 13.745	20.895	1.0941	3975 "	3975 " 21
6. 13.784	20.05	1.0973	3984 "	3983 " 20
7. 13.711	18.805	1.0875	3960 "	3963 " 19
8. 13.626	17.94	1.0826	3967 "	3967 " 18
9. 13.657	17.05	1.0748	3930 "	3930 " 17
10. 13.735	16.06	1.0818	3933 "	3932 " 16
11. 13.928	15.02	1.0971	3934 "	3934 " 15
12. 13.657	14.015	1.0820	3931 "	3931 " 14
13. 13.659	13.43	1.0770	3937 "	
14. 13.629	12.93	1.0669	3908 "	3908 " 13
15. 13.719	12.01	1.0634	3867 "	3867 } 3877 " 12
16. 13.620	11.90	1.0600	3886 "	
17. 13.627	10.005	1.0541	3162 "	3862 " 10
18. 13.625	8.00	1.0506	3846 "	3846 } 3842 " 8
19. 13.686	7.95	1.0511	3834 "	
20. 13.670	5.97	1.0442	3813 "	3813 " 6
21. 13.673	3.93	1.0342	3776 "	3778 " 4
22. 13.643	3.08	1.0227	3742 "	3741 } 3745 " 3
23. 13.656	2.525	1.0219	3735 "	

Series with Thermometer '61 A.

24. 13.705	24.93	1.0892	3970 cal.	3970 cal. at 25°
25. 13.640	23.895	1.0862	3975 "	3975 " 24
26. 13.618	22.95	1.0866	3977 "	3977 " 23
27. 13.648	21.89	1.0830	3964 "	3965 " 22
28. 13.644	20.91	1.0814	3960 "	3960 " 21
29. 13.660	19.99	1.0760	3935 "	3935 " 20
30. 13.639	18.95	1.0734	3932 "	3932 " 19
31. 13.689	18.00	1.0797	3940 "	3940 " 18
32. 13.601	16.90	1.0709	3934 "	3934 " 17
33. 13.640	15.93	1.0757	3939 "	3939 " 16
34. 13.618	15.04	1.0726	3930 "	3930 " 15
35. 13.716	13.98	1.0777	3925 "	3925 " 14
36. 13.675	13.04	1.0674	3902 "	3902 " 13
37. 13.666	11.925	1.0612	3878 "	3879 " 12
38. 13.665	10.98	1.0552	3856 "	3856 " 11
39. 13.688	9.05	1.0568	3856 "	3856 " 9
40. 13.610	7.935	1.0452	3835 "	3836 " 8
41. 13.620	6.925	1.0413	3818 "	3820 " 7
42. 13.698	4.98	1.0353	3774 "	3774 " 5
43. 13.638	2.985	1.0223	3739 "	3740 " 3

<i>w.</i>	<i>t.</i>	$(t-t')^{\circ}$	M at t°	M at T.	Whole degrees C.
Series with Thermometer '08 B.					
44. 13·607	24·905	1·0813	3957 cal.		3957 cal. at 25°
45. 13·619	23·01	1·0798	3960 "		3960 " 23
46. 13·614	21·095	1·0856	3982 "		3982 " 21
47. 13·617	19·04	1·0740	3939 "		3940 " 19
48. 13·639	16·87	1·0754	3937 "		3938 " 17
49. 13·606	14·94	1·0696	3925 "		3926 " 15
50. 13·588	14·04	1·0638	3909 "		3908 " 14
51. 13·567	12·01	1·0553	3884 "		3884 " 12
52. 13·659	9·925	1·0574	3865 "		3865 " 10
53. 13·597	9·03	1·0500	3855 "		3854 " 9
54. 13·707	7·97	1·0540	3838 "		3838 " 8
55. 13·654	5·935	1·0418	3809 "		3810 " 6

Series with Thermometer '61 B.

56. 13·668	25·00	1·0885	3978 cal.		3978 cal. at 25°
57. 13·614	22·945	1·0875	3990 "		3990 " 23
58. 13·643	20·975	1·0871	3980 "		3981 " 21
59. 13·623	18·955	1·0790	3953 "		3956 " 19
60. 13·652	16·885	1·0763	3938 "		3938 " 17
61. 13·616	14·96	1·0721	3933 "		3933 " 15
62. 13·583	13·975	1·0660	3920 "		3920 " 14
63. 13·655	11·975	1·0673	3903 "		3904 " 12
64. 13·584	9·96	1·0532	3872 "		3973 " 10
65. 13·692	9·04	1·0581	3859 "		3856 " 9
66. 13·670	7·97	1·0526	3845 "		3845 " 8
67. 13·647	5·915	1·0418	3812 "		3814 " 6

Series with Thermometer '61 C.

68. 13·703	23·955	1·0920	3983 cal.	3983	} 3980 cal. at 24°
69. 13·666	23·93	1·0875	3977 "	3977	
70. 13·670	21·93	1·0902	3984 "		3984 " 22
71. 13·638	20·1	1·0817	3961 "		3960 " 20
72. 13·663	18·075	1·0811	3952 "		3951 " 19
73. 13·643	17·00	1·0793	3951 "	3951	} 3950 " 17
74. 13·639	17·01	1·0787	3950 "	3950	
75. 13·625	15·10	1·0728	3933 "		3933 " 15
76. 13·582	14·065	1·0648	3915 "		3914 " 14
77. 13·599	12·90	1·0636	3905 "		3906 " 13
78. 13·626	11·93	1·0626	3895 "		3895 " 12
79. 13·648	10·93	1·0574	3878 "		3879 " 11
80. 13·669	9·06	1·0532	3848 "		3848 " 9
81. 13·610	8·07	1·0464	3839 "		3838 " 8
82. 13·621	6·08	1·0429	3823 "		3822 " 6

TABLE K.—*Heat of Dissolution of Hydrated Sodium Acetate,*
 $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O} = 135.755; \frac{1}{6} \text{ mol.} = 22.625 \text{ grams.}$

