

systems are of two sorts, viz., a point may lie on or off a line. We may therefore graphically represent such a system by using two sorts of graphical units, a pair of which, one of each sort, are either connected by a link or not, according as the point represented by one lies on the line represented by the other or not. The laws regulating the distribution of the links are stated, and the various forms which collections of three and four points and collections of three lines can assume are considered.

§§ 362—375. *Collinear Points.*

From the results of the sections under the preceding heading the form of a system of collinear points is deduced. It is shown to be a triadic group. The forms of tetrads of points of the system, both harmonic and anharmonic, are discussed.

§§ 376—380. *Ordinary Algebra.*

From the preceding sections we naturally pass to the ordinary algebraic treatment of collinear points, and the nature of quantities.

§§ 381—387. *Coplanar Points and Lines.*

These admit of discussion as a double system. The distribution of the connecting pairs of the two systems is defined, and the algebraic treatment deduced.

§§ 388—389. *Coplanar Points, Lines, and Conics.*

These sections refer briefly to the nature of the treble system composed of coplanar points, lines, and conics.

§§ 390—426. *Logic.*

The memoir concludes with the consideration of the forms of systems of which the units are classes. The investigation leads to a recognition of the fact that on certain points a modification of the views held by modern logicians is necessary.

IV. "On the Influence of Temperature on the Heat of Dissolution of Salts in Water." By WILLIAM A. TILDEN, D.Sc. Lond., F.R.S., Professor of Chemistry in the Mason College, Birmingham. Received May 18, 1885.

The experiments described in this paper were undertaken in the hope of obtaining some light upon the vexed question of the condition in which a solid exists when dissolved in a liquid, and were directed more especially towards the investigation of the well-known remarkable phenomena exhibited by sodium sulphate.

Crystallised sodium sulphate melts at about  $34^{\circ}$ , and at this temperature the salt begins to show signs of dissociation by depositing the anhydrous compound. According to Wiedemann,\* indeed, indications of change are observable at a few degrees lower. He finds by observation of the volume of the crystallised salt at different temperatures, that whereas slight expansion occurs from  $17^{\circ}$  to about  $30^{\circ}$ , contraction then sets in, at first slowly, then, at  $33^{\circ}$  to  $34^{\circ}$ , very rapidly, till the salt melts. The melted salt expands regularly in proportion as the temperature is raised to near  $100^{\circ}$ . Nicol† has made experiments upon the expansion of solutions of the same salt, and with similar results.

The solubility of sodium sulphate increases rapidly from ordinary temperatures up to  $34^{\circ}$ , when it attains a maximum. From this point upwards the solubility again diminishes very rapidly to between  $40^{\circ}$  and  $50^{\circ}$ , and then less rapidly, till at  $100^{\circ}$  to  $160^{\circ}$  it becomes nearly stationary. At temperatures higher than  $160^{\circ}$  the solubility slowly increases again.‡

In 1874 it was observed by De Coppet§ that heat is developed by contact of water with anhydrous sodium sulphate at temperatures considerably above  $34^{\circ}$ , at which point the ordinary hydrate is broken up. This circumstance was attributed by Thomsen to the formation of a monohydrate,  $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , and he ascribed this composition to the crystals which are deposited on heating a concentrated solution of sodium sulphate, and which had always been believed to be anhydrous. Thomsen's assumption has, however, been shown to be groundless,|| and therefore the fact noticed by De Coppet remains without adequate explanation.

Below the temperature of  $34^{\circ}$  it seems probable that the sodium sulphate dissolved in water is in the state of hydrate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . In what condition is it at temperatures higher than  $34^{\circ}$ ? In other words, does the solution contain the usual hydrate or the anhydrous salt, or both?

This is the question which I have endeavoured to attack by comparing the thermal changes attending the act of solution of the anhydrous salt in water at temperatures above this critical point with the corresponding change at temperatures below. Some interesting results have been obtained, but they do not supply a final answer to this question. My few earlier experiments, communicated in a short note to the British Association at Montreal, gave erroneous results, partly

\* "Pogg. Ann.," 1882, 561.

† "Ber. Deut. Chem. Ges.," xv, 1931 b.

