On Some Physical Constants of Saturated Solutions

Earl of Berkeley

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VIII. *On some Physical Constants of Saturated Solutions.*

By the EARL OF BERKELEY.

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INTRODUCTION.

THE following work was undertaken with a view to obtaining data for the tentative application of VAN DER WAALS' equation to concentrated solutions. It is evidently probable that if the ordinary gas equation be applicable to dilute solutions, then that of VAN DER WAALS', or one of an analogous form, should apply to concentrated solutions—that is, to solutions having large osmotic pressures.

Saturated solutions were taken for investigation because they presumably have the greatest osmotic pressures, and also because there is reason to believe that, in concentrated solutions at a given temperature, the greater the concentration the less the relative dissociation. For the purpose in view, measurements of volume, pressure and temperature are required.

Volume.

This term of the equation is deducible from observations of the density of a saturated solution and of the solubility of the salt at varying temperatures. In Part I., I give the densities and solubilities obtained, together with a description of the methods and apparatus used.

Pressure.

I am at present engaged, with the collaboration of Mr. E. G. HARTLEY, in testing a method of directly observing large osmotic pressures. Should the method fail, I propose to determine the vapour pressures of the saturated solutions at different temperatures and from these calculate the corresponding osmotic pressures. The observations and details will be given in Part II.

Temperatures.

The temperatures at which the densities, solubilities and osmotic pressures were determined are given with those quantities respectively.

Part III. will be devoted to the application of the results to theory.

The selection of the particular salts whose solutions were examined was governed by the following considerations :—

(1.) Fairly soluble salts should be used, so that differences between the ordinary phenomena of dilute and those appertaining to concentrated solutions may be the more marked ;

(2.) They should have as wide a range of molecular weights as possible, so as to bring into prominence any effect the interacting masses may have on the space occupied by the molecules ;

(3.) For the purpose of comparing members of the same family of elements the salts should be isomorphous, the presumption being that isomorphous salts give similarly constructed molecules in solution.

PART I. (A).

Determination of the Constants.

The densities were obtained by the following method : An approximately saturated solution was kept in contact with crystals of the salt at a definite temperature by means of a thermostat, and continuously stirred. When a sufficient length of time had elapsed, a pyknometer, whose capacity was known, was immersed in the solution and filled to a mark, then washed and dried by means of pure alcohol, and weighed against a counterpoise which had been similarly washed and dried. The solubilities were determined by washing the contents of the pyknometers into platinum crucibles and weighing them after evaporating to dryness. It was found in the course of the work that, in the case of very soluble salts, this method was not satisfactory, because a crust of salt formed on top of the solution in the platinum crucible, and the accumulation of steam under it, on finding its way out, carried particles of solution with it. Glass bulbs, represented in fig. 1 and made of Jena glass, were therefore substituted for the platinum crucibles and the solution evaporated to dryness in them. This was effected by passing a current of dry air through the tubes while they were being heated to 110°–170° in an air oven, the air current and the

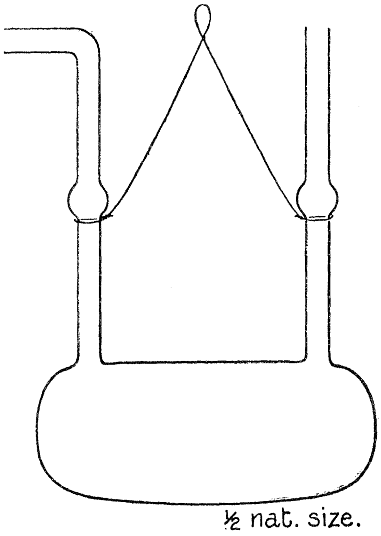

Fig. 1.

heating being continued until the bulbs had attained a constant weight. The air current was obtained by means of a Fleuss pump. The same filling of a pyknometer gave, therefore, both the density and the solubility. As a check on the latter, the contents of a pyknometer were occasionally analysed.

Pyknometers.

At first Sprengel pyknometers of various shapes and sizes were tried, but were found to be unsatisfactory. This was because it was almost impossible to prevent the solution from crystallizing in the capillary during the time the level of the liquid was being adjusted to the mark.

The following was the form finally adopted and found quite satisfactory. A pear-shaped bulb, of about 5 cub. centims. capacity, terminating above in a stem composed of a graduated capillary 120 millims. long, and below in a finer capillary, bent as in fig. 2, was used for salts of medium solubility. For somewhat insoluble salts a similar pyknometer, but of about 11 cub. centims. capacity, was found to be more suitable, while for very soluble salts, such as sodium sulphate, which have great differences in solubility at different temperatures, it was necessary to have similar pyknometers made of thicker glass, so that when the crystals formed and practically filled the whole of the bulb, the latter would withstand the pressure. It was also found necessary to make the capillaries of a larger internal diameter, so as to be able to fill quickly. And the shape of the lower capillary (see fig. 3) was altered and its end fitted with a glass cap to prevent the solution from "creeping" out when on the balance. The stem was also fitted with a cap to prevent evaporation.

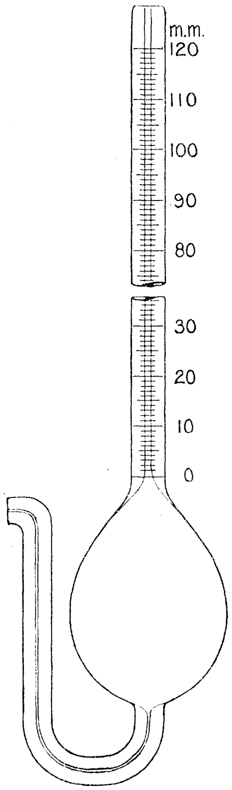

Fig. 2.

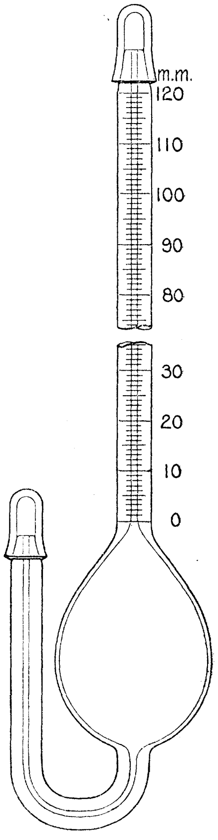

Fig. 3.

Determination of the Capacities of the Pyknometers.

Before determining the capacities, the pyknometers were heated rapidly and repeatedly to 200° C., being allowed to cool to the temperature of the room between each heating; by this means it was hoped that the gradual shrinking in volume would be accelerated. The graduated capillaries were then calibrated by the usual method of running a thread of mercury along the bore, measuring its length, and then weighing it.