<i>w.</i>	<i>t</i> °.	<i>(t-t')</i> °.	<i>m</i> at <i>t</i> °.	<i>m</i> at T.	Whole degrees C.	M. at T.°
Series with Thermometer '08 A.						
1. 22.458	24.96	1.3100	-4902 cal.	-4903 cal. at 25°	+ 7 cal.	
2. 22.481	23.92	1.3044	-4876 "	-4878 "	24 + 18 "	
3. 22.547	22.85	1.3038	-4860 "	-4862 "	23 + 8 "	
4. 22.701	21.975	1.3083	-4844 "	-4845 "	22 + 0 "	
5. 22.611	20.895	1.2919	-4802 "	-4805 "	21 + 13 "	
6. 22.460	20.045	1.2818	-4796 "	-4796 "	20 "	
7. 22.506	18.82	1.2792	-4776 "	-4779 "	19 - 16 "	
8. 22.791	18.01	1.2918	-4765 "	-4765 }	-4760 "	18 - 13 "
9. 22.545	17.935	1.2752	-4753 "	-4754 }	-4764 "	17 - 49 "
10. 22.606	17.07	1.2818	-4765 "	-4764 "	17 - 49 "	
11. 22.425	16.02	1.2651	-4740 "	-4740 "	16 - 50 "	
12. 22.736	15.05	1.2781	-4725 "	-4726 "	15 - 61 "	
13. 22.440	14.02	1.2612	-4723 "	-4723 "	14 - 85 "	
14. 22.320	13.43	1.2486	-4700 "			
15. 22.773	12.01	1.2657	-4671 "	-4671 "	12 - 85 "	
16. 22.595	10.01	1.2495	-4647 "	-4647 "	10 - 108 "	
17. 22.722	8.00	1.2455	-4606 "	-4606 "	8 - 122 "	
18. 22.836	3.93	1.2498	-4598 "	-4598 "	4 - 220 "	
19. 22.724	3.08	1.2448	-4602 "	-4602 "	3 - 252 "	
Series with Thermometer '61 A.						
20. 22.708	23.895	1.3183	-4875 cal.	-4875 cal. at 24°	+ 21 cal.	
21. 22.670	22.95	1.3144	-4875 "	-4876 "	23 - 6 "	
22. 22.558	21.89	1.3016	-4850 "	-4854 "	22 - 9 "	
23. 22.716	20.905	1.3061	-4833 "	-4836 "	21 - 18 "	
24. 22.726	19.99	1.2999	-4808 "	-4809 "	20 - 13 "	
25. 22.732	18.955	1.2706	-4798 "	-4799 "	19 - 36 "	
26. 22.770	18.01	1.2933	-4774 "	-4774 }	-4772 "	18 - 31 "
27. 22.558	17.915	1.2792	-4768 "	-4770 }		
28. 22.655	16.905	1.2818	-4756 "			
29. 22.668	15.915	1.2773	-4736 "	-4736 "	16 - 46 "	
30. 22.497	15.00	1.2656	-4728 "	-4728 "	15 - 63 "	
31. 22.804	13.975	1.2792	-4716 "	-4717 "	14 - 79 "	
32. 22.607	13.035	1.2626	-4694 "	-4694 "	13 - 81 "	
33. 22.813	10.98	1.2647	-4661 "	-4661 "	11 - 99 "	
34. 22.793	9.045	1.2575	-4637 "	-4636 "	19 - 126 "	
35. 22.673	6.91	1.2415	-4602 "	-4604 "	7 - 147 "	
36. 22.771	4.985	1.2501	-4614 "	-4615 "	5 - 212 "	
37. 22.766	3.965	1.2477	-4606 "	-4606 "	4 - 228 "	
38. 22.650	2.99	1.2436	-4598 "	-4598 "	3 - 248 "	

TABLE L.—*Heat of Dissolution of Anhydrous Rochelle Salt.*

$$\text{KNaC}_4\text{H}_4\text{O}_6 = 209\cdot665; \frac{1}{12} \text{ mol.} = 17\cdot472 \text{ grams.}$$

<i>w.</i>	<i>t</i> °.	(<i>t'</i> – <i>t</i>)°.	M at <i>t</i> °.	M at T. Whole degrees C.
Series with Thermometer '08 A.				
1. 17·457	20·935	0·3657	–2677 cal.	–2676 cal. at 21°
2. 17·447	20·03	0·3438	–2686 „	–2688 „ 20
3. 17·452	17·965	0·3868	–2834 „	–2831 „ 18
4. 17·469	16·885	0·3720	–2871 „	–2868 „ 17
5. 17·443	16·005	0·3960	–2903 „	–2903 „ 16
6. 17·496	12·01	0·4302	–3144 „	–3144 „ 12
7. 17·528	10·01	0·4495	–3278 „	–3278 „ 10
8. 17·479	7·995	0·4651	–3401 „	–3401 „ 8
9. 17·474	6·96	0·4834	–3536 „	–3530 „ 7
10. 17·469	5·97	0·4919	–3599 „	–3598 „ 6
11. 17·445	3·93	0·5198	–3808 „	–3702 „ 4
12. 17·455	3·085	0·5207	–3813 „	–3817 „ 3

Series with Thermometer '61 A.

13. 17·499	24·925	0·3397	–2484 cal.	–2480 cal. at 25°
14. 17·466	23·895	0·3465	–2538 „	–2538 „ 24
15. 17·515	22·95	0·3538	–2584 „	–2583 „ 23
16. 17·457	21·89	0·3592	–2633 „	–2630 „ 22
17. 17·414	20·895	0·3675	–2700 „	–2694 „ 21
18. 17·425	19·94	0·3697	–2721 „	–2720 „ 20
19. 17·475	18·955	0·3813	–2791 „	–2791 „ 19
20. 17·4 3	18·005	0·3868	–2843 „	–2843 „ 18
21. 17·464	16·905	0·3989	–2885 „	–2880 „ 17
22. 17·555	15·905	0·4007	–2920 „	–2917 „ 16
23. 17·475	15·01	0·4084	–2990 „	–2989 „ 15
24. 17·524	13·99	0·4173	–3046 „	–3046 „ 14
25. 17·499	13·04	0·4241	–3106 „	–3107 „ 13
26. 17·436	10·98	0·4367	–3202 „	–3202 „ 11
27. 17·453	9·05	0·4569	–3348 „	–3350 „ 9
28. 17·446	6·93	0·4694	–3440 „	–3437 „ 7
29. 17·490	4·98	0·5018	–3668 „	–3668 „ 5
30. 17·502	2·99	0·5195	–3795 „	–3795 „ 3

Series with Thermometer '08 D.