‡ Tilden and Shenstone, "Phil. Trans.," 1884, I, 23.

§ "Comp. Rend.," 79, 167.

|| De Coppet, "Ber. Deut. Chem. Ges.," xii, 248, and Pickering, "Jour. Chem. Soc.," 1884, 689.

because I was then unaware of the existence of the allotropic modifications of anhydrous sulphate of sodium since discovered by Mr. Pickering (*loc. cit.*), and partly from errors of experiments, which have since been corrected.

The apparatus I have used consists of two parts, the calorimeter and the constant temperature bath. The calorimeter is a brass drum 9 cm. high and 7 cm. diameter, having a paddle which works in a socket in the centre of the vessel, and the spindle of which passes through the lid. At the top of the spindle is a reel, round which passes a silk cord, the ends of which are weighted and drawn over pulleys placed at a little distance on opposite sides. By gently pulling the cord at either end the paddle is made to spin round. Immediately above the blades of the paddle is a wide brass tube perforated with holes, and the bottom of which is immersed in the water, which is placed in the calorimeter. In this tube is placed a thin glass bulb containing the weighed quantity of salt and sealed at the blowpipe. Standing in the tube is a thin brass rod having a fork at the end to act as pulveriser, the top which projects through the lid of the calorimeter, being provided with a wooden handle. The thermometer stands in a perforated tube on the opposite side of the calorimeter. The cover of the calorimeter is provided with three holes, one for the stem of the thermometer, one in the centre for the paddle, and the third for the handle of the pulveriser. The vessel is supported on three sharp boxwood points within a covered brass case silvered inside, the space between the calorimeter and the case being about 1 cm. all round.

The bath employed for maintaining a constant temperature is practically identical with that described by Nicol,\* but is provided with a well in the middle, into which fits closely the outer case of the calorimeter. The temperature of the water or oil is remarkably constant, and when the temperature does not exceed  $30^{\circ}$  a thermometer in different parts of the bath does not vary by more than  $\cdot 05^{\circ}$ . To assist in maintaining this constancy the bath is covered closely, and is enveloped in thick felt. Three thermometers were used—A, from  $8^{\circ}$  to  $26^{\circ}$  C., divided into twentieths; B, from  $25^{\circ}$  to  $50^{\circ}$ , and C, from  $42^{\circ}$  to  $76^{\circ}$ , both divided into tenths Centigrade, and the temperature could easily be read to  $\cdot 005^{\circ}$  and  $\cdot 01^{\circ}$  respectively, or even half this.

The course of an experiment is as follows:—The water having been introduced into the calorimeter, and the thermometer inserted into its tube, the whole is placed in an oven until the thermometer indicates a temperature about half a degree above that to which the bath has been previously heated. The calorimeter is then put into the bath, the cover of the case is put on, and the thermometer read from time to time till the temperature is either quite stationary or is falling steadily at a rate which is recorded, and from which a correction can be intro-

\* "Phil. Mag.," 1883, 339.

duced into the observed result. The glass bulb is then broken, and the paddle gently worked by one person whilst another reads the thermometer by the telescope. In every case a definite interval (usually one or two minutes) is allowed to elapse before the final reading is taken, not only to allow time for solution, but for the alteration of temperature in the liquid to be imparted to the calorimeter. In those cases in which the calorimeter had been in the bath for some time at a rather high temperature, and there was reason to fear that slight loss had occurred by evaporation, the whole was weighed after the experiment was concluded, and a correction introduced accordingly. The amount thus lost never exceeded a gram or thereabouts, and as the thermal equivalent of the calorimeter and its contents amounted to 100 grams and upwards, the result is not appreciably affected.

In the accompanying tables the numbers contained in the column headed "Water equivalent of the calorimeter," include the values of the calorimeter, the glass bulb, the thermometer, and the solution, the specific heat of which is taken generally from Thomsen's numbers.

Three series of experiments were undertaken with sulphate of sodium, and the results are embodied in the three tables, A, B, and C.

For A the salt had been heated to redness, not to fusion, about a fortnight before.

For B the salt had been heated to redness one day before.

