THE SOLUBILITY OF STRONTIUM SULPHATE
IN WATER
AND IN DILUTE SULPHURIC ACID.

by

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CONTENTS.

Page.

INTRODUCTION.

In 1793, Thomas Charles Hope, a graduate of Edinburgh University and at that time Professor of Medicine in the University of Glasgow, communicated to the Royal Society of Edinburgh a paper entitled "An Account of a Mineral from Strontian and of a Peculiar Species of Earth which it contains", in which he announced the discovery of a new "earth". This discovery was the first recognition of strontia as distinct from baryta. (Trans. Roy. Soc. Edin., 1798, 4, 3). In 1795 Hope was appointed joint Professor of Chemistry with Joseph Black in Edinburgh University. A fine specimen of strontia, prepared by Hope and contained in the original flask together with the solution from which it had crystallised, may be seen in the chemistry museum there. The discoverer of strontia was the occupant of the Chair of Chemistry in Edinburgh for nearly fifty years and this fact alone gives the University a special interest in the chemistry of strontium and its compounds.

An account is here given of an investigation that was undertaken with the object of determining the solubility of strontium sulphate in water and in dilute sulphuric acid. An accurate knowledge of the solubility of this salt is of the highest importance/

importance in analytical chemistry, seeing that strontium is most conveniently determined by precipitation in the form of the sulphate.

Strontium sulphate, which occurs naturally as the mineral celestine, was prepared in the laboratory for the first time by Hope (loc.cit. p.10), who obtained it by the action of sulphuric acid on the Strontian mineral (strontium carbonate) and investigated some of its properties. He writes, "The sulphate of strontites is in the form of a white powder. It has no taste and very little solubility in water. I boiled one grain for some minutes in four ounces of distilled water, half a grain was dissolved." There can be no doubt that this experiment of Hope's was the first attempt to determine the solubility of strontium sulphate.

Since Hope's time, the solubility of strontium sulphate has been frequently investigated. Andrews (Phil. Mag., 1830, 1, 4061), states that "900 grains of the solution in pure water were evaporated to dryness and left a residue of sulphate of strontia, which weighed 0.25 grain, from which it follows that one part of sulphate of strontia requires about 3600 parts of water at the temperature of 60° for solution".

Brandes (Archiv. Apothekerver., 1830, 33, 61) found that a litre of water dissolved 0.0665 gram of/

of the salt at 11° and 0.282 gram at 100°.

According to Fresenius (Annalen, 1846, 59, 120), one part of strontium sulphate dissolves in 6895 parts of water at 14°, and in 9638 parts of water at 100°.

Marignac (Archiv. Science Genève, 1858, 97, 222) states that, at room temperature, one part of strontium sulphate dissolves in 6000 to 6500 parts of water. Schweitzer (Amer. Assoc. Proc., 1877, 26, 197) found that strontium sulphate is less soluble in hot water than in cold water; that the freshly precipitated salt is less soluble than the ignited precipitate; and that the solution always had a slightly acid reaction.

More recently, the solubility was determined by Wolfmann (Osterr.- ung. Zeit. Zuckerindustrie, 1896, 25, 986) at temperatures ranging from 0° to over 100°. Some, if not all, of his experiments appear to have been conducted on a technical scale with unusually large quantities of materials, e.g. for temperatures over 100° he used a large iron boiler, capable of withstanding a pressure of 6 atmospheres, containing 15 cubic metres of water to which he added 5 kilograms of strontium sulphate. He found the solubility to increase very rapidly with temperature between 10° and 20° and thereafter slowly but steadily up to 100°.

All the above investigators used gravimetric methods. The method of determining the solubilities of/

of sparingly soluble salts by measuring the electrical conductivities of their saturated solutions originated with Hollemann (Zeit. physikal. Chem., 1893, <u>12</u>, 125) and Kohlrausch and Rose (ibid., 1893, <u>12</u>, 234), and has since been studied by others. The solubility of strontium sulphate according to Kohlrausch (ibid., 1908, <u>64</u>, 129) is the same at 18° and 32° and amounts to 114.3 milligrams per litre. The solubility of strontium sulphate at higher temperatures has not been determined by the conductivity method.