31. 17·456	21·005	0·3653	–2677 cal.	–2677 cal. at 21°
32. 17·466	20·10	0·3800	–2713 „	–2720 „ 20
33. 17·440	17·96	0·3878	–2843 „	–2840 „ 18
34. 17·418	16·98	0·3932	–2888 „	–2888 „ 17
35. 17·435	16·00	0·4015	–2944 „	–2944 „ 16

Series with Thermometer '08 E.

36. 17·458	20·935	0·3650	–2673 cal.	–2670 cal. at 21°
37. 17·440	19·945	0·3758	–2756 „	–2753 „ 20

<i>w.</i>	<i>t.</i> °	(<i>t</i> - <i>t'</i>)°	M at <i>t</i> °	M at T. Whole degrees C.
Series with Thermometer '61 D.				
38. 17·461	20·97	0·3691	-2699 cal.	-2697 cal. at 21°
39. 17·495	20·06	0·3753	-2745 "	-2747 } -2751 " 20
40. 17·418	20·05	0·3747	-2753 "	-2755 }
41. 17·446	17·99	0·3882	-2848 "	-2848 " 18
42. 17·462	17·005	0·3952	-2897 "	-2897 " 17
43. 17·456	15·935	0·4029	-2950 "	-2948 " 16
Series with Thermometer '61 C.				
44. 17·457	20·9	0·3671	-2691 cal.	-2686 cal. at 21°
45. 17·453	19·96	0·3774	-2767 "	-2765 " 20

TABLE M.—*Heat of Dissolution of Hydrated Rochelle Salt.*

$$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O} = 281.505; \frac{1}{12} \text{ mol.} = 23.459 \text{ grams.}$$

<i>w.</i>	<i>t</i> °	(<i>t</i> - <i>t'</i>)°	M at <i>t</i> °	M at T. Whole degrees C.	M at T.°
Series with Thermometer '08 A.					
1. 23·163	24·955	1·6438	-12307 cal.	-12306 cal. at 25°	-5746 cal.
2. 23·006	23·92	1·6358	-12331 "	-12329 " 24	-5801 "
3. 23·155	22·84	1·6470	-12335 "	-12334 " 23	-5841 "
4. 23·141	21·975	1·6497	-12362 "	-12362 " 22	-5903 "
5. 23·403	20·897	1·6673	-12355 "	-12353 " 21	-5929 "
6. 23·491	20·05	1·6772	-12383 "	-12385 " 20	-5995 "
7. 22·869	18·81	1·6399	-12453 "	-12427 " 19	-6072 "
8. 23·456	17·955	1·6866	-12470 "	-12470 " 18	-6149 "
9. 23·440	17·07	1·6909	-12510 "	-12511 " 17	-6223 "
10. 23·416	16·04	1·6863	-12490 "	-12493 " 16	-6239 "
11. 23·481	15·00	1·6938	-12510 "	-12510 " 15	-6291 "
12. 23·576	14·02	1·7079	-12565 "	-12564 " 14	-6380 "
13. 23·369	13·43	1·6959	-12584 "		
14. 23·603	12·01	1·7141	-12595 "	-12595 " 12	-6479 "
15. 23·452	10·01	1·7098	-12699 "	-12699 " 10	-6653 "
16. 23·522	8·00	1·7278	-12738 "	-12738 " 8	-6760 "
17. 23·325	5·97	1·7312	-12870 "	-12870 " 6	-6941 "
18. 23·488	3·93	1·7578	-12976 "	-12973 " 4	-7136 "
19. 23·271	3·08	1·7433	-12991 "	-12993 " 3	-7193 "

<i>w.</i>	<i>t</i> °.	(<i>t</i> − <i>t'</i>)°.	M at <i>t</i> °.	M at T.	Whole degrees C.	M at T°.
Series with Thermometer '61 A.						
20. 23·210	24·935	1·6510	−12342 cal.		−12340 cal. at 25°	−5782 cal.
21. 23·161	23·885	1·6508	−12365		−12362 " 24	−5834 "
22. 23·348	22·965	1·6624	−12355 "		−12355 " 23	−5862 "
23. 23·332	21·90	1·6686	−12406 "		−12404 " 22	−5945 "
24. 23·361	20·91	1·6712	−12411 "		−12410 " 21	−5986 "
25. 23·464	19·95	1·6783	−12408 "		−12408 " 20	−6018 "
26. 23·502	18·96	1·6887	−12464 "		−12463 " 19	−6108 "
27. 23·432	18·00	1·6848	−12472 "		−12472 " 18	−6151 "
28. 23·430	16·905	1·6891	−12505 "		−12504 " 17	−6216 "
29. 23·155	15·92	1·6697	−12506 "		−12505 " 16	−6251 "
30. 23·373	15·005	1·6900	−12540 "		−12540 " 15	−6321 "
31. 23·576	13·98	1·7109	−12587 "		−12589 " 14	−6415 "
32. 23·455	13·035	1·7053	−12610 "		−12610 " 13	−6460 "
33. 23·448	10·975	1·7083	−12638 "		−12638 " 11	−6656 "
34. 23·440	9·05	1·7166	−12703 "		−12705 " 9	−6691 "
35. 23·456	6·905	1·7295	−12791 "		−12786 " 7	−6842 "
36. 23·483	4·98	1·7486	−12915 "		−12915 " 5	−7043 "
37. 23·473	2·995	1·7601	−13005 "		−13005 " 3	−7201 "
Series with Thermometer '08 D.						
38. 23·573	24·945	1·6808	−12371 cal.	−12372 }	−12387 cal. at 25°	−5829 cal.
39. 23·365	24·94	1·6704	−12401 "	−12402 }		
40. 23·326	19·99	1·6650	−12374 "		−12374 " 20	−5984 "
41. 23·372	16·98	1·6882	−12510 "		−12510 " 17	−6222 "
Series with Thermometer '61 D.						
42. 23·430	24·835	1·6625	−12313 cal.		−12310 cal. at 25°	−5753 cal.
43. 23·485	21·94	1·6695	−12335 "		−12333 " 22	−5874 "
44. 23·355	19·86	1·6651	−12370 "		−12368 " 20	−5978 "
45. 23·298	17·005	1·6693	−12430 "	−12430 }	−12438 " 17	−6150 "
46. 23·502	16·93	1·6864	−12450 "	−12447 }		
With Thermometer '61 E.						
48. 23·429	23·995	1·6674	−12350 cal.		−12350 cal. at 24°	−5822 cal.
49.						
50. 23·332	19·96	1·6680	−12403 "		−12402 " 20	−6012 "
51. 23·310	16·82	1·6804	−12506 "		−12502 " 17	−6214 "