For C the precipitated salt had been dried at  $120^{\circ}$ .

These varieties were taken on account of the differences in the heat of dissolution of sulphate of sodium which have been observed by Mr. Pickering (*loc. cit.*).

Sodium Sulphate,  $\text{Na}_2\text{SO}_4$ , in 100 molecules of Water, or 142 parts in 1800 parts.

Weight of Salt used . . . . . 6·311 grams.

Weight of Water used . . . . . 80·000 „

Specific heat of Solution  $\text{Na}_2\text{SO}_4 \cdot 100\text{H}_2\text{O} = \cdot 927$ .

Number of expt.	Water equiv. calorim., &c.	Temperature.		Correction.	Total rise.	Molecular heat of dissolution.
		Before solution.	After solution.			
SERIES A.						
1	110·7	33·46	34·00	+ ·006	·546	1360
2	110·7	33·30	33·86	+ ·010	·570	1419
3	110·6	33·24	33·79	+ ·005	·555	1381
4	110·7	34·97	35·55	0	·580	1444
5	110·6	34·90	35·49	0	·590	1468
6	110·6	35·01	35·58	0	·570	1418
7	110·7	35·41	35·93	+ ·010	·530	1320
8	110·7	39·70	40·30	0	·600	1494
9	110·7	39·60	40·20	0	·600	1494
10	110·7	44·07	44·68	— ·010	·600	1494
SERIES B.						
11	110·7	31·19	31·70	0	·510	1270
12	110·6	31·50	32·01	0	·510	1269
13	110·7	44·28	44·98	— ·016	·684	1703
14	110·7	44·755	45·490	0	·735	1830
15	110·7	44·57	45·20	— ·01	·620	1544
16	110·7	45·01	45·71	+ ·009	·709	1766
17	110·6	63·51	64·30	+ ·022	·812	2020
18	110·7	67·80	68·69	0	·890	2216
SERIES C.						
19	110·7	31·60	32·06	0	·460	1146
20	110·6	31·54	32·00	0	·460	1146
21	110·7	45·00	45·55	0	·550	1369
22	110·8	44·98	45·50	+ ·006	·526	1311
23	110·7	60·10	60·84	+ ·01	·750	1869
24	110·7	64·20	64·94	+ ·01	·750	1869
25	110·6	64·20	64·96	+ ·052	·812	2020

## Mean Results.

No. in table.	Temp. approx.	Heat of dissolution.		
		A.	B.	C.
11, 12	31°	..	1270	
19, 20	32	..	..	1146
1, 2, 3	33	1387		
4, 5, 6, 7	35	1412		
8, 9	40	1494		
10A, 13B	44	1494	1703	
14, 15, 16B, 21, 22C	45	..	1713	1340
23	60	..	..	1869
17B, 24, 25C	64	..	2020	1945
18	68	..	2216	

From these figures it appears that although the manner in which the salt has been prepared influences the result very notably, yet in each series, comparing together the effects of dissolving the same kind of anhydrous sodium sulphate, the heat of dissolution increases progressively with rise of temperature. That this would be the case might be predicted by applying the principle originally indicated by Person,\* and since discussed by Berthelot† and by Thomsen,‡ and embodied in the general equation  $Q_T = Q_t + U - V$ , where  $Q_T$  and  $Q_t$  are the quantities of heat evolved in the act of solution at the temperatures  $T^\circ$  and  $t^\circ$ , and  $U$  represents the sum of the capacities for heat of the salt and the water, and  $V$  represents the capacity of the solution between the temperatures  $T^\circ$  and  $t^\circ$ .

The salt A must be regarded as being in the most stable condition of the three, and the following comparison of the numerical values of the thermal change observed and calculated, applies to the A series of experiments:—

$$U = (18n + C)(T - t).$$

$n$  is the number of water molecules.

$C$  is the molecular heat of the salt.

$$V = (18n + K)(T - t).$$

$$C = 32.2 \text{ (Kopp).}$$

$$18n + K = 1815 \text{ (Marignac).}$$

Take  $Q_t$  at  $34^\circ = 1400$ , which is the mean of numbers given above for  $33^\circ$  and  $35^\circ$ ,

\* "Ann. Chim. Phys." [3], xxxiii, 449.