The capacities were found by weighing the pyknometers filled with water at 0° C. and at 90° C. respectively; the volume occupied by the water was taken to be that given in Landolt and Börnstein's tables for water which is air-free. The difference between the capacities thus determined gave the expansion from 0° C. to 90° C., and for intermediate temperatures it was assumed to be proportional to the temperature interval; this assumption was tested with one of the pyknometers, and it was found that the resulting difference was within the experimental errors. With the 11 cub. centim. pyknometers, however, it was deemed advisable to examine the error more closely, and for this purpose the capacities were determined at five approximately equal intervals of temperature between 0° C. and 90° C. The numbers obtained were plotted against the corresponding temperatures, and a bent-ruler curve passed through the points; the capacities for intermediate temperatures were taken from it. The maximum difference between this curve and a line joining the penultimate observations represented a difference of ·0015 cub. centim. This is a quantity which is barely greater than the experimental errors, as will be seen from the following numbers obtained with one of the pyknometers:—

Temperature.	Capacity.	Temperature.	Capacity.	Temperature.	Capacity.	Temperature.	Capacity.	Temperature.	Capacity.
° C.	cub. centims.	° C.	cub. centims.	° C.	cub. centims.	° C.	cub. centims.	° C.	cub. centims.
91·85	11·4406	68·60	11·4321	45·40	11·4239	25·85	11·4181	0·70	11·4111
91·35	·4397	68·40	·4317	45·30	·4239	25·80	·4186	0·60	·4113
91·10	·4394	68·00	·4313	45·15	·4239	25·40	·4176	0·50	·4111
—	—	—	—	45·30*	·4238*	—	—	—	

On re-determining the capacities after an interval of several months no change was apparent.

As the table used for the expansion of water gives numbers derived from air-free water, and as the pyknometers had been filled with water which had not been freed from dissolved air, it was thought possible that an error had been introduced in this way; a pyknometer was therefore filled, in a vacuum, with water which had been boiled in that vacuum for three-quarters of an hour; it was then withdrawn and brought to a constant temperature in the thermostat and weighed in the usual manner. The results of three observations carried out thus did not differ from those obtained with ordinary water by more than the latter differed among themselves. Taking into consideration that the solutions themselves are not air-free, it was considered unnecessary to pursue the matter any further.

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* This observation was one made with air-free water.

In weighing the pyknometers care was always taken that they should be slung on the balance in such a way that the end of the lower capillary was at a higher level than the level of the liquid in the stem; this, as a rule, was sufficient to prevent any loss of weight by evaporation, but such observations as did show a loss were rejected.

Stirring.

The stirring was obtained by means of a small platinum rod, fitted with a two-bladed screw, suspended vertically in the solution, and rotated by a cord and a small electric motor. The speed of rotation could be varied from 2 to 20 revolutions per second. During the last two years of the course of this work the separate motors were replaced by a shafting driven by an electric motor; pulleys of various sizes were fixed on it and driving cords taken to the stirrers as required. This shafting also worked the Fleuss pump mentioned above.

Constant Temperatures.

At 0° C. the beaker containing the solution was surrounded by ice and water. At 15° C. it was placed in a copper vessel, in which was suspended a thermostat, and through which a current of cold water passed. The former actuated a gas burner and kept the temperature constant. From 30° C. to 90° C. the solution was placed in a platinum beaker of 300 cub. centims. capacity which formed part of a D'Arsonval thermostat. The platinum beaker (see fig. 4), having a flange welded on to it three-

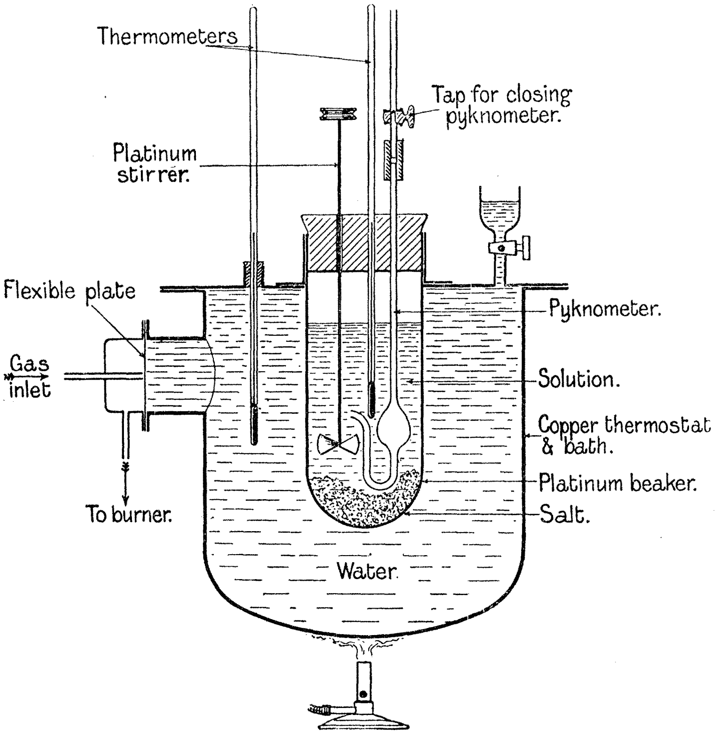

Fig. 4.

quarters of an inch from the top, was passed through the top plate of the thermostat and soldered in position. The body of the thermostat was of copper and held about three litres of water, and the expansion and contraction of this was enough to actuate the flexible diaphragm (the iron plate of the receiver of a telephone) sufficiently to keep the temperature of the thermostat constant to about 0°·2 C.; that is to say, that for 2 or 3 hours before taking an observation, the temperature in the beaker would only show, at the utmost, a change of 0°·05 C., but in the course of 24 hours after setting the temperature of the thermostat, and consequently that of the solution, might slowly rise or slowly fall to the extent mentioned, and then remain constant to 0°·05 C.

Means employed for Determining the Point of Saturation.

After numerous experiments the following general method was found to be the most satisfactory. The thermostat was set at 90° C., and water, together with a quantity of salt more than necessary to saturate it, placed in the platinum beaker, and the mixture stirred very rapidly until it was thought that saturation had been attained; an observation of the density was then made, and the stirring continued for a further period of 2 or 3 hours, and then another density determination made. If the two observations agreed within the experimental errors, it was considered that saturation had been practically reached; if the two observations did not agree, the stirring was continued and the density taken at intervals until it became constant. The temperature of the thermostat was then lowered 2 degrees, and after stirring 2 or 3 hours the density again taken. The mean of this and of the constant density previously mentioned was considered to be the density of a saturated solution at the mean of the respective temperatures. The temperature of the thermostat was then lowered to the next point of observation, and after 2 or 3 hours' stirring the density was taken; water was then added to the solution and the stirring continued until the density, taken at intervals of from 4 to 12 hours, was constant—the mean of the first and the last observations, which usually differed by an amount slightly greater than the experimental errors, was taken as giving the true density. The process was then repeated for the other temperatures. It should be noted that whether working with supersaturated or an unsaturated solution, the liquid is always stirred in contact with a large excess of solid salt.

In the case of salts whose solubilities decrease with an increase of temperature, the process is reversed; with Na_2SO_4, for example, which has a maximum solubility at 32°·5 C., the thermostat was set at 33° C., and stirring continued until constant density was obtained; the temperature was then raised 1° C. and the density again determined, and the mean of this and of the constant density above mentioned was taken as the true density of a solution saturated at the mean of the respective temperatures. The temperature of the thermostat was then raised to the next point of observation, the density taken, boiling water added and a constant density obtained, the numbers being "meaned" as before. The process was then continued for the next higher temperature, and so on. The object of adding boiling water is to make sure that the solution is unsaturated, for if cold water were added the temperature of the solution would fall, and if the rate of attaining saturation be greater than the rate at which the solution comes back to the constant temperature, you get a solution supersaturated with respect to that temperature.

It will therefore be seen that the method adopted resolves itself into this: at any given temperature, two observations of density and solubility are taken; one is obtained by stirring a supersaturated solution in contact with the solid salt, the other by stirring an unsaturated solution in contact with an excess of salt—and the true density or solubility is considered to be the mean of the two observations.