TABLE N.—*Heat of Dissolution of Potassium Sulphate.*

$$\text{K}_2\text{SO}_4 = 173.88; \frac{3}{40} \text{ mol.} = 13.041 \text{ grams.}$$

<i>w.</i>	<i>t</i> °.	(<i>t</i> − <i>t'</i>)°.	M at <i>t</i> °.	M at T.	Whole degrees C.
Series with Thermometer '08 A.					
1. 12·956	19·935	0·7799	−6398 cal.		−6397 cal. at 20°
2. 12·998	16·88	0·8148	−6662 „		−6650 „ 17
3. 12·997	14·945	0·8348	−6826 „		−6822 „ 15
4. 13·038	13·925	0·8466	−6899 „		−6893 „ 14
5. 12·940	12·05	0·8616	−7074 „		−7080 „ 12
6. 13·093	10·09	0·8981	−7287 „		−7297 „ 10
7. 13·012	6·90	0·9324	−7613 „		−7605 „ 7
8. 13·036	3·08	0·9885	−8056 „		−(8063) „ 3

<i>w.</i>	<i>t</i> °.	(<i>t</i> − <i>t'</i>)°.	M at <i>t</i> °.	M at T. Whole degrees C.
Series with Thermometer '61 B.				
9. 13·032	16·95	0·8157	−6653 cal.	−6650 cal. at 17°
10. 13·061	14·91	0·8395	−6833 „	−6823 „ 15
11. 12·977	13·94	0·8448	−6920 „	−6912 „ 14
12. 12·966	11·93	0·8657	−7096 „	−7086 „ 12
13. 13·029	9·985	0·8964	−7311 „	−7310 „ 10
14. 13·019	6·955	0·9273	−7569 „	−7554 „ 7
15. 13·009	2·99	0·9784	−7992 „	−7952 „ 3
Series with Thermometer '61 B.				
16. 13·036	19·91	0·7866	−6415 cal.	−6405 cal. at 20°
17. 13·057	16·95	0·8191	−6684 „	−6665 „ 17
18. 13·012	14·96	0·8427	−6842 „	−6838 „ 15
19. 13·030	13·98	0·8487	−6922 „	−6922 „ 14
20. 13·076	11·97	0·8742	−7105 „	−7103 „ 12
21. 13·096	9·965	0·8995	−7299 „	−7295 „ 10
22. 13·051	7·045	0·9316	−7586 „	−7592 „ 7
23. 12·487	4·16	0·9719	−7864 „	−7877 „ 4

TABLE O.—*Heat of Dissolution of Anhydrous Magnesium Sulphate.*

$$\text{MgSO}_4 = 119\cdot76; \frac{3}{40} \text{ mol.} = 8\cdot982 \text{ grams.}$$

Series with Thermometer '08 B.				
1. 8·936	19·965	2·5055	20492 cal.	20496 cal. at 20°
2. 8·930	16·855	2·4803	20292 „	20304 „ 17
3. 8·918	13·395	2·4416	20000 „	20010 „ 13·5
4. 8·955	7·01	2·3857	19451 „	19451 } 19450 „ 7
5. 8·979	6·965	2·3906	19444 „	
6. 8·982	3·08	2·3498	19104 „	19094 „ 3
Series with Thermometer '61 B.				
7. 8·939	19·865	2·5086	20510 cal.	20512 cal. at 20°
8. 8·916	16·955	2·4821	20345 „	20349 „ 17
9. 8·918	13·45	2·4451	20034 „	20034 „ 13·5
10. 8·959	9·925	2·4172	19711 „	19716 „ 10
11. 8·955	7·04	2·3840	19450 „	19445 „ 7
12. 9·014	3·04	2·3561	19093 „	19088 „ 3

TABLE P.—*Heat of Dissolution of Hydrated Magnesium Sulphate.*

$$\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 245.58; \frac{3}{40} \text{ mol.} = 18.411 \text{ grams.}$$