† "Ann. Chim. Phys." [4], vi, 329.

‡ "Thermochemische Untersuchungen," I.

Then  $Q_T = 1503$  when  $T = 40^\circ$ .

= 1537 when  $T = 42^\circ$ .

= 1572 when  $T = 44^\circ$ .

From  $40^\circ$  to  $44^\circ$  observed 1494.

There is not much difference here, but the observed is less than the calculated number.

Carbonate of sodium was next examined on account of its close resemblance to sulphate of sodium in water of crystallisation, melting point, and solubility.

Sodium Carbonate,  $\text{Na}_2\text{CO}_3$ , in 100 molecules of Water, or 106 parts in 1800 parts by weight.

Weight of Salt used .. .. 5.005 grams.

Weight of Water used.. .. 85.0 „

Specific Heat of Solution  $\text{Na}_2\text{CO}_3.100\text{H}_2\text{O} = .933$ .

Number of expt.	Water equiv. calorim., &c.	Temperature.		Correction.	Total rise.	Molecular heat of dissolution.
		Before solution.	After solution.			
26	116.2	21.85	24.37	+ .075	2.595	6388
27	116.3	21.80	24.25	+ .058	2.508	6177
28	117.5	22.545	25.050	+ .1075	2.6125	6485
29	117.4	22.39	24.82	+ .079	2.509	6238
30	116.2	35.60	38.40	0	2.800	6887
31	116.2	35.28	38.08	0	2.800	6887
32	116.2	35.70	38.50	0	2.800	6887
33	116.3	38.18	40.90	+ .004	2.724	6708
34	116.3	38.97	41.60	+ .112	2.742	6753
35	116.1	43.55	46.30	+ .015	2.765	6785
36	116.3	50.40	53.16	+ .020	2.780	6846
37	115.1	55.25	58.08	0	2.790	6783
38	114.9	54.73	57.58	0	2.850	6923
39	116.1	54.60	57.50	- .002	2.898	7128
40	116.2	54.30	57.18	0	2.880	7067
41	115.1	56.00	58.875	0	2.875	7004

The carbonate of sodium used in these experiments had been heated to redness, but at times which varied from a few hours to several days before the experiment. Some of the irregularities in the numbers may be not improbably due to this circumstance. But the mean results show on the whole an increase in the heat of dissolution with rise of temperature.

Experiment number.	Approximate temperature.	Mean heat of dissolution.
26 to 29 .....	22° .....	6322
30 „ 33 .....	35—40° .....	6842
34 „ 35 .....	40—45° .....	6769
36 „ 41 .....	50—55° .....	6958

Calculated from the figure for 22° = 6322, taking  $C = 26.1$  (Kopp),  $18n + K = 1778$  (Thomson),  $T = 55^\circ$ .

$Q_T = 7909$ , which is much higher than 7128, the greatest observed value at 55—56°.

For the sake of comparison sulphate of potassium, which always crystallises without water, was taken with the following results:—

Potassium Sulphate,  $K_2SO_4$ , in 100 molecules of Water, or 174 parts in 1800 parts by weight.

Weight of Salt used .. .. 7.733 grams.

Weight of Water used.. .. 80.00 „

Specific Heat of Solution  $K_2SO_4.100H_2O = .8965$ .

Number of expt.	Water equiv. calorim., &c.	Temperature.		Correction.	Total fall.	Molecular heat of dissolution.
		Before solution.	After solution.			
43	110.4	15.23	13.015	— .004	2.211	5494
44	110.3	15.02	13.02	+ .03	2.03	5037
45	110.4	15.105	13.050	+ .100	2.155	5348
46	110.3	15.70	13.52	+ .03	2.21	5472
47	109.4	23.665	21.560	— .006	2.099	5166
48	109.4	23.90	21.78	0	2.12	5219
49	109.3	36.86	34.93	— .006	1.924	4720
50	109.4	37.60	35.53	— .01	2.06	5073
51	109.3	36.99	35.00	— .008	1.982	4865
52	109.3	45.00	43.13	+ .075	1.945	4782
53	109.3	45.06	43.20	+ .046	1.906	4678

Approximate temperature.	Mean heat of dissolution.
15° .....	—5338
24 .....	—5192
37 .....	—4886
45 .....	—4730

Take  $Q_t$  at 15° = —5338.