In the earlier part of this work it was found that, in many cases, a very long time elapsed before the densities obtained, when starting with an unsaturated solution, approached sufficiently closely to that derived by starting with a supersaturated one—this was partially remedied by increasing the speed of stirring from 2 to 20 revolutions per second—but even then there was generally a difference in the two densities of some few units in the 4th decimal place. The cause of this discrepancy was eventually traced to the fact that a considerable length of time was also required for the point of saturation to be attained by a supersaturated solution, even when stirred in contact with its salt. It was owing to this that some 300 density and solubility determinations had to be discarded—for preliminary observations had shown that concordant results could be obtained by merely covering the top of the beaker with a glass perforated for the stirrer to pass through, and removing the plate while the pyknometer was being filled. At the higher temperatures the removal of the plate caused a fall in the temperature of the solution and a consequent supersaturation. This, however, was not suspected (because when the results were plotted the curve was regular) until I was dealing with very soluble salts, which, on the removal of the plate, tended to form crusts of salt on the surface of the solution. The difficulty was overcome by closing the beaker by an india-rubber stopper, which was perforated for the stirrer, the thermometer, and the pyknometer. The latter was closed at the upper end by a tap attached by rubber tubing. The tap served two purposes: it was kept closed on immersing the pyknometer, so that no liquid could enter during the time that the pyknometer was attaining the temperature of the solution, and it was closed after filling the pyknometer, so that no liquid could flow back during the withdrawal of the rubber stopper.

As an extreme example of the necessity of giving an unsaturated solution plenty of time to attain saturation, and also as showing the importance of having a sufficiency of salt in contact with the solution, I extract the following numbers from my note-book. An unsaturated solution of thallium alum, together with a quantity of the salt, was placed in the beaker, which was at the constant temperature of 61°·0 C. This was stirred for 12 hours at the rate of 10 to 20 revolutions per second; at the end of this period the density was found to be 1·2539 (temperature 61°·00 C.). Having reason to believe, from previous work, that saturation had been reached, the temperature of the thermostat was lowered 1° C. and the solution stirred for another 3 hours; its density was then 1·2546 (temperature 59°·85 C.).

The next day it was 1·2555 (temperature 59°·90 C.).
,, ,, ,, 1·2572 (,, 60°·00 C.).
,, ,, ,, 1·2591 (,, 60°·00 C.).

Between each observation about 10 hours' continuous stirring was given to the solution, and all the time there had been about 5 cub. centims. of solid salt in contact with the solution; another 20 cub. centims. of salt was then added, and the stirring continued for 12 hours, with a resulting density 1·2810 (temperature 60°·00 C.). And a further 12 hours gave 1·2813 (temperature 60·00 C.).

On the other hand, the following shows the reverse phenomenon, *i.e.*, that a considerable time must elapse before a supersaturated solution attains its true point of saturation. A solution of Na_2SO_4, saturated at 60° C., was heated to the constant temperature of 75° C. (it must be remembered that Na_2SO_4 is more soluble at 60° C. than at 75° C.) and stirred at the rate of 13 revolutions per second in contact with the anhydrous salt for $3\frac{1}{2}$ hours; the density of the solution was found to be 1·2738 (temperature 75°·00 C.). The next day, after 12 hours' stirring, the density was 1·2729 (temperature 75°·00 C.); 20 cub. centims. of boiling water was then added (if cold water had been added, as before explained, the solution would have become supersaturated), and after 12 hours' stirring its density was 1·2727 (temperature 75°·00 C.).

Where it was suspected that the solutions, when at the higher temperatures, might decompose non-reversibly, the observations for the lower temperatures were first recorded, in the manner already outlined, and those for the higher temperatures were obtained by heating to the constant temperature required and stirring the solution until the density was constant; the temperature was then lowered by 1 or 2 degrees, and after a sufficient length of time the density again determined; the mean of this last observation, and of the constant density first obtained, was considered to be the density of a solution saturated at the mean of the corresponding temperatures.

The following are the important points to be observed in obtaining a saturated solution:—

(1) A sufficiency of solid salt should always be in contact with the solution;
(2) A thorough stirring should be continuously kept up;
(3) A sufficient length of time should be allowed to elapse before taking the required observation. This last condition seems to depend on the nature of the salt, the speed of stirring, and on the temperature.

I had hoped to have been able to determine both the rate of attainment of saturation, and the time at which it is attained, by observing the change in the electric conductivity of the solution while it is becoming saturated, and I have made a few somewhat unsatisfactory experiments on the method, but hope to be able to return to it shortly.

Measurement of Temperature.

Thermometers whose graduations were sufficiently open to allow of an estimation to 0°·01 C. were used. They were standardized at Kew, and the rise of the zero point was determined after an interval of 18 months. The rise of the zero point was assumed to be proportional to the elapsed time, and all observations are corrected on that assumption. Corrections were also applied for the emergent column by suspending an auxiliary thermometer half way up the exposed stem and calculating in the usual manner; in no case did this correction amount to more than 0°·37 C.

The temperatures given in the tables are corrected to the hydrogen scale of the Bureau International at Paris.

Experimental Errors.

On page 192 I have already given an example of the results obtained in determining the capacities, and it will be seen that the largest difference between any two observations at the same temperature is ·0012 cub. centim., which is roughly ·01 per cent. To give an idea of the order of accuracy of the observations of density and solubility, the actual figures obtained with NaCl are appended below. NaCl was selected because the differences between the two sets of densities are fairly typical, while, on account of the small change in the solubility of the salt, those between the solubilities, besides being typical, show the experimental errors without the necessity of correcting for small changes of temperature.

Starting supersaturated.			Starting unsaturated.		
Temperature.	Density.	Solubility.	Temperature.	Density.	Solubility.
° C.			° C.		
0·35	1·20900	35·75	0·35	1·20896	35·74
15·05	1·20209	35·83	15·35	1·20193	35·85
30·05	1·19556	36·22	30·05	1·19555	36·19
45·30	1·18908	36·62	45·50	1·18902	36·59
61·80	1·18221	37·30	61·60	1·18227	37·26
75·85	1·17644	37·86	75·45	1·17637	37·80
90·50	1·17009	38·53	91·25	1·16971	lost

The largest difference between two densities at the same temperature is ·00038 at 91° C., which, if the observation at 90°·5 C. be corrected to 91°·25 C., is reduced to a difference of ·00020, and this corresponds to an error of about 0·02 per cent. In solubilities, however, the largest difference is ·06 at 75° C., and this corresponds to an error of 0·16 per cent. This large difference in the two percentage errors is remarkable, and I have not yet been able to account for it—it is manifested in most of the salts hitherto worked with. A fact which may possibly throw light on the subject is noticeable in the above table, and is one which most of the salts also show, namely, that the solubilities obtained when starting with an unsaturated solution, tend to be slightly less than those obtained when starting with a supersaturated one, and this although the corresponding densities are practically identical. I hope to investigate the matter while determining the electric conductivities of these solutions.

