II. *On the Solubility of Salts in Water at High Temperatures.*

By WILLIAM A. TILDEN, *D.Sc. Lond., F.R.S.; Professor of Chemistry in the Mason Science College, Birmingham, and* W. A. SHENSTONE, *F.I.C., F.C.S., Lecturer on Chemistry in Clifton College, Bristol.*

Received June 19,—Read June 21, 1883.

[PLATES 1, 2.]

THE experiments of which an account is given in the following paper originated in a desire to investigate further the remarkable anomalies which have been observed in the solubility of sulphate of sodium in water. It appears to have been first discovered by GAY LUSSAC (Ann. Chim. Phys., xi., 313) that whilst the solubility of this salt in water increases rapidly with rise of temperature above zero, it attains a maximum at 33° or thereabouts, and above that temperature diminishes till the boiling point (about 103°) of the saturated solution is reached.

On referring, however, to the curve of solubility for this salt traced by GAY LUSSAC, or to the numbers published many years afterwards by LÖWEL (Ann. Chim. Phys. [3], xlix., 32), it will be seen that the rate of decrease of solubility, though at first rapid, soon slackens, and the descending curve becomes nearly parallel with the axis of the abscissæ representing temperatures. It appeared probable that if the solubility of sulphate of sodium could be traced through a range of higher temperatures, the solubility would be found once more to increase, and the curve resume an upward direction.

It was not possible, however, to undertake the investigation of an isolated case of this kind without extending the inquiry to the phenomena of solution in general, and we have thus been led to consider several questions, which were not immediately involved in the subject of our first experiments. One important point which our experiments illustrate is the relation, hitherto assumed rather than determined, between fusibility and solubility.

In our earlier experiments the ordinary crystallised sulphate of sodium containing ten molecules of water of crystallisation was enclosed together with a suitable quantity of water in glass tubes, either bent in the middle to an angle of 130°–140°, or straight and divided midway by a strainer of fine platinum wire gauze.

In either case the materials were placed at one end of the tube, which was held in an inclined position within an air bath, with double walls, and provided with a

The Royal Society is collaborating with JSTOR to digitize, preserve, and extend access to *Philosophical Transactions of the Royal Society of London.* www.jstor.org

thermometer at each end, and a thermostat. The tube and its contents were then exposed to the desired temperature for a considerable time, usually about four-and-a-half to five hours, so as to ensure complete saturation. By then gradually tilting the air bath, which was slung upon suitable supports, the solution was caused to drain away from the undissolved residue of the salt, and the whole was then allowed to cool. Finally the tube was cut open, the end containing the solution was weighed, and, after removing the solution to a tared dish, was reweighed. The solution was then evaporated to dryness with due precautions, and the weight of the dry residue determined. From the data so obtained the proportion of anhydrous salt to water in the solution was calculated.

Throughout these operations two tubes were invariably employed in each experiment, and two determinations thus made simultaneously. The mean of the results was taken. Preliminary experiments were also made which indicated that by a proper disposition of the four BUNSEN burners used as the source of heat, and the employment of the mercurial gas regulator, the temperature of the air bath could be maintained within a range of $\pm$ 2° for many hours. We also satisfied ourselves of the efficiency of the platinum gauze strainers, by frequently examining the decanted solution whilst still warm and liquid. It may also be added that the salts operated upon were pure and were almost always specially prepared in the form of agglomerated masses of small crystals, with the object alike of exposing a greater surface to the action of the solvent, and of allowing the solution to flow away freely when the tube was reversed.

The employment of bent glass tubes was soon abandoned, owing to the difficulty of keeping both ends of the tube at precisely the same temperature, also in consideration of the greater risk of bursting to which they were liable. The employment of tubes of glass under any form is, in the case of sulphate of sodium, undesirable, as we find that this salt has the power of attacking glass at high temperatures in an unexpected degree. Consequently, although we succeeded in satisfying ourselves that the solubility of sodium sulphate in water at temperatures above the normal boiling point of the solution does increase in the manner we anticipated, the numerical results of the successive experiments were not sufficiently concordant to show clearly the form of the continuation of GAY LUSSAC'S curve. It therefore became necessary to employ tubes of metal, and of a somewhat different construction.

In arranging the experiments, which were afterwards extended to many other metallic salts, the following considerations had to be taken into account :—

1. It is necessary to allow the solution to drain away completely from the undissolved residue of salt before allowing the tube to cool; otherwise a part of the dissolved salt may be deposited, and the solution collected for analysis would be weaker than it should be. Provision is made against this source of error in the metal tube we have used in the later experiments.

2. If the two extremities of the tube are not kept at absolutely equal temperatures,

distillation of water from one part to another will take place. A paraffin bath appeared to offer greater probability of uniformity than an air bath, and was consequently employed in most of the best experiments.*

3. Further, it is obvious that the part of the tube not occupied by salt and solution must be filled with vapour of water, which, on cooling, will condense to the liquid state, and mix partly with the undissolved residue and partly with the solidified solution which has been drained away. Unfortunately, too, this circumstance is complicated by the fact that the tension of such water vapour is not that which would be given by pure water, but is the smaller tension given by the saline solution contained within the tube.

By ascertaining the volume of this vapour, approximate correction of the results can be effected with the aid of the tables of vapour tension of salt solutions, published by WÜLLNER (POGGEND. Ann., ciii., 529; cx., 564).

In any case the error on this account could not be great, but we nevertheless thought it advisable to make a few experiments with the object of testing directly its probable magnitude.