The following tabulation gives a summary of the results hitherto obtained.

TABLE./

Name and Year	Temperature	Solubility (grams per litre)
Hope, 1793	100°	0.3
Andrews, 1830	60°	0.267
Brandes, 1830	11°	0.0665
"	100°	0.282
Fresenius, 1846	14°	0.145
"	100°	0.104
Marignac, 1858	Room temperature	0.154 - 0.167
Schweitzer, 1877	20°	0.128
"	100°	0.0972 - 0.0998
Wolfmann, 1896	10°	0.099
"	20°	0.148
"	50°	0.163
"	98°	0.179
Hollemann, 1893	16°	0.0993
	26°	0.0997
Kohlrausch, 1890-1908	2.85°	0.1133
	10.18°	0.1135
	18°	0.1143
	32.26°	0.1143

Judging from the figures given above, there is no agreement among the results hitherto obtained, seeing that some authors state that strontium sulphate is more soluble in hot water than in cold water, whereas others state the converse.

It/

It was proposed, in the present investigation, to determine the solubility of the salt by (1) the direct gravimetric method and (2) the indirect conductivity method. The first method is undoubtedly preferable when practicable, especially for solubility determinations at high temperatures, and it was hoped that, by using modern resistance-glass vessels, it would be possible to make accurate determinations of the solubility by evaporation of the saturated solution and weighing the residue. If one litre of solution, saturated at 18°, were evaporated, the residue should weigh (according to Kohlrausch) about 114 milligrams, so that, with quite ordinary precautions, the error in weighing need not much exceed about 0.2 per cent.

It was also proposed to determine the solubility of strontium sulphate in dilute sulphuric acid and to examine the data obtained from the point of view of the interionic attraction theory of ionised solutes.

DETERMINATION OF THE SOLUBILITY OF STRONTIUM SULPHATE IN WATER BY THE GRAVIMETRIC METHOD.

There are various preliminary experiments to be done before the actual determination of the solubility by the gravimetric method can be undertaken. In the description of the investigation that follows, the first section deals with the purification of strontium chloride and the preparation of strontium sulphate; the second part describes preliminary experiments with the apparatus and reagents to be used; and the last section is devoted to the main solubility determinations and includes a statement of the results obtained by the gravimetric method.

I. Preparation of pure Strontium Chloride and Strontium Sulphate.

It was proposed to prepare strontium sulphate by mixing solutions of strontium chloride and sulphuric acid. The first essential was to prepare pure strontium chloride. In order to obtain this, advantage was taken of the method used by Richards (J. Amer. Chem. Soc., 40, 1918, 89) in connection with his work on the transition point of the dihydrate and hexahydrate of strontium chloride.

Purification of Strontium Chloride.

The main difficulty is to eliminate traces of barium and calcium from the strontium chloride. Richards found that if the salt was crystallised as dihydrate above the transition point (61.34°), the resulting crystals contain barium but no calcium, whereas if the salt was crystallised as hexahydrate below the transition point, the crystals contain calcium but no barium. These two contrasting phenomena open the way for the complete purification of the salt, merely by crystallising first above the transition point to eliminate barium from the mother liquid, and then crystallising the mother liquid below the transition point so as to obtain a mother liquid free from calcium (and barium).

Since no detailed description of the apparatus used or the procedure followed is given in Richard's paper, the present author constructed a special thermostat for the purpose. The thermostat consisted of a large glass beaker containing water which was heated with a small flame, and the temperature as well as the water level were controlled by a flow of water through narrow inlet and outlet capillary tubes. By regulating the water flow, it was found possible to maintain the temperature constant to within 0.1°, or to raise or lower it by 0.1° at will.