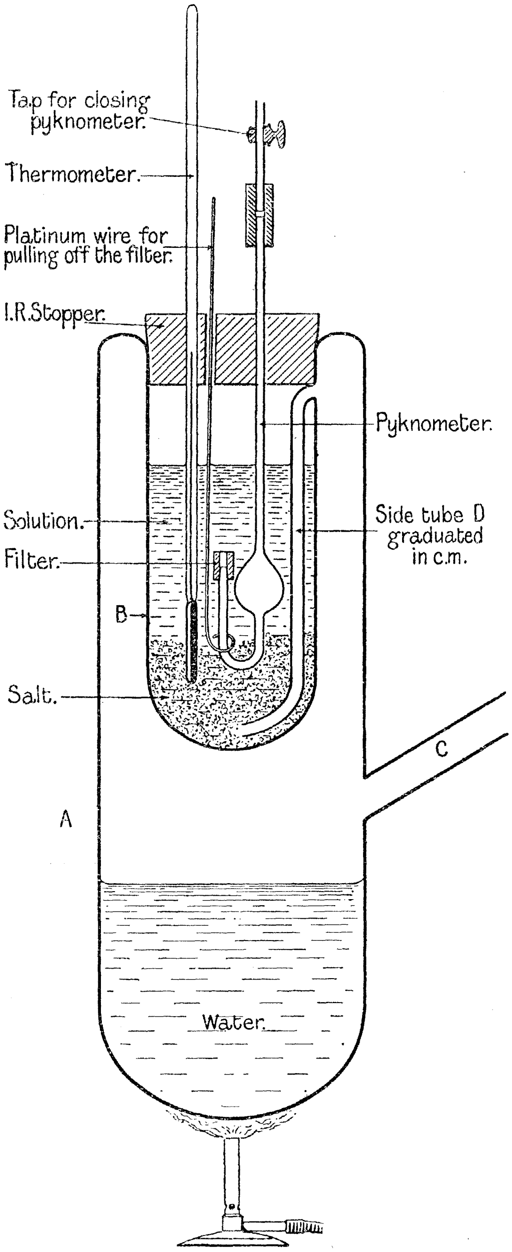

Fig. 5.

The Densities and Solubilities at the Boiling-point.

Attempts were made to determine these in a Beckmann apparatus, but without success—the difficulty of keeping a constant temperature being too great—so recourse was had to a method first suggested by, I believe, BUCHANAN.

In the apparatus shown in fig. 5, the outer glass tube A contains water, and the inner tube B the salt and solution; by boiling the water vigorously and closing the side tube C, steam, passing through the tube D, is forced to bubble rapidly through the solution (D is graduated in centimetres so that the level of the solution may be estimated while the pyknometer is in the solution). The steam, if passed rapidly enough through the solution, stirs it thoroughly, and the temperature rises up to the boiling-point of the saturated solution and remains constant at this point as long as there is enough undissolved salt left. The constancy of the temperature therefore indicates that saturation is attained.

Determination of the Density.

When it is seen that the steam is passing freely through the solution, an india-rubber plug, through which the thermometer and pyknometer pass, and which is also perforated to allow the steam to escape, is inserted into the top of the inner tube. When the temperature becomes constant, the pyknometer, with the tap closed and with the end of the lower capillary covered by a filter, is forced through the stopper, so that the bulb and capillary are completely immersed; when the temperature is again constant, the tap is opened and the pyknometer quickly filled by gentle suction, and the tap closed. The filter is then removed from the end of the capillary, the level of the solution in the stem is read, and both thermometer and pyknometer are taken out of the solution by the withdrawal of the rubber stopper; the pyknometer is then washed, dried, and weighed in the usual manner.

It was found advisable to use the pyknometers described on p. 191 and shown in fig. 3, not only on account of the pressure set up when the salt crystallized out, but because they could be more quickly filled, and therefore less condensed steam formed in the stem; a further reason for using these pyknometers was that the larger bore of the stem and lower capillary enabled them to be emptied with less difficulty.

Determination of the Solubility.

When the pyknometer had been weighed, its contents were emptied into a beaker, and the solution washed into a Jena glass bulb (described on p. 190 and shown in fig. 1), and evaporated to dryness as before.

Great difficulty was experienced in emptying the pyknometers when filled with the solutions of rubidium nitrate, thallium nitrate, or cæsium alum, and the only way of doing so was by alternate heating and cooling when completely immersed in nearly boiling water—the operation taking in some cases as long as 6 hours. It is interesting to note that on testing the boiled saturated solutions of the nitrates of sodium and rubidium for nitrites by means of fuchsine, the conversion of a small quantity of the nitrate into the nitrite was distinctly indicated.

Modification of Apparatus Necessary to Meet the Case of Extremely Soluble Salts.

In the case of the nitrates of rubidium and thallium, which are extremely soluble at the boiling-point, the apparatus described on the foregoing page was found to be unsuitable, because a constant temperature could not be maintained for a sufficient length of time to allow the pyknometer to be filled. Two things are essential for maintaining the solutions at their boiling-points: that thorough stirring should take place, and that there should be a sufficiency of undissolved salt left in contact with the solution; with extremely soluble salts the larger quantity of steam necessary for thorough stirring dissolves so much salt that by the time this stirring is attained the solution is nearly clear, and shortly after, all the salt is dissolved and the temperature begins to fall.

A modification of the method was adopted in which steam, generated in a boiler A (see fig. 6), is forced through a tube B and delivered at the bottom of the large test-tube C, which contains the solution. The test-tube is immersed in an oil bath D

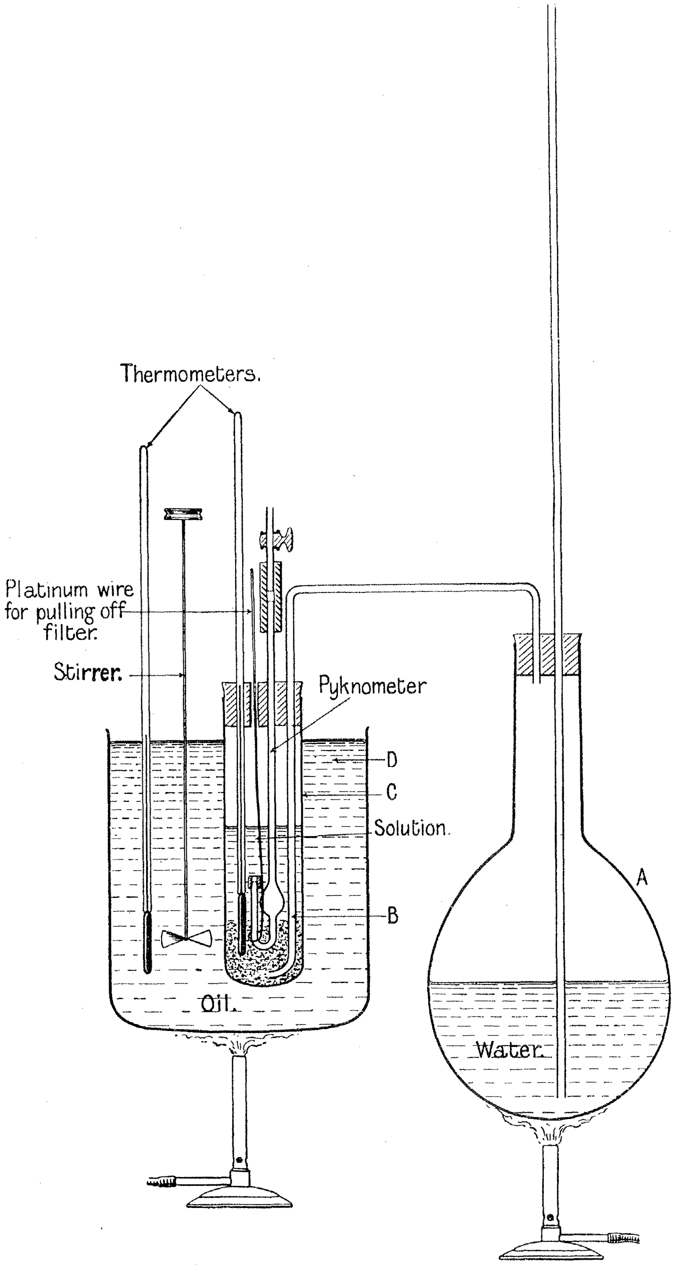

Fig. 6.

maintained at a temperature close to that of the boiling-point of the saturated solution, the oil in the bath being vigorously stirred by a stirrer driven from the main laboratory shafting. When the temperature of the oil bath was below the boiling-point, salt dissolved; when above, salt was thrown out of solution. By carefully adjusting the temperature of the oil bath, two densities could be obtained, one while the temperature of the solution was close to the boiling-point, but slowly rising, and the other when it was above the boiling-point, but close to it and slowly falling. The former gave the density of a slightly unsaturated solution, and the latter that of a slightly supersaturated solution when referred to a solution saturated at its boiling-point. The mean of these two observations was considered to be the density of the solution saturated at the boiling-point—and similarly with the resulting solubilities.