A number of bent glass tubes containing crystals of sodium sulphate, $Na_2SO_4.10H_2O$, in one limb, were sealed up and heated in a paraffin bath to temperatures ranging from 115° to 150°, the experiment being conducted in all respects as if a solubility were to be determined, except that the solution was not decanted. They were then allowed to cool, cut in two at the bend, and the end remote from the salt was at once closed by a stopper and weighed. It was then dried and re-weighed. Subsequently its capacity was ascertained. The following were the results:—

Experiment.	Weight of Water.		Difference.
No.	Calculated.	Found.	
	grm.	grm.	grm.
1	·0103	·0153	+·0050
2	·0102	·0116	+·0014
3	·0141	·0129	−·0012
4	·0067	·0061	−·0006
5	·0151	·0137	−·0014
6	·0106	·0173	+·0067

As the quantity of solution dealt with was never less than 4 grms., and was generally about 8 grms., it is obvious that the greatest error to be expected on account of occasional slight distillation from inequality of temperature, or on account of the water vapour always present, is inappreciable. When the metal tube is used the error is still less, because its greater mass and superior conducting power are favourable to the maintenance of a constant temperature.

Attempts were made to employ a metal tube provided with valves of various kinds,

* The bath was in fact carefully tested, and the constancy of its temperature ascertained.

arranged so that after draining the solution from the residual crystals it was shut off in a portion of the tube of known capacity, further entrance or escape of vapour being prevented, the risk of an impoverished solution continuing to drain into it during cooling being also done away with. But though we were successful in getting such a tube constructed, the difficulty of working it and of keeping it in working order, led us to abandon it in favour of a simpler form.

4. The influence of pressure.—Mr. SORBY's experiments (Proc. Roy. Soc., xii., 538) show that pressure exerts an influence upon the solubility of salts in water, but the effect due to the pressure existing at high temperatures in our tubes is too small to affect materially these estimations of solubility. In our experiments, with only two or three exceptions, the pressure of the vapour in the tube could never have exceeded some 10 or 12 atmospheres.

5. The choice of salts at our disposal is more limited than might be expected.—In some cases the solubility becomes so great at temperatures above 100°, that quantitative experiments were found to be impracticable. In others, as may be supposed, water at high temperatures decomposes the salts with formation of precipitates, or other signs of chemical change.

In one case, namely, chloride of barium, the crystals of the salt fall to a powder, from which it was found impossible to withdraw the solution.

6. We intended originally to have made a much larger number of determinations at temperatures above 200°, but it was not found practicable, partly in consequence of the difficulty of maintaining constant so high a temperature in the air bath (and paraffin could not be used), partly because the pressure at 250° and above becomes so considerable (amounting probably to about 30 atmospheres), that the lead washer in the joint of the metal tube was forced out, no matter how tightly the parts were screwed together.

The melting point of the most fusible salt tried (silver nitrate, m.p. 217°), is easily reached, but its solubility at temperatures far below this was so excessive that further determinations became impossible.

The apparatus finally adopted is represented (half-size) in Plate 1, figs. 1 and 2. The tube is made of gun metal, electroplated with silver all over. The two parts screw together at C. Each of the faces, *b*, *b*, *b′*, *b′*, has two circular grooves cut in it, an electroplated lead washer fits between these two faces, and when the proper amount of pressure is applied in screwing up, the lead is forced into these grooves. Plate 1, fig. 1 B, shows the end of B. It is hexagonal for convenience in screwing up. *a*, *a*, is a disk or screen of silver having a semicircular opening, *e*, cut through it. When the tube is closed, *a* does not quite touch *f*. By means of the handle *h*, the tube may be turned round its longitudinal axis in its support during an experiment, so that liquid may be free to flow from A to B through *e*, or not, as may be desired. In using the tube the materials are placed in A, a disk of platinum gauze is placed above at about *g*, and the two parts are screwed together very firmly. The tube is then placed

in an adjustable cradle (Plate 1, fig. 2), which consists of a stout beam of wood, B, supported by a horizontal rod of iron which passes through *o*, and serves as a pivot on which the beam can turn. Attached to the upper side of this beam is an index, which moves against the face of a semicircle of wood S, fixed rigidly to the rod on which B turns. The index can be pinned to the semicircle at the holes *h*, *h*, *h*, *h*, so that the beam can be inclined to the horizontal at any desired angle. The cradle of sheet copper, C, is supported by the wires *w*, *w*, and in this the tube lies.

The tube being in position in the cradle, with the end B slightly elevated, and the opening *e* in the screen downwards, the whole is lowered into a paraffin bath by lowering the rod which supports the beam, and which is itself fixed by an ordinary clamp to the upright of a large retort stand. After heating at a steady temperature for four-and-a-half or five hours, the end A of the tube is raised, and B depressed, very gradually, keeping the whole tube below the surface of the paraffin. When time has been allowed for the solution to drain away, the tube is turned half round its long axis by the handle *h*, so that the screen is interposed between the solution and the residual salt, and so liquid from the latter is prevented from continuing to drain into the former. The tube is then placed in a position more nearly horizontal, but still with the end A raised somewhat higher than B, which now contains the solution.

The cradle, with the tube, is then lifted from the bath, and allowed to cool in the air. When cold it is opened, the disk is removed, and a stopper placed in the mouth of B. After cleansing the outside of the tube by washing in benzoline, the tube and solution are weighed. Then the solution, which is usually in a solid or semi-solid state, having been removed to a tared dish for analysis, the dry tube is finally reweighed.

The capacity of B to the mouth was 16·4 cub. centims.

The results given below with sodium sulphate show that the process yields very satisfactory results. It necessitates, however, a good deal of trouble, and each experiment occupies more than a day.