$C = 34.1$  (Kopp) and  $18n + K = 1781$  (Marignac).

$T = 45^\circ$ .

$Q_T = -3745$ . Observed —4730. Difference, 985.



In the solution of anhydrous carbonate and sulphate of sodium in water, evolution of heat occurs, and the amount of heat evolved increases with the temperature, but is not so great as would be inferred from the application of Person's formula. On the other hand, sulphate of potassium, the solution of which is attended by absorption of heat, gives a gradually diminishing absorption as the temperature is raised, but the observed absorption is greater at the higher temperature than the calculated amount. That is to say, in all these cases, whether the act of solution is attended by rise or fall of temperature, there is a consumption of energy corresponding to an absorption of heat, which is not accounted for by the difference between the specific heats of the materials, and of the solution which results from their union.

From the connexion already established between fusibility and solubility,\* and from *à priori* considerations, it seemed probable that the thermal change attending the solution of a solid must vary according as by raising the temperature the cohesion of the solid is diminished, or by lowering the temperature the cohesion is increased. For if a salt dissolves in water with absorption of heat, this absorption will be less at higher temperatures when the cohesion of the solid has been reduced, and therefore the energy required for its liquefaction by the solvent also lessened. On the other hand, if a salt dissolves with evolution of heat, the heat evolved must be greater at higher temperatures for the same reason.

Some very fusible salts were therefore taken in order to ascertain whether the difference between the observed and calculated heats of solution was notably greater or less than the difference observed in the case of the sodium carbonate and sulphate and potassium sulphates.

\* Carnelley, "Phil. Mag.," March, 1882 Tilden ; and Shenstone, "Phil. Trans.," 1884, I ; Tilden, "J. Chem. Soc.," July, 1884.

Potassium Nitrate,  $\text{KNO}_3$ , in 100 molecules of Water, or 101.1 parts in 1800 parts by weight.

Weight of Salt used .. .. 4.774 grams.

Weight of Water used .. .. 85 „

Specific Heat of Solution  $\text{KNO}_3.100\text{H}_2\text{O} = .942$ .

Number of expt.	Water equiv. calorim., &c.	Temperature.		Correction.	Total fall.	Molecular heat of dissolution.
		Before solution.	After solution.			
54	116.8	15.55	12.30	0	3.25	8028
55	116.7	15.50	12.30	0	3.20	7906
56	116.7	34.42	31.30	0	3.12	7703
57	116.7	34.61	31.39	-.006	3.214	7926
58	116.7	52.72	49.60	-.015	3.105	7662
59	116.7	53.88	50.87	-.004	3.006	7421

Mean.

Approximate temperature.	Heat of dissolution.
15° .....	-7967
34 .....	-7814
53 .....	-7541

From the values  $C=23.2$  (Kopp),  $18n+K=1791$  (Thomsen), and  $Q_t=-7967$  at  $15^\circ$ ,  $Q_T=-6751$  when  $T=53^\circ$ .

Sodium Nitrate,  $\text{NaNO}_3$ , in 100 molecules of Water, or 85 parts in 1830 parts by weight.

Weight of Salt used .. .. 4.013 grams.

Weight of Water used .. .. 85.0 „

Specific Heat of Solution  $\text{NaNO}_3.100\text{H}_2\text{O} = .950$ .