The results obtained at the boiling-point were found not to be as concordant as those at the other temperatures; doubtless the greater part of this is due to the exceptional difficulties of the experiments. The following are some of the sources of error. It was impossible to prevent the condensation of steam in the stem of the pyknometer, and it was therefore necessary to estimate the length of each drop, and add this length to the reading of the level in the stem. There was also an error introduced by the fact that, for the purpose of reading its level, the solution had to be sucked into the cold part of the stem which projected through the indiarubber stopper; on reaching this colder part, salt immediately crystallises out; the total volume thus changes, and the observed level is not that which the solution would otherwise have attained. The maximum error possible from this cause was calculated for the case of rubidium nitrate, and was found to be such as to give an error in the density of 0·1 per cent.

Another and a much more important source of error was that the reduction of pressure on the surface of the solution in the pyknometer, unavoidable when filling by suction, very often caused steam bubbles to form. As it was essential to fill whilst a large excess of undissolved salt was still being stirred by the steam, the solution surrounding the pyknometer was often semi-opaque, and consequently it might happen that part of the space inside the pyknometer was occupied by an unseen steam bubble, and might thus be an unobserved source of error. Numerous fillings had to be rejected on this account, the steam bubbles showing themselves on the withdrawal of the pyknometer from the solution. The numbers tabulated below are those derived from fillings in which there were no observed steam bubbles.

Determination of the Temperature.

As mentioned above, the boiling-point of the saturated solution was considered to be the constant temperature which the solution and salt reached when steam was rapidly bubbled through them; this temperature was indicated by mercury thermometers, and is given in the table of results. They are, however, uncorrected for emergent column, because it was found to be practically impossible to apply a satisfactory correction. It is hoped that, later on, when determining the osmotic pressures,* these boiling-points will be accurately ascertained by means of platinum

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* These experiments are in progress, but not complete.

thermometers. In the expectation of this the total pressures under which each solution was boiling when its density was taken was noted, and is given in the table. This total pressure is made up of the barometric pressure, together with the pressure due to the height of the boiling liquid. To ascertain the effect of the latter, observations were made on the boiling-point of water of varying depths, and through which steam was being rapidly blown. The results showed that the boiling-point was increased by an amount equal to that which a pressure equal to half the depth of the liquid would create; this, of course, was what was to be anticipated, provided the stirring was thorough. It was assumed that a similar result would hold for the solutions, and the total pressures given are those calculated on this basis.

Results.

The first table gives the results obtained by means of the apparatus shown in fig. 5.

Column I. gives the approximate boiling-point, which is also the temperature at which the pyknometer was filled.

Column II. gives the total pressure in millimetres of mercury, at the time of filling.

Columns III. and IV. give the corresponding densities and solubilities; the latter are in parts of anhydrous salt dissolved by 100 parts of water.

TABLE I.

	I. Boiling-point.	II. Pressure.	III. Density.	IV. Solubility.
	° C.			
NaCl	107·5	740·1	1·1634	39·57
,,	107·8	749·1	1·1629	39·72
KCl	107·4	738·7	1·2118	58·09
,,	107·4	739·4	1·2118	58·12
RbCl	112·9	756·6	1·6146	146·65
,,	112·9	756·6	1·6149	146·65
CsCl	119·3	754·2	2·0855	290·04
,,	119·5	757·6	2·0863	289·93
TlCl	99·2	736·5	·9787	2·42
,,	99·6	746·9	·9786	2·40
Na_2SO_4	101·9	750·6	1·2451	42·15
,,	101·9	751·0	1·2449	42·21
K_2SO_4	101·0	752·6	1·1206	24·23
,,	101·0	752·6	1·1207	24·18
Rb_2SO_4	102·4	742·4	1·4752	82·57
,,	102·4	742·4	1·4753	82·56
Cs_2SO_4	108·5	737·2	2·0927	224·24
,, *	108·6	737·6	2·0942	224·75
Tl_2SO_4	99·7	748·7	1·1164	18·45
,,	99·6	747·5	1·1165	18·45
KNO_3	114·0	745·5	1·6266	311·79
,,	114·0	745·1	1·6272	311·48
$CsNO_3$	106·0	747·6	1·8642	219·29
,,	106·3	749·2	1·8664	221·12

[*] These observations are derived from pyknometer fillings which were considered to be particularly good; they are therefore given double weight when taking the "means" for the tables at the end of the paper.

The second table gives the results obtained with the apparatus shown in fig. 6. Columns I., II., III., and IV. give the temperature of filling, the total pressure, the density, and the solubility, respectively, when the temperature of the oil bath was below the boiling-point, but close to and rising; while columns V., VI., VII., and VIII. give the same, when the oil-bath temperature was higher than the boiling-point, but close to and falling.

TABLE II.

	I. Temperature.	II. Pressure.	III. Density.	IV. Solubility.	V. Temperature.	VI. Pressure.	VII. Density.	VIII. Solubility.
	° C.				° C.			
$NaNO_3$	119·0	737·7	1·5369	208·27	118·9	734·8	1·5379	209·42
$RbNO_3$	118·1	739·6	2·1867	614·27	118·4	729·2	2·1867	619·94
$TlNO_3$	104·1	756·8	3·1725	583·39	104·8	768·1	3·2086	604·46
CsAlum	100·3	757·8	1·1278	22·47	100·4	758·0	1·1292	23·21

Purity of the Salts—the Chlorides.

The alkali chlorides were obtained from Messrs. MERCK, and were sold as the purest they made; the thallous chloride came from Messrs. KAHLBAUM, and was also sold as pure.

The solutions of the potassium and sodium salts did not require filtering, and were tested for purity by an analysis of their chlorine contents. The sodium salt giving 60·58 per cent. (calculated 60·59 per cent.) and the potassium 47·60 per cent. (calculated 47·54 per cent.). The rubidium chloride was tested spectroscopically for the presence of potassium and cæsium by first locating the chief lines of these metals by observation of their spectra on the graduated circle of the spectroscope, and then exploring the rubidium spectrum for them. No definite evidence of impurities was obtained. An analysis of the chlorine content gave 29·34 per cent. (calculated 29·32 per cent.). From the appearance of the cæsium chloride it was thought necessary to filter the solution and recrystallise several times; the mother liquor of the first recrystallisation was distinctly yellow, that of the second faintly so, while the third was colourless. A spectroscopic examination, similar to that mentioned above for the rubidium salt, revealed, it was thought, a trace of rubidium. An analysis of the chlorine content gave 21·13 per cent. (calculated 21·06 per cent.).