In order that our results might be readily compared with the determinations made by other experimenters at lower temperatures, we have added many of these latter to the tables. The numbers are taken from the several original sources, and have been recalculated to show the weight of salt in 100 parts of water when not so given in the memoir referred to. In the curves which accompany the tables the results of other experimenters are put in dotted lines. We have also added at the head of each table the melting point of the salt. For these we have adopted the values obtained by Professor T. CARNELLEY (Jour. Chem. Soc., 1876, i., 489; 1878, i., 273), though in one or two cases, where data were not to be found, a rough determination of the melting point has been made by ourselves.

SOLUBILITY of sodium sulphate.—Melting point 860° C.

Observer.	Temperature.		Anhydrous salt Na_2SO_4 in 100 parts of water.
	°		
GAY LUSSAC (Ann. Chim.	0	..	5·02
Phys., xi., 312)	11·6	..	10·12
	13·3	..	11·74
	17·9	..	16·73
	25·0	..	28·10
	28·7	..	37·35
	30·7	..	43·05
	31·8	..	47·37
	32·7	..	50·65
LÖWEL (Ann. Chim. Phys.	33	..	50·76
[3], xlix., 42)	34	..	55·00
	40·1	..	48·78
	45·0	..	47·81
	50·4	..	46·82
	59·7	..	45·42
	70·6	..	44·35
	84·4	..	42·96
T. and S.	100·0	..	42·41
GAY LUSSAC	103·1	..	42·65
T. and S.	120	*a.* 41·9 *b.* 42·0	Mean 41·95 }
	140	*a.* 41·9 *b.* 42·1	„ 42·00 } In the
	160	*a.* 42·8 *b.* 43·0	„ 42·90 } metal
	180	*a.* 44·2 *b.* 44·3	„ 44·25 } tube.
	230		„ 46·40 }

In this table and curve (Plate 1), the results of LÖWEL between 33° and 34° are substituted for those of GAY LUSSAC, as being probably more correct. At 34°, or a fraction above, crystals of the ordinary salt with $10H_2O$ melt, and, if the experiment be conducted with due care, without separation of anhydrous salt. Such a liquid is a solution of 78·8 parts of Na_2SO_4 in 100 parts of water, and falls naturally into its place at the highest point of the curve.

The solubility of sodium sulphate at 100° was determined in several ways, in order to ascertain whether the mode of operating had any influence on the result.

(*a.*) By heating up crystals of the decahydrated salt, without addition of water, in a bath of constant temperature.

(*b.*) By dropping crystals of the same salt into water, heated and maintained at 100°.

(*c.*) By adding the anhydrous salt to water at 100°.

The result was the same in each case.

Reference to the curve will show that, as we anticipated, the solubility of sodium sulphate does increase again when the temperature is carried high enough.

The peculiarities of sodium sulphate in regard to its solubility have always formed an interesting problem, but we venture to think its interest is enhanced by this

discovery, because it seems impossible, by appeal to the commonly received theories of solution, to find a satisfactory explanation of all the facts of the case. If we admit that sodium sulphate, placed in contact with water at temperatures below 34°, dissolves in virtue of its power of entering into union with water to form liquid hydrates, the diminished solubility above that temperature must be due to dissociation of these hydrates, and production of the anhydrous salt, which is apparently much less soluble. What then is the cause of the much greater solubility of the ordinary crystals in which the salt is already united with a large quantity of water, and how can we explain the fact that the anhydrous salt increases in solubility in accordance with the common rule when the temperature is raised? The explanation appears to be found in the difference of fusibility of the two compounds, $Na_2SO_4 10H_2O$ melting at 34°, and Na_2SO_4, which melts at 860°.

There is nothing new in the idea that readiness to melt by heat is associated with disposition to dissolve by contact with liquid solvents, for even so far back as 1819 we find GAY LUSSAC quoting with approval a still older explanation given by LAVOISIER ('Traité Elem. de Chimie.,' ii., 39)* of the action of heat in causing increase of solubility. But we are not aware that it has been definitely brought to the test of experiment before.

Supposing a substance heated with a solvent to the melting point of the former, three cases might present themselves :—

(*a.*) The liquids might be miscible in all proportions.

This is true of sulphate of sodium at 34°. The melted salt, $Na_2SO_4 10H_2O$, may be mixed with an indefinitely small quantity of water, or in other words is infinitely soluble.

We have also ascertained that it is nearly true of benzoic acid, which melts at 120°. This compound is stated to be soluble in about 600 parts of water at 0°, in 200 parts at 18°, in 25 parts at 100°. By sealing it up with water in a glass tube and heating to a few degrees beyond the melting point, intermixture occurs in all proportions, and the liquid so obtained on cooling to 120°, or about 1° lower, becomes turbid from deposition of oily drops, which, however, immediately crystallise.

(*b.*) The solvent might become saturated and the excess of undissolved substance remain over in a liquid state.

(*c.*) Or both might become saturated, the one with the other, forming two distinct liquids.

This occurs in the case of phenol (carbolic acid) and certain of the fatty series of acids, besides other well-known substances.

Supposing either *b* or *c* to occur, the two liquids become miscible when the temperature is raised, as may easily be shown in either of the cases referred to.

But the connexion between fusibility and solubility, though proved, does not wholly explain the nature of the initial stage in the process of solution of a solid. It does,

* In the reprint of LAVOISIER'S works, vol. i., p. 305.

however, strongly support a kinetic theory of solution based on the mechanical theory of heat. The solution of a solid in a liquid would accordingly be analogous to the sublimation of such a solid into a gas, and proceeds from the intermixture of molecules detached from the solid with those of the surrounding liquid.