A saturated solution of strontium chloride was prepared, /

prepared, at about 70°, from the best commercial salt. This was placed in a Jena-glass beaker together with a stirrer and a thermometer. Another thermometer and stirrer were placed in the thermostat. Many trials had to be made in order to ascertain the best conditions under which to conduct the various crystallisations. The temperature was lowered slowly and the concentration of the solution was carefully adjusted by the addition of small drops of water through a capillary tube, so that, after the addition of a nucleus of anhydrous strontium chloride, the dihydrate (recognised as square glistening plates) began to crystallise at about 64°. The temperature of the thermostat was then lowered to 62°, and this temperature was maintained for an hour during which the solution with the dihydrate crystals was stirred.

The solution was then filtered at the same temperature into another Jena-glass beaker. This beaker containing the first mother liquid was placed in the thermostat. The temperature was slowly lowered and the concentration of the solution was carefully adjusted by the addition of small drops of water, until it was found that, after the addition of a nucleus of the hexahydrate, a suitable amount of needle-like crystals of the hexahydrate was formed, after the temperature had fallen to about 36°. This temperature was maintained for an hour with continuous stirring/

stirring. The crystals and mother liquid were separated by filtration, and the final product obtained from the mother liquid by double recrystallisation. The hexahydrate crystals obtained in this way were examined spectro-photographically for calcium and barium, but no trace of either was detected.

Preparation of Strontium Sulphate.

When strontium sulphate is prepared by precipitation from dilute solutions, the precipitate consists of rhombic crystals of the anhydrous salt. According to Lambert and Hume-Rothery (J.C.S., 1926, 2638), the rhombic crystals, although varying in size and form, depending on the temperature of precipitation, belong to the same crystal system identical with that of the mineral celestine. Under certain conditions, an unstable, hydrated form of the salt is obtained by precipitation, but the only form of strontium sulphate stable in contact with its saturated solution between 0° and 100° is the anhydrous salt.

It was decided to prepare the strontium sulphate by mixing hot decinormal solutions of strontium chloride and sulphuric acid. The strontium chloride solution (800 cc.) was placed in a two litre Pyrex-glass beaker in which a stirrer was arranged. The solution was heated to about 90° and, while stirring vigorously, slightly less than the calculated quantity of/

of dilute sulphuric acid was added drop by drop. The mixture was kept near the boiling-point and stirred for half an hour. The precipitate was examined microscopically; only rhombic crystals could be seen. The strontium sulphate was filtered and washed thoroughly until no trace of chloride could be detected in the washings. It was dried at 100°.

II. Preliminary Experiments with the Vessels and the Reagents to be employed.

It was proposed to prepare the saturated solutions of strontium sulphate in silica or Pyrex-glass flasks of about two litres capacity, and to evaporate the solutions, after filtration, in Pyrex-glass flasks or in a large platinum basin. It was necessary, therefore, to make special experiments to ascertain whether water or the solutions would dissolve a weighable amount of the glass under the existing conditions - in short, to ascertain whether "clean" evaporations were possible in such vessels.

The water used in all the experiments was specially distilled and its conductivity was usually about 1.5×10^{-6} mhos. at room temperature. Besides water, the only other reagent required was hydrochloric acid. It was obtained by diluting the A.R. acid with an equal volume of water and distilling.

The/

The distillate was tested by evaporating 50 cc. in a platinum basin and weighing the residue. It amounted to 0.3 milligram.

The suitability of the silica and glass flasks for the solubility determinations was tested by evaporating in each vessel 1 litre of distilled water at the boiling-point until the volume was reduced to about 50 cc. The liquid was transferred to a weighed platinum basin and, after evaporation to complete dryness, the weight of the residue was ascertained. The following results were obtained.

Silica Flask.

No. of Experiment.	Weight of residue obtained.
1.	1 mgrm.
2.	1 mgrm.
3.	0.1 mgrm.
4.	nil.
5.	nil.

Pyrex Flasks.