The thallous chloride was found to be free from lead, and an analysis of the thallium content gave 85·40 per cent. (calculated 85·21 per cent.). Owing to the insoluble nature of this salt, the solubility determination cannot be relied on to as great a degree of accuracy as in the other determinations.

The Sulphates.

The alkali sulphates came from Messrs. MERCK, and were sold as their purest; the thallium salt came from Messrs. KAHLBAUM. Neither the sodium nor the potassium salts required recrystallising, nor did their solutions require filtering; analyses of their sulphuric acid contents gave for the sodium salt 67·37 per cent. (calculated 67·57 per cent.) and for the potassium 55·20 per cent. (calculated 55·12 per cent.). Not having purchased enough of the rubidium salt, the balance was made good by treating pure rubidium carbonate (also purchased from Messrs. MERCK) with pure sulphuric acid in just sufficient quantity to neutralise the solution, and then crystallising out. The two quantities of salt were then added together and recrystallised, and the crystals examined spectroscopically, in the manner before stated, for potassium and cæsium, but with no definite indication of either. An analysis of the sulphuric acid content gave 36·05 per cent. (calculated 35·99 per cent.).

The cæsium sulphate was recrystallised three times, and the spectroscopic examination gave no definite indication of either potassium or rubidium. An analysis of the sulphate content gave 26·62 per cent. (calculated 26·55 per cent.). The thallium sulphate was recrystallised three times and found to be free from lead. An analysis of the thallium content gave 80·96 per cent. (calculated 80·95 per cent.).

The Nitrates.

All the salts were Messrs. MERCK's purest, except the thallium salt, which came from KAHLBAUM. The alkali nitrates were all recrystallised two or three times, and were examined spectroscopically and found to be free from impurities. The thallium nitrate, however, was found to contain some lead; it was freed from this by repeated recrystallisation. An analysis of the thallium content gave 76·89 per cent. (calculated 76·69 per cent.).

On account of the difficulty of obtaining accurate analyses of the alkali nitrates they were not analysed, but after the first recrystallisation a series of densities and a corresponding series of solubilities at different temperatures were obtained, and these series were compared with similar series obtained from the solution of the crystals of the next recrystallisation. The two differed by no more than the experimental errors.

During the evaporation to dryness in the Jena glass bulbs for the purpose of determining the solubilities, it was found that a trace of nitrate almost invariably came over with the condensed water, and those observations in which more than a trace came over were rejected. It was also noticed that, except in the case of cæsium nitrate, the dried salt remaining in the bulbs contained a trace of nitrites. The quantities in both cases were so small that it was not considered necessary to apply any corrections to the resulting solubility.

The Alums.

The potassium alum purchased as pure from Messrs. Merck was found to contain a small quantity of both iron and ammonium, and repeated recrystallisation did not purify it. Pure aluminium and pure potassium sulphates were therefore purchased, and the pure alum made from these. An analysis of the sulphuric acid content of this salt, when recrystallised, gave 40·33 per cent. (calculated 40·49 per cent.). The remainder of the alums, purchased as pure from Messrs. Merck, were recrystallised several times, and the spectroscopic examination showed no impurities. Analyses gave, for the rubidium salt, 36·69 per cent. SO (calculation being 36·89 per cent.), and, for the cæsium salt, 33·67 per cent. SO (calculation being 33·80 per cent.).

The thallium alum was analysed by determining the thallous sulphate content, giving 39·29 per cent., the calculated value being 39·43 per cent. It will be noticed that the tables of results give no values for potassium alum above 60° C., for the rubidium alum above 70° C., and for thallium alum above 60° C.—this is because it was found that the prolonged heating at 68° C., at 80° C., and at 75° C. respectively decomposed the solutions, and a white insoluble precipitate was formed. The cæsium alum, however, could be heated to the boiling-point without decomposition.

The solubilities of the potassium and rubidium alums could not be determined to so close a degree of accuracy as that of the other salts, for it was almost impossible to dry the contents of the pyknometers to a constant weight, without decomposing the salt. The method finally adopted was to evaporate to partial dryness in the Jena glass bulbs at 115° C., then raise the temperature of the oven gradually to 175° C. (dry air passing the while), and, when all perceptible moisture had been driven off, to heat the bulb gently with a naked flame, care being taken not to heat to a temperature high enough for the glass to give a sodium flame. With cæsium alum a constant weight was obtained by keeping the oven at 130° C. to 140° C.

The Observed Densities and Solubilities.

In the following tables the numbers in each column are obtained as follows:—

Column I. gives the temperatures to which the observation recorded in the remaining columns refer. These temperatures are corrected for emergent column, and are, as before stated, the mean temperature corresponding to the meaned density and the meaned solubility.

Column II. gives the density of the saturated solution, obtained as already stated. It summarizes over 600 observations, excluding the 300 mentioned on p. 195.

Column III. gives the corresponding solubilities in parts of anhydrous salt dissolved by 100 parts of water, and is also a summary of some 450 observations exclusive of the above mentioned 300.

Column IV. gives the number of gram-molecules of salt in 1 litre of solution saturated at the temperature recorded in column I. The numbers are obtained by dividing the weight of salt found in the litre by the molecular weight of that salt.

Column V. gives the number of gram-molecules of water in the litre. The numbers are derived by dividing the weight of the water in 1 litre of saturated solution by the molecular weight of water. Throughout this work the atomic weights used are those based on hydrogen as unity and oxygen as equal to 15·88.

Column VI. gives a measure of the concentration—it is the ratio of the number of salt molecules to the sum of salt and water molecules in the same volume of solution.

Column VII. gives the solubilities, taken from COMEY's 'Dictionary of Solubilities,' of such salts as have already been investigated.

SODIUM Chloride.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from COMEY'S dictionary.	
° C.							
0·35	1·2090	35·75	5·484	49·81	10·083	35·7	
15·20	1·2020	35·84	5·462	49·49	10·061	35·9	1·2025
30·05	1·1956	36·20	5·473	49·09	9·969	36·3	1·1960
45·40	1·1891	36·60	5·488	48·69	9·872	36·8	1·1895 *
61·70	1·1823	37·28	5·529	48·17	9·712	37·4	1·1827
75·65	1·1764	37·82	5·560	47·74	9·586	38·2	1·1769
90·50	1·1701	38·53	5·606	47·24	9·427	39·1	
Boiling-point 107·0	1·1631	39·65	5·688	46·58	9·189	40·2	

The solubilities were determined by evaporating to dryness in Jena glass bulbs.

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* The numbers in this column are the densities of the saturated solution of NALL obtained by ANDRIA ('J. Prakt. Chem.,' [2], 30, 305), and reduced to the temperatures given in column I.

POTASSIUM Chloride.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Con-centration.	VII. Solubility, from COMEY'S dictionary.	*
° C.							
0·70	1·1540	28·29	3·438	50·31	15·633	28·7	28·23
19·55	1·1738	34·37	4·057	48·84	13·038	34·6	34·06
32·80	1·1839	38·32	4·432	47·87	11·801	38·2	38·05
59·85	1·1980	45·84	5·088	45·95	10·031	45·5	45·47
74·80	1·2032	49·58	5·389	44·99	9·348	49·6	
89·45	1·2069	53·38	5·676	44·01	8·753	53·6	
Boiling-point } 108·0	1·2118	58·11	6·018	42·87	8·124	58·5	

The solubilities were determined by evaporating to dryness in platinum crucibles, those at boiling-point in Jena glass bulbs.