Such a process is promoted by rise of temperature, partly because the molecules of the still solid substance make longer excursions from their normal centre, partly because they are subjected to more violent encounter with the moving molecules of liquid. Such a view does not necessarily involve the assumption of an "attraction" between the molecules of the solvent and those of the solvend (compare Dossios, Jahresb., 1867, 92; and Nicol, Phil. Mag., Feb., 1883).

Indeed, it is difficult to disconnect "attraction" from the idea of combination resulting from such attraction. In some of the cases we are considering, as for instance the solution of anhydrous sulphate of sodium in water at 100°, nothing like combination between the water and salt seems to occur.

We have satisfied ourselves by direct experiment that anhydrous sulphate of sodium at the temperature of 100° dissolves in water at the same temperature without any sign of previous combination, and the solution so prepared contains exactly the same amount of solid as the solution made by gradually heating up a solution prepared at a lower temperature. But when anhydrous sulphate of sodium is introduced into water below 34°, all the phenomena of combination are manifested, and the salt sets into a solid crystalline mass previous to dissolving.

Whilst, therefore, we still think the act of hydration a factor in a great many cases of solution, it appears that it must be abandoned as a hypothesis of general applicability.

We now proceed to describe the results we have obtained with other salts.

Calcium sulphate.—Melting point a red heat.

Sullivan (Rep. Brit. Assoc., 1859, 292) states that he has proved this salt to be insoluble in water at 150°, but we can find no detail of any experiments of his. Cousté (Ann. des Mines [5], v., 140–144) describes experiments upon the solubility of calcium sulphate at high temperatures, but they appear to have been all made with sea-water, and there are many objections that might be raised to his mode of operating.

In our experiments pure precipitated calcium sulphate, which had been most thoroughly washed, was used and distilled water. Glass is rapidly attacked by the solution, and the determinations were therefore made in the silvered metal tube.

Observer.	Temperature.		Parts of $CaSO_4$ in 100 of water.
Poggiale (Ann. Chim. Phys. [3], viii., 469)	0°	..	·205
	20	..	·241
	35	..	·254
	70	..	·244
	100, &c.	..	·217, &c.
T. and S.	140	Exp. 1. ·080	
		„ 2. ·076	Mean ·078
		„ 3. ·080	
	160–165	„ 1. ·056	
		„ 2. ·056	„ ·056
	175–185	„ 1. ·024	
	178–183	„ 2. ·030	„ ·027
	240	..	·018
	250	..	·018

(See Plate 2.)

This curve is interesting as having considerable resemblance to that of sodium sulphate. Experiments at 250° were repeated, but without any indications that the solubility was about to increase, and this was the highest temperature at which we have been able to work. Calcium sulphate is much less fusible than sodium sulphate, and we could not therefore expect that a change would be observable in the direction of the curve, unless the temperature were carried much higher than we found it possible to go.

Potassium sulphate.—Melting-point ?.

Temperature.	Parts of K_2SO_4 in 100 parts of water.	
	Gay Lussac.	T. and S.
0°	8·3	..
12·7	10·5	..
16	..	9·76
20	..	10·30
28	..	12·59
36	..	13·28
39	..	14·21
49	16·9	..
59	..	17·39
63·9	19·2	..
98	..	23·91
101·5	26	..
120	..	26·5
143	..	28·8
170	..	32·9

(See Plate 1.)

These results give a curve which is nearly a straight line. Our figures are uniformly somewhat lower than those of Gay Lussac. Curves constructed with the

two sets of figures are nearly parallel. Hence we think it possible that the salt used by GAY LUSSAC may have been slightly acid. On the other hand, our own results at temperatures above 120° may be somewhat too low.

COPPER sulphate.

Temperature.	Parts of $CuSO_4$ in 100 parts of water.
120°	90·1
135	85·5
140	84·4
157	82·0
188	74·5

These results are of no value as showing the solubility of the salt, for at temperatures above 120° chemical action ensues, with production of a green basic sulphate. And even at 120° there is reason to suppose that decomposition has commenced, inasmuch as 90·1 is below the solubility that would be inferred from a consideration of the solubilities (see POGGIALE, Ann. Chim. Phys. [3], viii., 467) determined at lower temperatures.

SODIUM chloride.—Melting point 772°.

Temperature.	Parts of salt in 100 parts of water.
118°	39·8 } exp. made in the metal tube.
140	42·1 }
160	43·6 }
180	44·9 }

(See Plate 2).

Reference to the curve shows that the solubility increases at temperatures above 100° faster than below.

POTASSIUM chloride.—Melting point 734°.

Temperature.	Parts of salt in 100 parts of water.
125°	59·6 in metal tube.
133	69·3 } in glass tube.
144	70·8 }
175	75·2 }
180	77·5 in metal tube.

POTASSIUM bromide.—Melting point 699°.

Temperature.	Parts of salt in 100 parts of water.
140°	120·9 in metal tube.
181	145·6

POTASSIUM iodide.—Melting point 634°.

Temperature.	Parts of salt in 100 parts of water.
124°	233·9 } in glass tube.
133	249·3
144	264·6
175	310·4

(See Plate 2.)

These results, when expressed graphically, correspond in each case very nearly to a straight line. And when the four preceding salts are compared together they serve to illustrate very well the relation of solubility to fusibility. In Plate 2, iodide of potassium, the most easily fusible, is shown to be not only the most soluble at common temperatures, but its solubility increases at a more rapid rate than either of the others, which follow in succession.

POTASSIUM nitrate.—Melting point 339°.

Two determinations of the solubility of this salt were done at 125°. At this temperature 100 parts of water dissolved—

Exp. I. 495·9 parts of salt, KNO_3.
Exp. II. 492·7 „ „ „

From the great solubility of the salt at higher temperatures, and the peculiar viscosity of the solution, in consequence of which it was difficult to separate it from the solid, no determinations of any value could be obtained in the experiments made at 180° and thereabouts.