<i>w.</i>	<i>t</i> °.	(<i>t</i> − <i>t'</i>)°.	<i>m</i> at <i>t</i> °.	<i>m</i> at T. Whole degrees C.	M at T.°
Series with Thermometer '08 A.					
1. 18.334	19.94	0.4670	−3874 cal.	−3875 cal. at 20°	8000 cal.
2. 18.310	16.875	0.4714	−3914 „	−3912 „ 17	7087 „
3. 18.035	14.945	0.4673	−3940 „	−3939 „ 15	6945 „
4. 18.195	13.925	0.4736	−3958 „	−3957 „ 14	6864 „
5. 18.263	12.05	0.4786	−3985 „	−3987 „ 12	6714 „
6. 18.177	10.085	0.4832	−4042 „	−4045 „ 10	6536 „
7. 18.247	6.895	0.4953	−4127 „	−4125 „ 7	6276 „
8. 18.298	3.075	0.5138	−4269 „	−4272 „ 3	5882 „
Series with Thermometer '61 A.					
9. 17.997	16.96	0.4648	−3928 cal.	−3927 cal. at 17°	7072 cal.
10. 18.268	14.91	0.4787	−3961 „	−3960 „ 15	6924 „
11. 18.091	13.94	0.4722	−3969 „	−3968 „ 14	6853 „
12. 18.203	11.935	0.4792	−4003 „	−4000 „ 12	6701 „
13. 20.151	9.98	0.5374	−4062 „	−4062 „ 10	6519 „
14. 18.239	6.96	0.4948	−4125 „	−4124 „ 7	6277 „
15. 18.257	2.99	0.5113	−4258 „	−4258 „ 3	5896 „
Series with Thermometer '61 B.					
16. 18.229	19.90	0.4672	−3899 cal.	−3898 cal. at 20°	7287 cal.
17. 17.941	16.95	0.4642	−3926 „	−3925 „ 17	7074 „
18. 18.251	14.955	0.4741	−3951 „	−3950 „ 15	6934 „
19. 17.979	13.975	0.4699	−3975 „	−3975 „ 14	6846 „
20. 18.295	11.965	0.4813	−4001 „	−4000 „ 12	6701 „
21. 18.321	9.96	0.4898	−4056 „	−4055 „ 10	6526 „
22. 18.143	7.04	0.4925	−4129 „	−4130 „ 7	6271 „
23. 18.323	3.935	0.5059	−4199 „	−4197 „ 4	6000 „

TABLE Q.—*Heat of Dissolution of Anhydrous Copper Sulphate.*

$$\text{CuSO}_4 = 158.84; \frac{3}{40} \text{ mol.} = 11.913 \text{ grams.}$$

<i>w.</i>	<i>t</i> °.	(<i>t</i> − <i>t'</i>)°.	M at <i>t</i> °.	M at T. Whole degrees C.
Series with Thermometer '08 B.				
1. 11.979	19.965	1.9914	16110 cal.	16112 } 16100 cal. at 20°
2. 11.880	19.97	1.9722	16087 „	16099 }
3. 11.958	16.855	1.9644	15918 „	15922 „ 17
4. 11.950	13.375	1.9369	15704 „	15711 „ 13.5
5. 11.999	7.01	1.8851	15219 „	15219 „ 7
6. 11.946	3.945	1.8489	14991 „	14996 „ 4

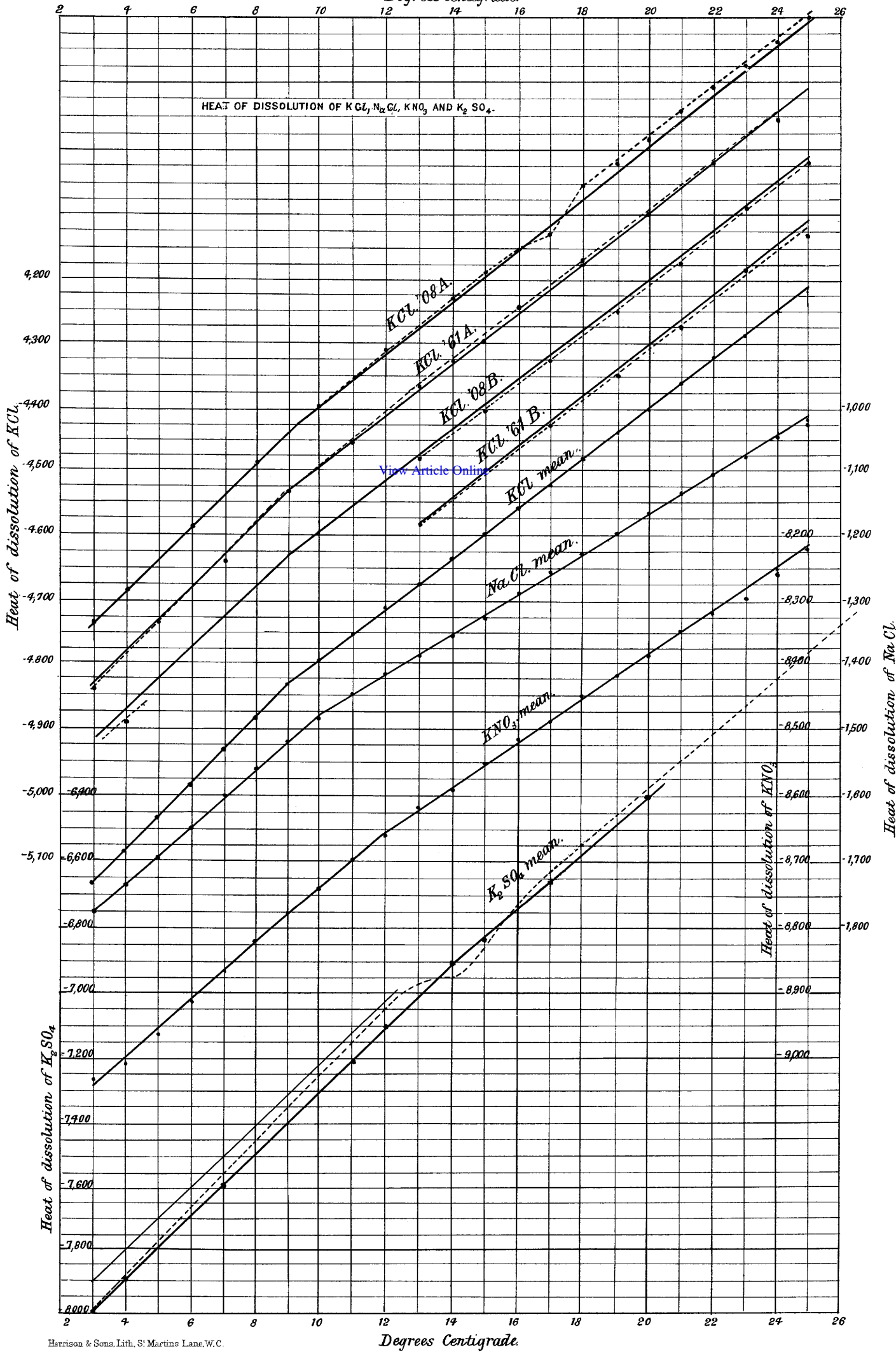
<i>w.</i>	<i>t</i> °.	(<i>t</i> − <i>t'</i>)°.	M at <i>t</i> °.	M at T. Whole degrees C.
Series with Thermometer '61 B.				
7. 12·009	19·91	1·9909	16070 cal.	16079 } 16089 cal. at 20°
8. 11·853	19·915	1·9679	16093 „	16102 } „ 17
9. 11·945	16·95	1·9615	15917 „	15919 „ 17
10. 11·937	13·45	1·9358	15717 „	15720 „ 13·5
11. 11·915	7·04	1·8759	15255 „	15251 „ 7
12. 11·894	3·985	1·8371	14966 „	14966 „ 4