No. of flask.	Weight of residue obtained.
1.	0.3 mgrm. (twice)
2.	0.2 mgrm. (twice)
3.	0.2 mgrm. (twice)

The silica flask was of opaque "Vitreosil" ware and it was only after it had become thoroughly cleaned as the result of the first two evaporations that the residue/

residue was entirely negligible. The glass flasks are more convenient, being transparent and more easily kept clean, and, seeing that the action of water on the glass under the above conditions is almost negligible, it was decided to use the Pyrex ware for the solubility determinations.

In order to prevent the separation of strontium sulphate during the evaporation of the saturated solutions in the Pyrex flasks, it was necessary to add hydrochloric acid to the solution, and special experiments were made to ascertain whether the acid had any marked action on the glass. One litre of approximately 0.3N hydrochloric acid was evaporated at the boiling-point in the flasks until the volume was reduced to 50 cc. The liquid was transferred to a weighed platinum basin and, after evaporation to complete dryness, the weight of the residue was ascertained. The following results were obtained.

No. of flask	Weight of residue.
1.	2.5 mgrm. (mean of 2 evaporations)
2.	1.7 mgrm. (mean of 3 evaporations)

The solubility of strontium sulphate in hydrochloric acid had also to be ascertained, in order to find how much acid would be required to prevent the precipitation of the salt during the evaporation of the saturated solutions in the main solubility determinations/

determinations. Preliminary experiments were therefore carried out with this end in view, the procedure being similar to that adopted in the main solubility determinations to be described later. Strontium sulphate was stirred with 800 cc. of 0.3067N hydrochloric acid in a Pyrex-glass flask for 24 hours at 25°. The solution was filtered at the temperature of the thermostat and a weighed portion was evaporated in a platinum basin. The residue was moistened with sulphuric acid and, after drying over an electric heater, was weighed. The following results were obtained:-

Weight of solution taken	Weight of residue obtained	Solubility (grams per litre)
493.5 grams	0.5055 gram	1.024
489.0 "	0.5050 "	1.033

The solubility of strontium sulphate in 0.3067N hydrochloric acid at 25° is therefore 1.03 gram per litre.

As a result of the above experiments, it was decided that, in the main solubility determinations, 10 cc. of 3N hydrochloric acid should be added to the saturated strontium sulphate solutions (usually about 1 litre) prior to evaporation. At the beginning of the evaporation, the concentration of hydrochloric acid in the solution was therefore about/

about 0.03N (only about 1/10 of the concentration used in the "blank" experiments described on p.13), and the correction to be applied to the results on account of the action of the acid solution on the glass is evidently very small. It was decided to deduct 0.3 mgrm. from the weight of the strontium sulphate residues found in those experiments in which the evaporations were conducted in Pyrex-glass flasks. As may be seen in the sequel, the results obtained in this way agree very closely with those obtained by evaporating the solutions in a platinum vessel, the latter results being uncorrected.

III. The Solubility of Strontium Sulphate in Water. Gravimetric Method.

The strontium sulphate solutions were prepared in a Pyrex-glass flask of two litres capacity, which was immersed in a thermostat. Each saturated solution, after filtration, was divided into two portions. One portion (about 1000 cc.) was evaporated in a Pyrex-glass flask and the other portion (about 600 cc.) in a large platinum basin. When the volume, in each case, had become reduced to 100 cc. - 50 cc., the solutions were transferred to weighed platinum basins in which the strontium sulphate residues were finally/

finally weighed, as described in detail below.