SILVER nitrate.—Melting point 217°.

Notwithstanding the extreme solubility of this compound, two pairs of concordant determinations were made.

Temperature.	Parts of salt dissolved in 100 parts of water.
125°	1622·5 } in glass tube.
133	1941·4

(See Plate 1.)

Beyond this temperature it was useless to attempt quantitative experiments, as we already have nearly 20 parts of salt dissolved in 1 part of water. It may be observed that this corresponds to rather more than two molecules of silver nitrate, $AgNO_3$, to one molecule of water. This, therefore, is an example of a solution in which it is difficult to conceive the existence of liquid hydrates. It must rather be regarded as melted silver nitrate mixed with a small quantity of water.

Potassium chlorate.—Melting point 359°.

Temperature.	Parts of salt in 100 parts of water.	
120°	73·7	in glass tube.
136	98·9	
160	148·0	
190	183·0	in metal tube.

(See Plate 2.)

Barium chlorate, $Ba(ClO_3)_2$.—Melting point of the anhydrous salt about 400°.

Temperature.	Parts of $Ba(ClO_3)_2$ dissolved by 100 parts of water.	
116°	195·5	in glass tube.
135	287·4	
146	365·6	
180	522·6	in metal tube.

(See Plate 2.)

This salt gave some trouble, partly on account of its considerable solubility, partly from the viscosity of the solution. No oxygen was found in any of the tubes after heating, but two tubes were split in a somewhat singular manner by the solution in process of solidification during cooling.

Potassium dichromate, $K_2Cr_2O_7$. —Melting point about 400°.

Temperature.	Parts of salt dissolved by 100 parts of water.	
117°	128·3	in glass tube.
129	153·8	
148	200·6	
180	262·7	

(See Plate 2.)

BARIUM acetate, $Ba(C_2H_3O_2)_2$.—Melting point of the anhydrous salt about 450°.

Temperature.	Anhydrous salt dissolved by 100 parts of water.	
°22	48·5	
40	76·5	
60	79·0	
110	79·3	in glass tube.
130	85·6	
136	91·9	
180	141·6	in metal tube.

(See Plate 2.)

This salt was examined chiefly because it had been represented as an example of solubility diminishing with rise of temperature. When these results are plotted out the curve does suggest a change of this kind, and it is possible that acetate of barium may resemble sulphate of sodium and sulphate of calcium in parting with its water of crystallisation when the solution is heated. It is known to yield crystals containing one molecule of water of crystallisation when deposited from a warm solution, or three molecules of water when crystallised by cooling a weaker solution. It is probable that the peculiarities of its solubility are connected with the fusibility of these hydrates respectively.

CALCIUM HYDRATE.

This compound is known to be less soluble in hot water than in cold water. We have made some experiments at temperatures above 100°, but as the solution seemed to attack the metal, and the quantity of liquid we could operate upon is but small, the results are of no quantitative value.

SUMMARY.

Altogether we have examined sixteen salts, whereof three, namely, barium chloride, copper sulphate, and calcium hydrate, gave no results at high temperatures for reasons already given. Barium acetate presents anomalies which cannot be explained without further inquiry. Sodium sulphate and calcium sulphate are salts which certainly exist in solution in two forms, that is, in chemical combination with water and in the anhydrous state.

The remaining ten salts, with one exception, barium chlorate, form crystals which, when deposited from solution at any ordinary temperatures, contain no water of crystallisation.

It is almost fair to infer, though of course it is not certain, that these salts do not combine with water when the temperature is raised, and therefore when in solution at high temperatures exist there in the anhydrous state.

Concerning these ten salts the following remark may be made. If we write them down in the order of their melting points, beginning with the most fusible, we do not indeed find that the figures expressing their solubilities follow the same order. Though it is true that one example of this may be seen in the iodide, bromide, and chloride of potassium, such a relation could hardly be expected to be general amongst the rest, differing as they do in composition and in other properties. But if their solubilities are compared at temperatures of 100° and above, we find that the *rate of increase of solubility follows the order of the melting points.* In other words the ratio of the solubility at, say, 180°, to the solubility at 100°, is greatest in the most easily fusible, whilst the rest follow in regular succession. This is shown in the following table.

Formula of salt.	Melting point.	Parts of salt* dissolved by 100 parts of water at				Ratio of VI. to IV.	Ratio of VI. to V.	Ratio of V. to IV.
		0°	100°	130°	180°			
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
$AgNO_3$	217°	121·9	830	1825	?	..	..	2·20
KNO_3	339	13·3	265	565	?	..	..	2·13
$KClO_3$	359	3·3	56·5	88·5	190	3·36	2·14	1·56
$K_2Cr_2O_7$	400	4·9	102	156	285	2·79	1·82	1·52
KI	634	130	204	243	327	1·60	1·34	1·19
KBr	699	53·4	102	118	143	1·40	1·21	1·15
KCl.	734	29·2	56·5	66	78	1·38	1·18	1.16
NaCl	772	35·5	36·6	40·3	44·9	1·23	1·11	1·10
Na_2SO_4	860	hydrates	hydrates	42·0	44·2	..	1·05	..
K_2SO_4 †	?	8·3	25	28	34	1·36	1·21	1·12

The only salt which does not fall strictly into order is potassium sulphate; but concerning this we are in doubt as to the melting point, and since it gave a good deal of trouble the determinations of solubility at the higher temperatures may not be quite exact. It is difficult to believe that the relation we have indicated is merely accidental.