TABLE R.—*Heat of Dissolution of Hydrated Copper Sulphate.*

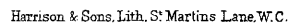
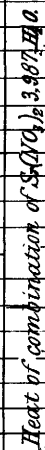
$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 248 \cdot 64; \quad \frac{3}{40} \text{ mol.} = 18 \cdot 648 \text{ grams.}$$

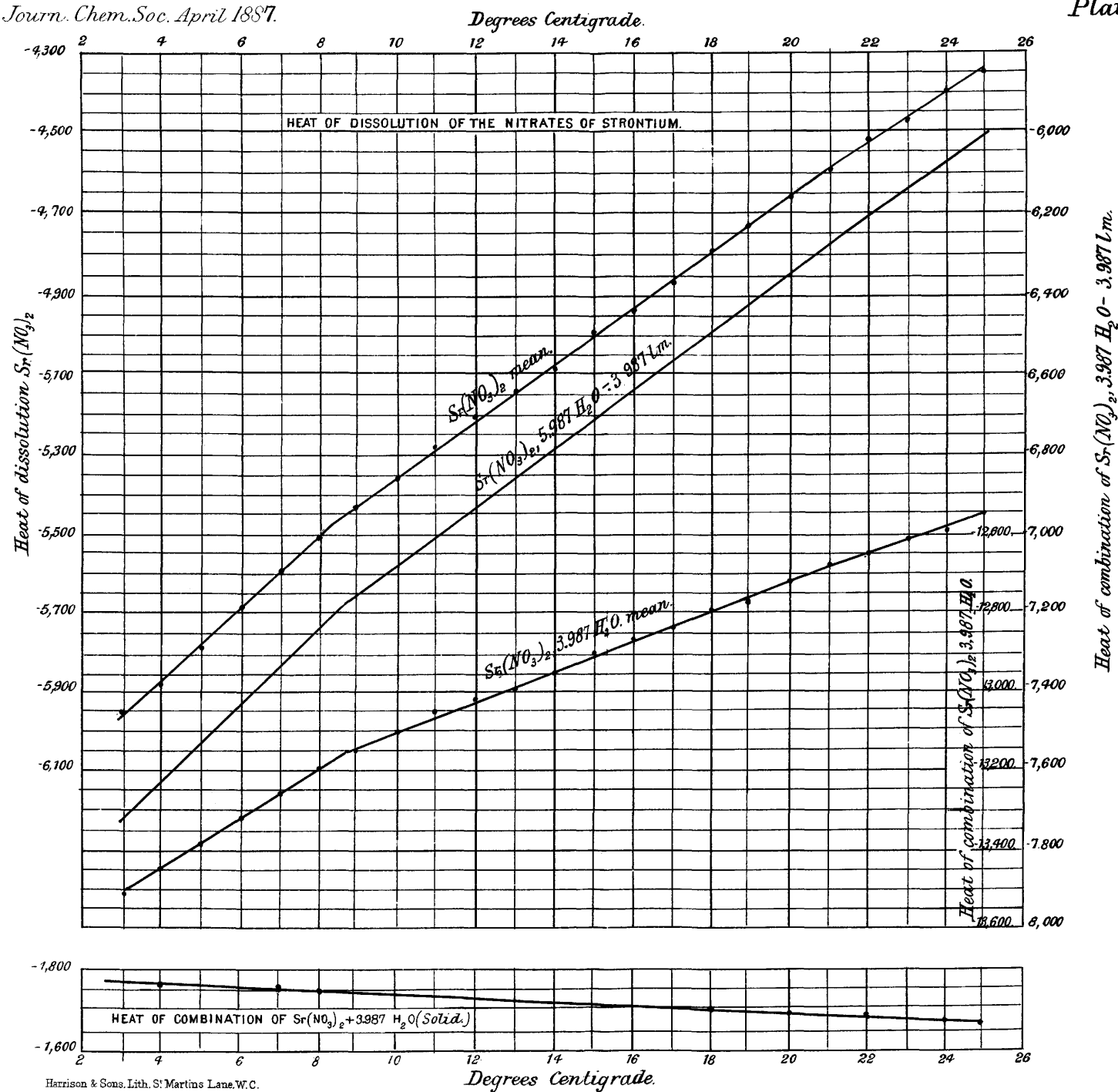
<i>w.</i>	<i>t</i> °.	(<i>t</i> − <i>t'</i>)°.	<i>m</i> at <i>t</i> °.	<i>m</i> at T. Whole degrees C.	M at T.°
Series with Thermometer '08 B.					
1. 18·905	19·97	0·3351	−2719 cal.	−2718 cal. at 20°	5217 cal.
2. 18·738	16·855	0·3429	−2807 „	−2805 „ 17	5052 „
3. 18·873	13·38	0·3542	−2879 „	−2877 „ 13·5	4830 „
4. 18·860	7·01	0·3796	−3087 „	−3087 „ 7	4343 „
5. 18·852	3·935	0·3929	−3196 „	−3192 „ 4	4106 „
Series with Thermometer '61 B.					
6. 18·935	19·905	0·3359	−2723 cal.	−2720 cal. at 20°	5267 cal.
7. 18·894	16·95	0·3457	−2808 „	−2808 „ 17	5049 „
8. 18·930	13·45	0·3522	−2855 „	−2854 „ 13·5	4858 „
9. 18·860	7·045	0·3763	−3061 „	−3062 „ 7	4368 „
10. 18·736	3·965	0·3859	−3159 „	−3158 „ 4	4140 „