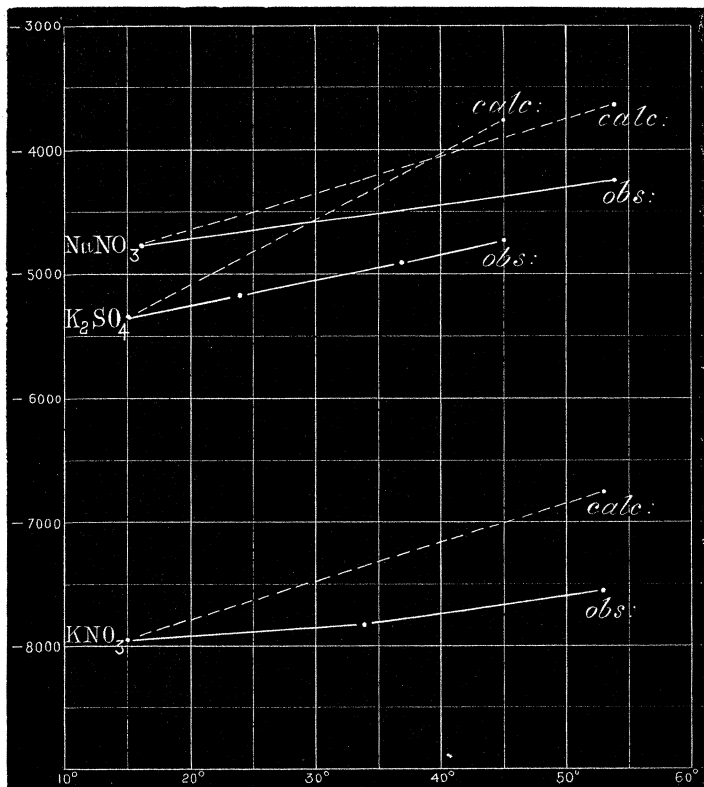
Number of expt.	Water equiv. calorim., &c.	Temperature.		Correction.	Total fall.	Molecular heat of dissolution.
		Before solution.	After solution.			
60	116.8	16.30	14.36	-.003	1.937	4776
61	116.8	16.05	14.15	+ .040	1.940	4796
62	116.8	54.42	52.67	-.004	1.746	4306
63	116.8	54.80	53.09	-.002	1.708	4204

Mean.

Temperature.	Heat of dissolution.
16° .....	-4786
54 .....	-4255

Calculated from the values  $C=21.8$  (Kopp),  $18nK=1791$  (Thomsen), and taking  $Q_t=-4786$  at  $16^\circ$ ,  $Q_t=-3616$  when  $T$  is  $54^\circ$ .

The observed and calculated numbers for potassium sulphate and nitrate and sodium nitrate are plotted out in the diagram below, where it is manifest that there is a difference between the two nitrates and the much less fusible and soluble sulphate. For tracing up the abscissa for  $45^\circ$ , we see that the difference between the observed and calculated numbers for potassium sulphate amounts to upwards of 900 calories, whilst the corresponding difference in nitrate of sodium is only about 500, and in nitrate of potassium about 700.



Experiments published in 1873 by Winkelmann,\* on the solution of the potassium, sodium, and ammonium chlorides and nitrates in water at different temperatures lead to similar conclusions. Thus taking Winkelmann's figure representing the heat of dissolution of nitrate of sodium, 1 gram of salt in 20·80 grams of water, which is very nearly 1 mol. of salt to 100 mols. of water—

At 2—3° gives as a mean  $-60\cdot30$  cal.

At 50—51° „ „ „  $-48\cdot70$  „

For a molecule of salt, or 85 grams—

$$60\cdot3 \times 85 = 5125\cdot5$$

$$48\cdot7 \times 85 = 4139\cdot5.$$

By the formula—

$$Q_T = Q_t + [(18n + C) - (18n + K)](T - t),$$

and using the values already given for sodium nitrate,

$$Q_T = -3646\cdot6,$$

and this is very nearly identical with the number calculated from my own experiment at 16°.

I have made a few determinations of heat of solution of the crystallised sulphate and carbonate of sodium. Whilst these salts dissolve at common temperatures, with great absorption of heat, the absorption at the melting point is very feeble, and at a few degrees higher is changed into evolution of heat. This last-named effect is probably due to the fact that when heated beyond their melting point, 34° (*circa*), these salts are partly deposited in a solid dehydrated state.

\* "Pogg. Annalen," cxlix, 1. Winkelmann's experiments were directed towards the object of determining the specific heat of the solutions of these six salts. One difficulty in the way of the general application of this method is the uncertainty attaching to the specific heats of the salts in the solid state, by reason of the variability of their properties according to the manner in which they have been prepared.