* The solubility, when not the result of a direct experiment, is taken from the curve by interpolation.

† The melting point of potassium sulphate is doubtful. It is probably higher than that of sodium sulphate. According to CARNELLEY (*loc. cit.*) the potassium salts generally melt at temperatures above the melting points of the corresponding sodium salts. Thus:

$NaNO_3$, m.p. 316°,	KNO_3, m.p. 339°.
$NaClO_3$, m.p. 302°,	$KClO_3$, m.p. 359°.
NaI, m.p. 628°,	KI, m.p. 634°.
Na_2CO_3, m.p. 814°,	K_2CO_3, m.p. 834°.

On the other hand—

KCl, m.p. 734°,	NaCl, m.p. 772°.

Fig. 1 A

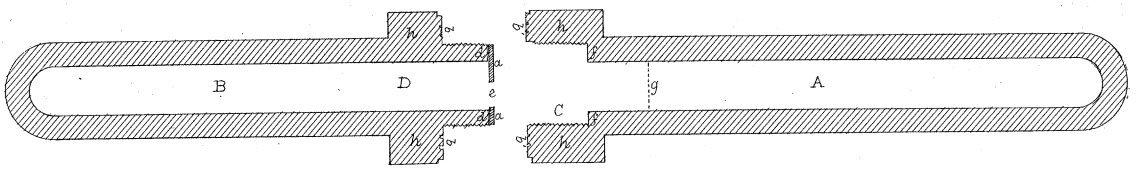


Fig. 1 B

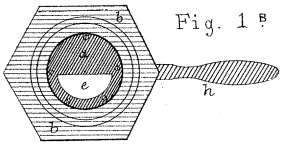
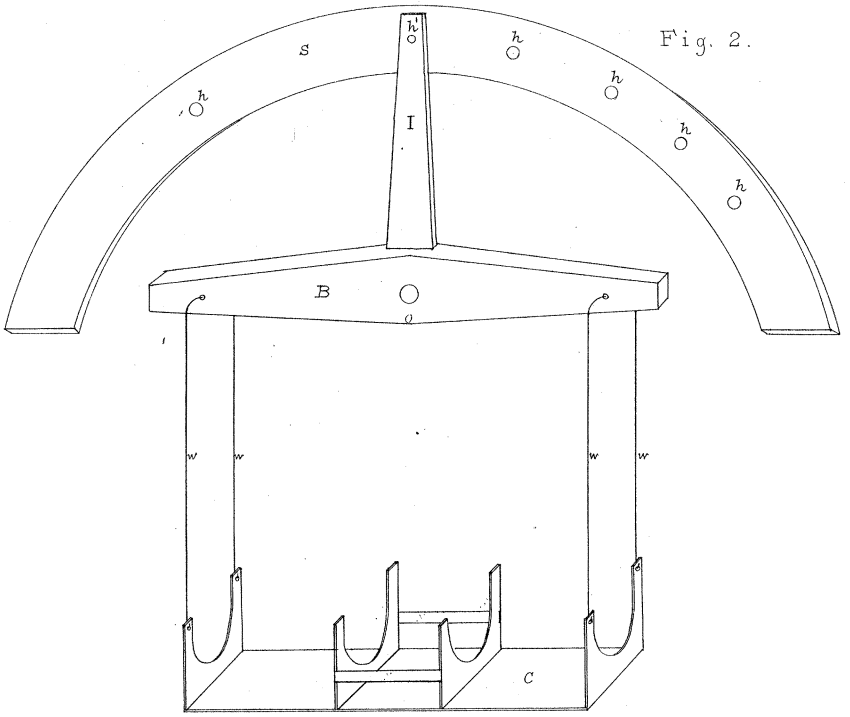
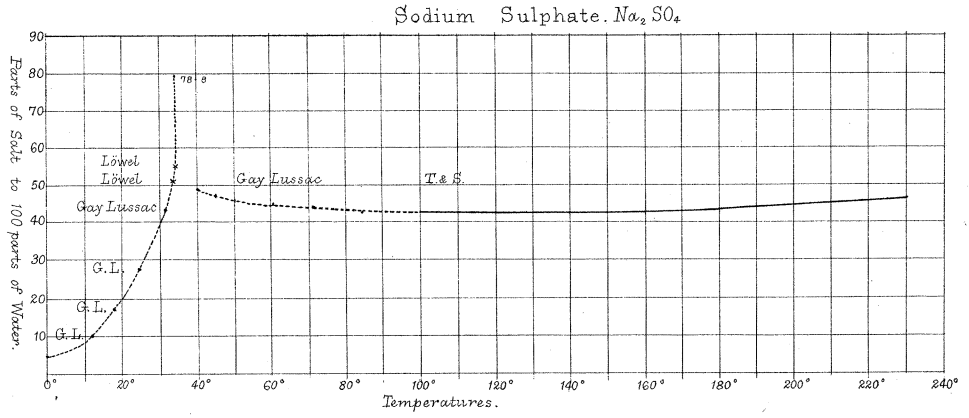
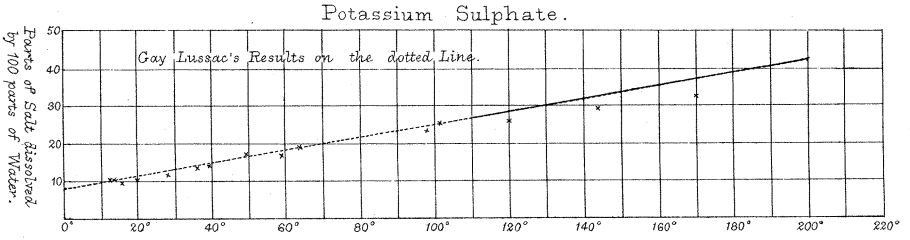
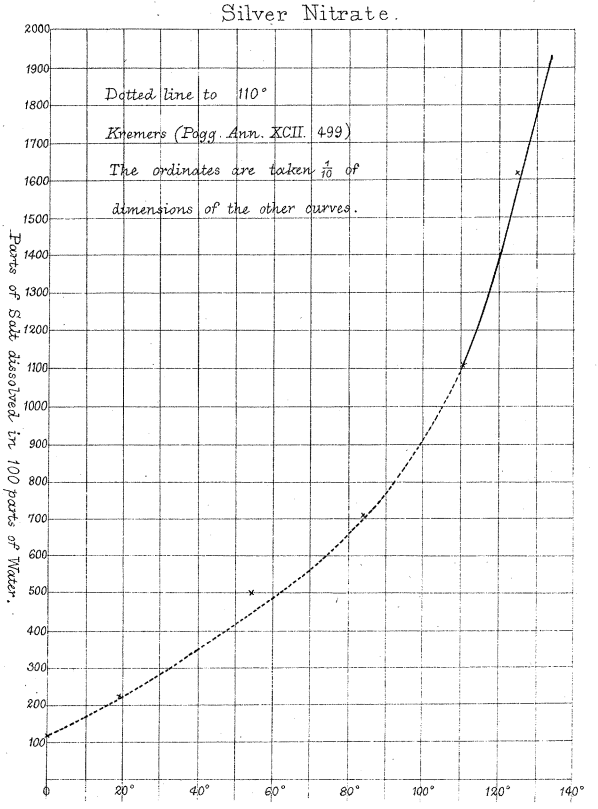