RUBIDIUM Chloride.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Con-centration.	VII. Solubility, from COMEY'S dictionary.
° C.						
0·55	1·4409	77·34	5·238	45·44	9·675	76·4 at 1° C.
18·70	1·4865	90·32	5·881	43·69	8·429	82·9 ,, 7° C.
31·50	1·5118	98·61	6·257	42·58	7·805	
44·70	1·5348	106·24	6·590	41·63	7·317	
60·25	1·5558	115·63	6·955	40·35	6·802	
75·15	1·5746	124·52	7·280	39·22	6·387	
89·35	1·5905	132·73	7·562	38·22	6·054	
Boiling-point } 114·0	1·6148	146·65	8·003	36·62	5·575	

The solubilities were determined by evaporating to dryness in platinum crucibles, those at boiling-point in Jena glass bulbs.

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* The numbers in this column are the solubilities given by ANDRIA ('J. Prakt. Chem.,' 137, 468) reduced to the temperatures given in column I.

Cæsium Chloride.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.
° C. 0·70	1·8458	162·29	6·836	39·36	6·758
16·20	1·8984	182·24	7·337	37·62	6·127
29·85	1·9359	197·17	7·688	36·43	5·739
45·55	1·9702	213·45	8·030	35·16	5·379
60·20	2·0012	229·41	8·342	33·98	5·073
76·10	2·0286	245·76	8·630	32·81	4·802
89·50	2·0500	259·56	8·858	31·88	4·599
Boiling-point 119·4	2·0859	289·98	9·283	29·92	4·223

The solubilities were determined in platinum crucibles, except those at the boiling-point, which were done in Jena glass bulbs.

Thallous Chloride.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from Comey's dictionary.
° C. 0·4	1·0013	0·17	·00707	55·91	7916	0·19
15·6	1·0017	0·29	·01199	55·86	4660	0·27
30·05	·9996	0·47	·01930	55·65	2930	0·40
45·20	·9964	0·72	·02976	55·33	1860	0·52
59·80	·9922	1·03	·04266	54·92	1288	0·74
75·65	·9870	1·48	·06060	54·40	896·6	1·03
89·65	·9821	1·96	·07964	53·87	677·4	1·32
Boiling-point 99·35	·9787	2·41	·09684	53·45	552·9	1·55

The solubilities were determined in platinum crucibles, except those at the boiling-point, which were done in Jena glass bulbs.

SODIUM Sulphate.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from COMEY'S dictionary.
° C.						
0·70	1·0432	4·71	·3327	56·05	168·46	5·0
10·25	1·0802	9·21	·6456	55·32	86·63	9·18
15·65	1·1150	14·07	·9747	54·67	57·07	14·12
20·35	1·1546	Lost	—	—	—	—
24·90	1·2067	27·67	1·8534	52·86	29·57	27·6
27·65	1·2459	34·05	2·2425	51·99	24·18	34·1
30·20	1·2894	41·78	2·6926	50·86	19·88	41·8
31·95	1·3230	47·98	3·0400	50·00	17·45	47·6
33·50	1·3307	49·39	3·1174	49·82	16·98	50·5
38·15	1·3229	48·47	3·0608	48·47	17·28	49·3
44·85	1·3136	47·49	2·9980	49·81	17·62	47·7
60·10	1·2918	45·22	2·8507	49·75	18·45	45·3
75·05	1·2728	43·59	2·7383	49·57	19·11	44·0
89·85	1·2571	42·67	2·6643	49·28	19·50	43·1
Boiling-point 101·9	1·2450	42·18	2·6175	48·97	19·71	42·3

Most of the solubilities were determined by evaporating to dryness in platinum crucibles, the remainder in Jena glass bulbs. On plotting out the results of the density and solubility determinations against the temperatures, it will be seen that both curves give the transition point at 32°·5. The direct estimation of the melting-point of hydrated sodium sulphate made by Messrs. RICHARDS and CHURCHILL* gave 32°·379 on the hydrogen scale.

POTASSIUM Sulphate.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from COMEY'S dictionary.	
° C.							
0·40	1·0589	7·47	·4253	55·11	130·66	8·5	7·42
15·70	1·0770	10·37	·5849	54·58	94·31	10·4	10·31
31·45	1·0921	13·34	·7429	53·89	73·52	12·5	13·22 †
42·75	1·1010	15·51	·8551	53·31	63·35	14·5	15·25
58·95	1·1086	18·01	·9792	52·53	54·65	17·6	17·99
74·85	1·1157	20·64	1·1036	51·72	47·86	20·8	
89·70	1·1194	22·80	1·2019	50·98	43·41	23·8	
Boiling-point 101·1	1·1207	24·21	1·2621	50·47	40·99	26·4	

The solubilities were determined by evaporating in platinum crucibles, those at the boiling-point in Jena glass bulbs.

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* 'Zeit. Phys. Chem.,' 26, 690 (1898).

† Reduced to the temperatures in column I., from ANDRIA'S solubilities, see 'J. Prakt. Chem.,' 137, 471.

Rubidium Sulphate.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from Comey's dictionary.
° C.						
0·50	1·2740	36·66	1·2903	52·14	41·41	36·3
15·80	1·3287	46·04	1·5810	50·89	33·19	45·3
31·60	1·3704	54·25	1·8193	49·69	28·32	55·9
44·20	1·3998	60·75	1·9970	48·70	25·35	65·5
57·90	1·4232	66·59	2·1475	47·78	23·24	71·2
74·75	1·4480	73·25	2·3111	46·74	21·22	74·5
89·45	1·4649	78·61	2·4337	45·87	19·84	77·5
Boiling-point 102·4	1·4753	82·57	2·5185	45·19	18·94	80·2

The solubilities were determined by evaporating to dryness in platinum crucibles those at the boiling-point in Jena glass bulbs.

Cæsium Sulphate.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from Comey's dictionary.
° C.						
0·70	1·9766	167·55	3·4467	41·32	12·99	158·7 at −2° C.
15·00	1·9992	176·02	3·5499	40·51	12·41	—
30·40	2·0202	184·35	3·6469	39·74	11·90	—
44·90	2·0365	192·49	3·7318	38·94	11·44	—
59·50	2·0512	199·35	3·8035	38·32	11·08	—
75·70	2·0664	207·89	3·8850	37·54	10·66	—
89·75	2·0774	214·82	3·9471	36·91	10·35	—
Boiling-point 108·6	2·0932	224·50	4·0323	36·08	9·95	—

The solubilities were determined by evaporating to dryness in the Jena glass bulbs.

THALLOUS Sulphate.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration	VII. Solubility, from COMEY'S dictionary.
° C.						
0·15	1·0248	2·72	·0541	55·80	1032·5	2·8
15·60	1·0384	4·32	·0858	55·67	649·9	4·6
29·80	1·0512	6·13	·1214	55·40	457·3	6·7
44·95	1·0652	8·39	·1647	54·97	334·7	8·8
60·40	1·0795	10·96	·2130	54·41	256·4	11·2
75·90	1·0941	13·84	·2654	53·76	203·5	13·8
90·05	1·1071	16·54	·3138	53·14	170·3	16·8
Boiling-point 99·7	1·1165	18·45	·3474	52·72	152·7	18·7

The solubilities were determined by evaporating to dryness in the Jena glass bulbs.