Sodium Sulphate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in 190 molecules of Water, or 322 parts by weight in 3420 parts of Water.

Weight of Salt used .. .. 8·05 grams.

Weight of Water used.. .. 85·5

Specific Heat of Solution  $\text{Na}_2\text{SO}_4 \cdot 200\text{H}_2\text{O} = \cdot 955$ .

Water equiv. calorim., &c.	Temperature.		Correction.	Total change.	Molecular heat of dissolution.	Mean.
	Before solution.	After solution.				
121·4	16·390	12·945	+·255	-3·700	-17939	-18035*
121·1	16·250	12·800	+·300	-3·750	-18131	
121·4	34·180	34·040	-·04	-0·136	- 660	
121·3	48·150	48·200	-·004	+0·046	+ 223	

Sodium Carbonate,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , in 180 molecules, or 286 parts in 3240 parts by weight of Water.

Weight of Salt used .. .. 7·150 grams.

Weight of Water used.. .. 81·00 „

Specific Heat of Solution  $\text{NaCO}_3 \cdot 190\text{H}_2\text{O} = \cdot 950$  approximately.

Water equiv. calorim., &c.	Temperature.		Correction.	Total change.	Molecular heat of dissolution.	Mean.
	Before solution.	After solution.				
117·3	15·025	12·020	+·1312	-3·1362	-14714	-14714
116·1	34·820	34·500	-·014	·306	- 1405 }	
116·1	34·300	34·050	+·005	·255	- 1171 }	- 1288
116·1	39·390	39·300	+·0075	·0975	- 446 }	
116·1	47·710	47·690	0	·020	- 91	- 91
116·1	48·040	48·100	0	+0·062	+ 275 }	+ 311
116·1	48·230	48·300	-·005	·075	+ 347 }	

The very rapid decline in the heat absorption attending the solution of these two salts cannot be accounted for by Person's principle, whatever value be considered probable for the specific heat of the solid salt.

The process of dissolving a solid in a liquid must be considered as involving several distinct operations. Person seems to have been the first to point out that the change of state from solid to liquid must

\* Thomsen's figure at 18° is -18509.

be distinguished from the intermixture of the liquefied solid with the water. Both these acts must be attended by heat-absorption. The dilution of watery solutions has been shown, especially by the researches of Thomsen, to be attended very generally by absorption of heat, notwithstanding that in most cases it is accompanied by contraction of volume, a process which must have an opposite effect.

In the solution of many anhydrous and even hydrated salts, we must believe, from the very energetic thermal change observed, that the salt enters into chemical union with a portion of the liquid. The extent to which this combination occurs will be greatly influenced by the temperature at which the experiment is made, and at sufficiently elevated temperatures it must be believed to be entirely annulled, whilst on the other hand, as the temperature is raised, chemical action, resulting in double decomposition between the water and constituents of the salt, becomes apparent. This action, which is manifested in the case of the salts of the heavy metals by the production of insoluble oxides, hydroxides, or basic salts, cannot be supposed to be altogether without effect in the case of the salts of the alkali metals such as I have been examining, and I incline strongly to the belief that a part of the difference which I have pointed out between the observed heat of solution and the same calculated according to Person's formula, is due to this decomposing action of the water.

It is manifest that no theory of solution can be accepted which does not take cognisance of all these facts.

In conclusion, I desire to acknowledge the intelligent assistance I have received in the conduct of these experiments from Mr. Harold P. White.

## V. "On Radiant Matter Spectroscopy. Part II. Samarium."

By WILLIAM CROOKES, F.R.S. Received May 21, 1885.

(Abstract.)

In the concluding sentence of the Bakerian Lecture which I had the honour to deliver before the Royal Society, May 31st, 1883, I said that the new method of Radiant Matter Spectroscopy there described had not only given me spectrum indications of the presence of yttrium as an almost invariable, though very minute, constituent of a large number of minerals, but had likewise revealed signs of another spectrum-yielding element. I stated that I had repeatedly seen indications of another very beautiful spectrum characterised by a strong red and a double orange band.