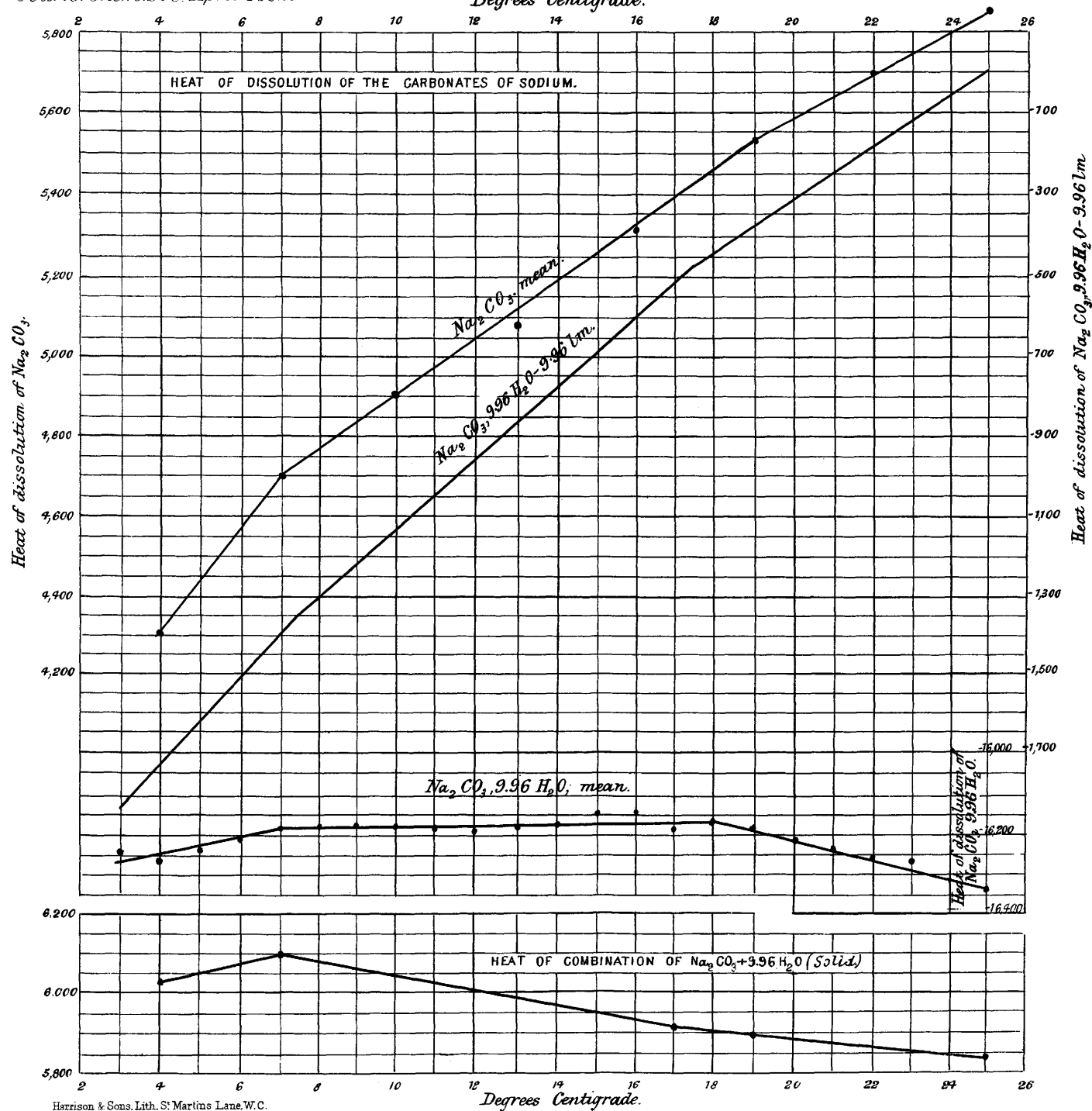
Degrees Centigrade.