SODIUM Nitrate.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from COMEY'S dictionary.
° C.						
0·30	1·3530	73·30	6·776	43·660	7·443	73·4
15·45	1·3769	84·48	7·466	41·74	6·591	85·7
30·00	1·3992	96·15	8·121	39·89	5·912	95·0
44·50	1·4210	109·10	8·779	38·01	5·329	106·5
60·00	1·4446	124·56	9·489	35·98	4·792	124·3
76·15	1·4701	143·15	10·248	33·81	4·300	142·1
90·25	1·4920	161·61	10·917	31·88	3·920	163·5
Boiling-point 119·0	1·5374	208·84	12·310	27·84	3·262	c̄ 220

The solubilities were determined by evaporating to dryness in Jena glass bulbs; and it is to be noted that a small trace of salt was always found in the distillate from the bulbs.

Potassium Nitrate

I. Temperature ° C.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI Con-centration.	VII. Solubility, from Comey's dictionary.	
0·40	1·0817	13·43	1·276	53·34	42·80	13·5	13·53
14·90	1·1389	25·78	2·326	50·64	22·77	25·9	25·75
30·80	1·2218	47·52	3·921	46·32	12·81	45·7	47·28 } *
44·75	1·3043	74·50	5·547	41·80	8·536	73·5	73·67
60·05	1·3903	111·18	7·291	36·83	6·051	111·1	110·02
76·00	1·4700	156·61	8·936	32·04	4·585	159·0	—
91·65	1·5394	210·20	10·391	27·75	3·767	212·6	—
Boiling-point } 114·0	1·6269	311·64	12·269	22·10	2·801	327·1	—

The solubilities were determined in platinum crucibles, those at the boiling-point in Jena glass bulbs.

Rubidium Nitrate.

I. Temperature. ° C.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Con-centration.	VII. Solubility, from Comey's dictionary.
0·60	1·1389	20·39	1·318	52·91	42·66	20·1 at 0° C.
15·85	1·2665	44·28	2·656	49·09	19·49	43·5 ,, 10° C.
31·55	1·4483	86·67	4·592	43·42	10·45	—
45·85	1·6216	139·38	6·450	37·90	6·875	—
63·40	1·8006	217·06	8·423	31·76	4·770	—
75·60	1·9055	284·06	9·630	27·75	3·881	—
90·95	2·0178	382·89	10·932	23·37	3·138	—
Boiling-point } 118·3	2·1867	617·11	12·858	17·05	2·326	—

The solubilities were determined by evaporating to dryness in platinum crucibles, except in the case of the observations at the boiling-point; these were done in Jena glass bulbs, and the distillate always showed a trace of nitrate as having come over.

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* These solubilities are calculated from those of Andria at slightly different temperatures, 'J. Prakt. Chem.,' 137, 474.

CÆSIUM Nitrate

I Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from COMEY'S dictionary.
° C.						
0·35	1·0701	9·54	·4815	54·64	114·35	10·58 at 3°·2 C.
15·95	1·1345	19·46	·9555	53·11	56·56	—
30·45	1·2219	34·50	1·6205	50·81	32·36	—
45·15	1·3306	55·58	2·4572	47·84	20·47	—
59·90	1·4565	83·50	3·4260	44·39	13·96	—
76·40	1·6068	124·64	4·6082	40·00	9·68	—
90·55	1·7307	165·18	5·5724	36·50	7·55	—
Boiling-point 106·2	1·8657	220·32	6·6351	32·56	5·91	—

The solubilities were determined by evaporating to dryness in platinum crucibles; those at the boiling-point in Jena glass bulbs.

THALLOUS Nitrate.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from COMEY'S dictionary.
° C.						
0·65	1·0346	4·07	·1532	55·60	363·92	—
15·40	1·0653	7·93	·2963	55·20	187·50	9·7 at 18° C.
30·60	1·1150	14·63	·5385	54·40	102·06	—
44·65	1·1891	24·98	·8995	53·22	60·13	—
57·30	1·2986	41·31	1·4369	51·40	36·77	43·5 at 58° C.
64·95	1·3957	56·33	1·9036	49·93	27·33	—
76·00	1·6096	91·93	2·9183	46·90	17·07	—
87·80	2·0258	174·02	4·8780	41·23	9·45	—
Boiling-point 104·5	3·1906	593·93	10·3366	25·72	3·488	588·2 at 107° C.

The solubilities were determined by evaporating to dryness in platinum crucibles; those at the boiling-point in Jena glass bulbs.

POTASSIUM Alum

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from COMEY'S dictionary.
° C.						
0·40	1·0292	3·01	·0586	55·88	954·6	3·05
15·30	1·0461	5·09	·0989	55·67	564·0	5·06
28·10	1·0661	7·83	·1510	55·28	367·1	7·50
43·20	1·1044	13·31	·2530	54·51	216·5	13·40
60·45	1·1835	25·06	·4624	52·93	115·5	25·7

The solubilities were determined in the Jena glass bulbs. Column IV. gives the number of gram molecules in the litre calculated on the assumption that the anhydrous salt is $K_2Al_2\ (SO_4)_4$.

RUBIDIUM Alum.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from COMEY'S dictionary.
0° C.						
0·40	1·0072	0·73	·0121	55·92	4607	0·73
15·20	1·0112	1·28	·0211	55·84	2645	1·33
32·20	1·0165	2·38	·0391	55·53	1420	2·44
45·80	1·0267	4·13	·0673	55·14	820·6	4·33
59·65	1·0466	7·27	·1241	54·57	440·8	7·97
69·75	1·0804	12·23	·1947	53·84	277·5	13·42

Solubilities in Jena glass bulbs. Column IV. gives the number of gram-molecules calculated on assumption that the anhydrous salt is $Rb_2Al_2\ (SO_4)_4$.

CÆSIUM Alum.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.	VII. Solubility, from COMEY'S dictionary.
0° C. 0·40	1·0017	0·21	·0030	55·91	18890	0·19
15·60	1·0022	0·35	·0050	55·85	11230	0·36
29·15	1·0010	0·58	·0082	55·66	6773	0·59
45·25	·9994	1·07	·0151	55·30	3658	1·07
60·60	1·0004	2·05	·0287	54·83	1911	2·04
75·35	1·0107	4·32	·0599	54·19	905·6	4·39
83·05	1 0250	6·86	·0934	53 67	575·6	5·87
90·85	1·0328	11·26	·1524	52·92	353·8	—
Boiling-point 100·4	1·1285	22·84	·3002	51·38	172·2	—

Solubilities in Jena glass bulb. Numbers in IVth column are derived from assumption that anhydrous salt is CS_2, $Al_2\,(SO_4)_4$.

THALLIUM Alum.

I. Temperature.	II. Density.	III. Solubility.	IV. Number of gram-molecules of salt.	V. Number of gram-molecules of aqua.	VI. Concentration.
0° C. 0·45	1·0299	3·22	·0382	55·81	1460
16·10	1·0503	5·61	·0664	55·62	839·3
29·85	1·0808	9·33	·1097	55·29	505·0
37·50	1·1090	13·09	·1527	54·85	360·2
45·20	1·1500	18·50	·2136	54·28	255·1
52·40	1·2051	25·39	·2904	53·75	186·1
60·05	1·2812	35·43	·3988	52·91	133·7

Solubilities in platinum crucibles. Numbers in IVth column are calculated for $N_2Al_2\,(SO_4)_4$.

In conclusion, I am glad to have this opportunity of thanking Mr. E. G. HARTLEY for his help in the observations on the densities at the boiling-points, and Messrs. NEVILLE and WHETHAM for the kind interest they have taken in the work, and for several suggestions.