Fig. 2.

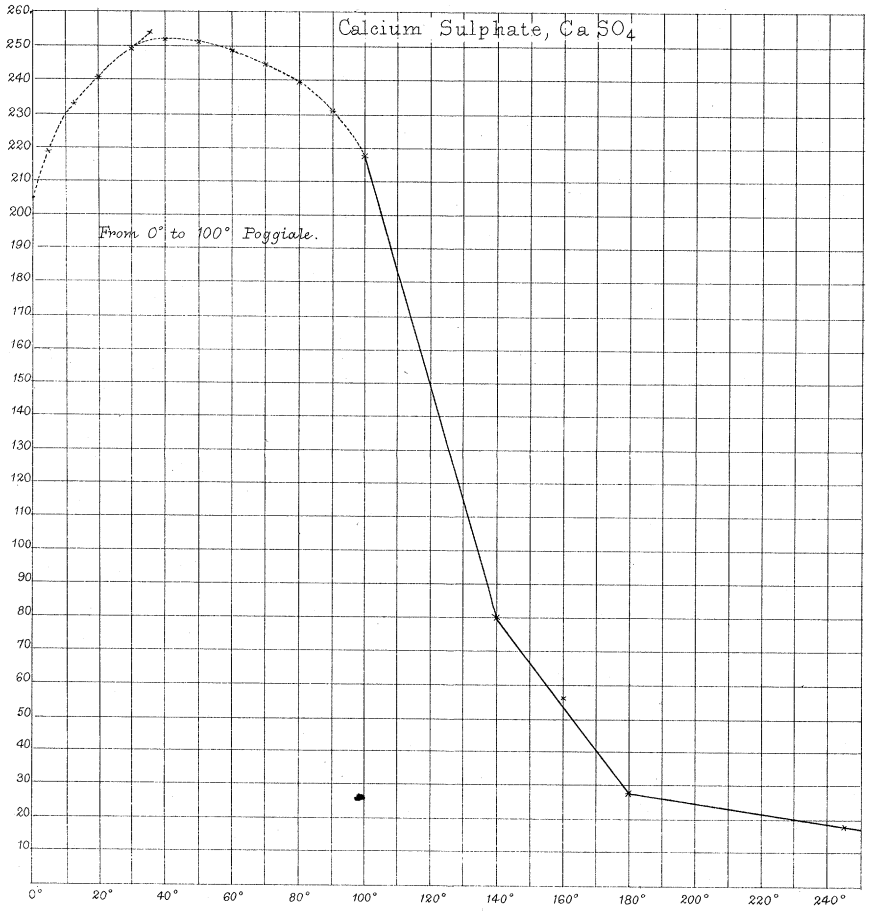


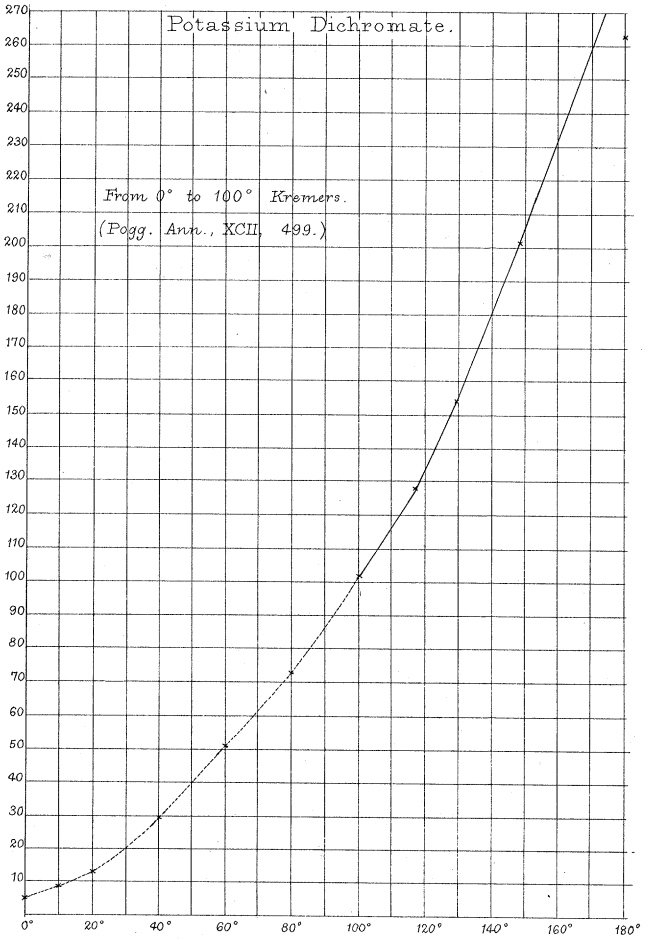


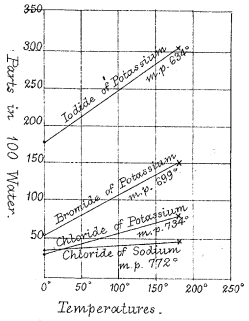


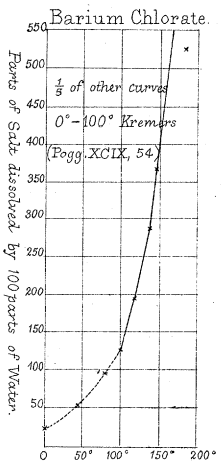