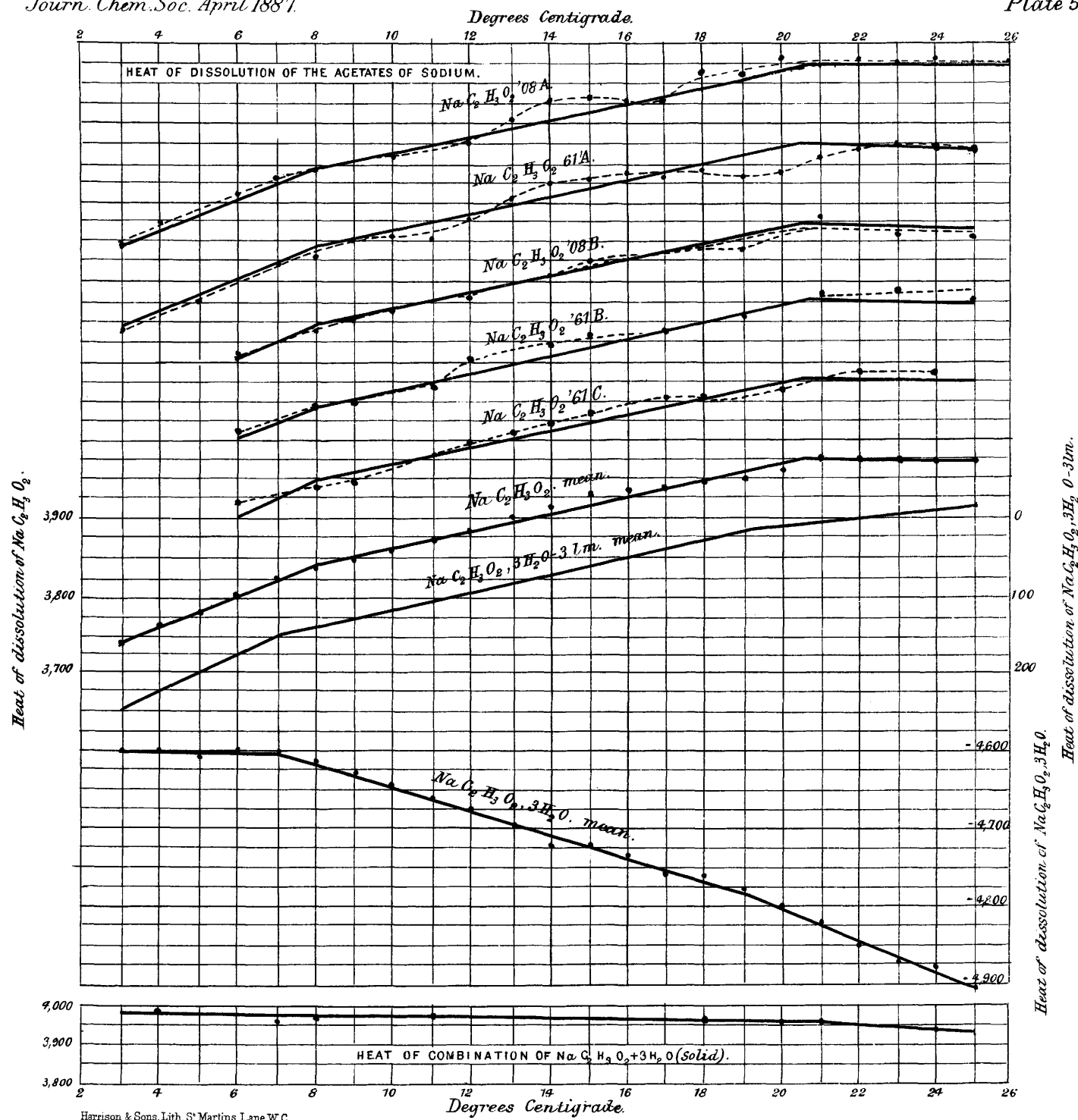


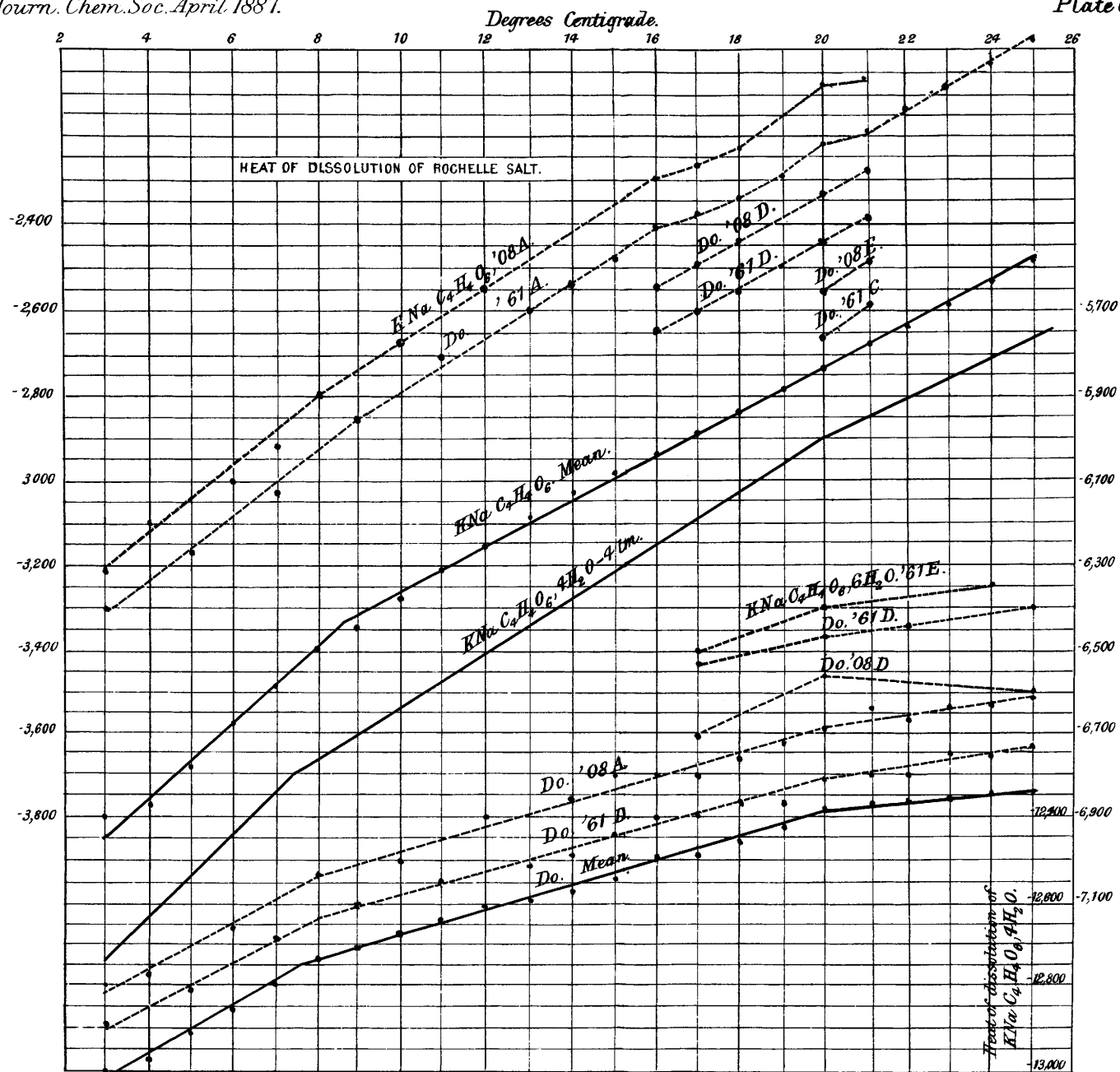
Degrees Centigrade.









Heat of dissolution of $\text{KNaC}_4\text{H}_4\text{O}_6$ Heat of dissolution of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O} - 4\text{lm.}$ 