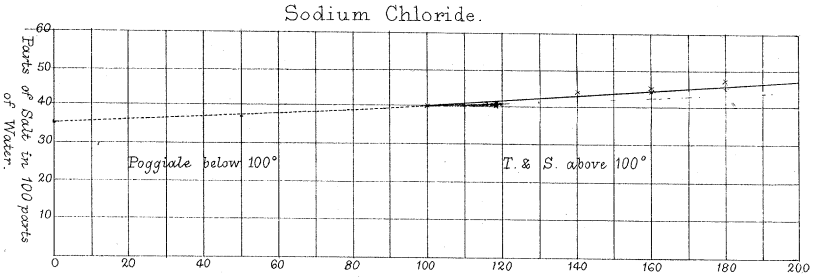
West Newman & Co lith.

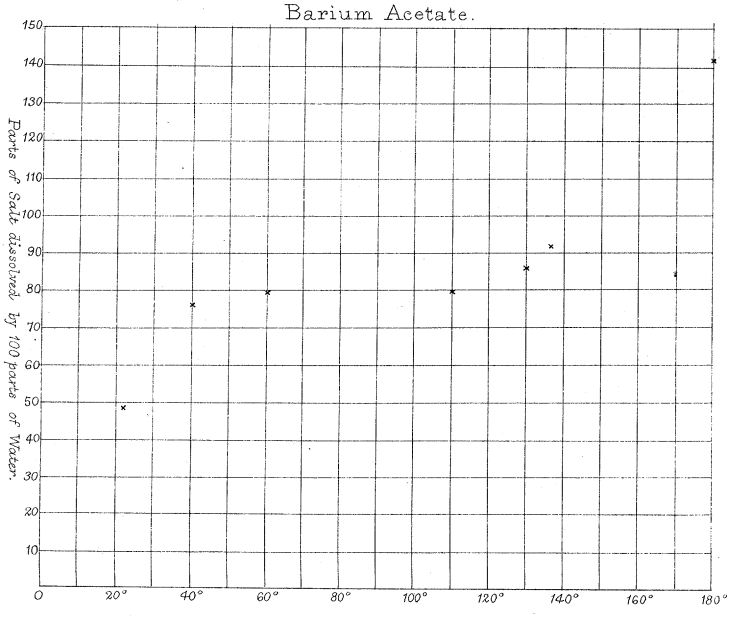


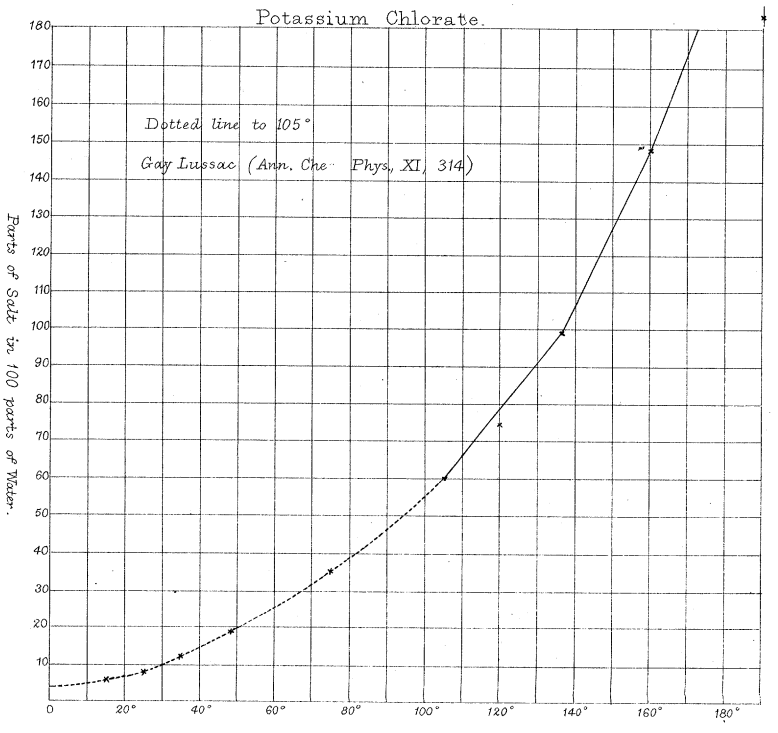












West Newman & Co lith.