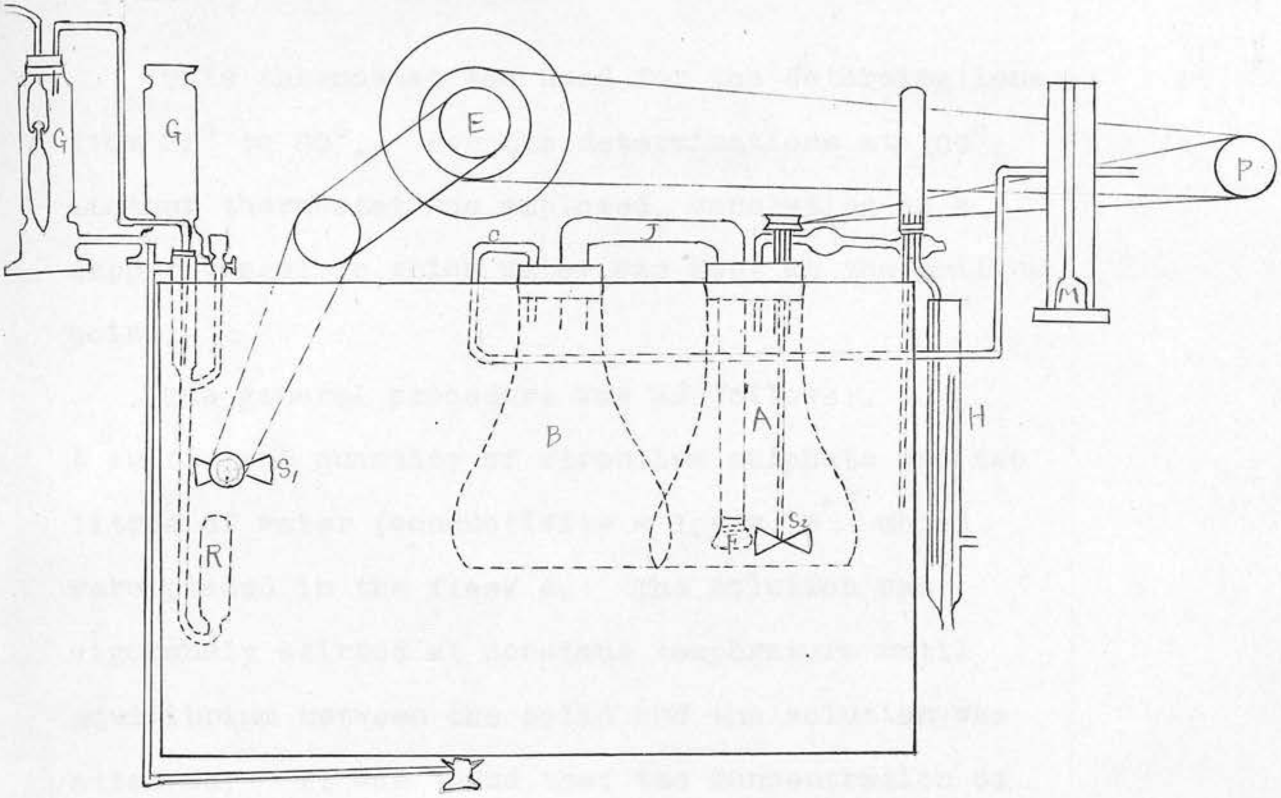
In the following description of the apparatus employed, the letters refer to the diagram given on a separate page.

A is a two litre Pyrex-glass flask, with a wide mouth, fitted with a glass stirrer S_2. J is a Jena-glass tube to one end of which is attached a filter F, the other end passing into a Pyrex-glass flask B used for receiving the filtered solution.

The filtering apparatus consists of a sheet of hardened filter paper inserted between two pieces of muslin which are tightly fixed to the Jena-glass tube by two rubber bands cut from high-pressure rubber tubing which had been carefully washed in boiling water. These rubber bands must fit very tightly in order that the filtration may be perfect. The tube C, leading from flask B, is connected to a suction pump through the mercury manometer M.

R is the gas regular (ordinary toluene type) employed to maintain constant temperature. G is a gas-pressure regulator which is required because the gas-pressure often fluctuates, thereby causing a change in the size of the flame. E is a hot-air engine transmitting power to the stirrer S_1 in the thermostat and, through the pulley P, to the stirrer S_2 in the flask A. H is a regulator to maintain a constant level of the water in the thermostat.

This/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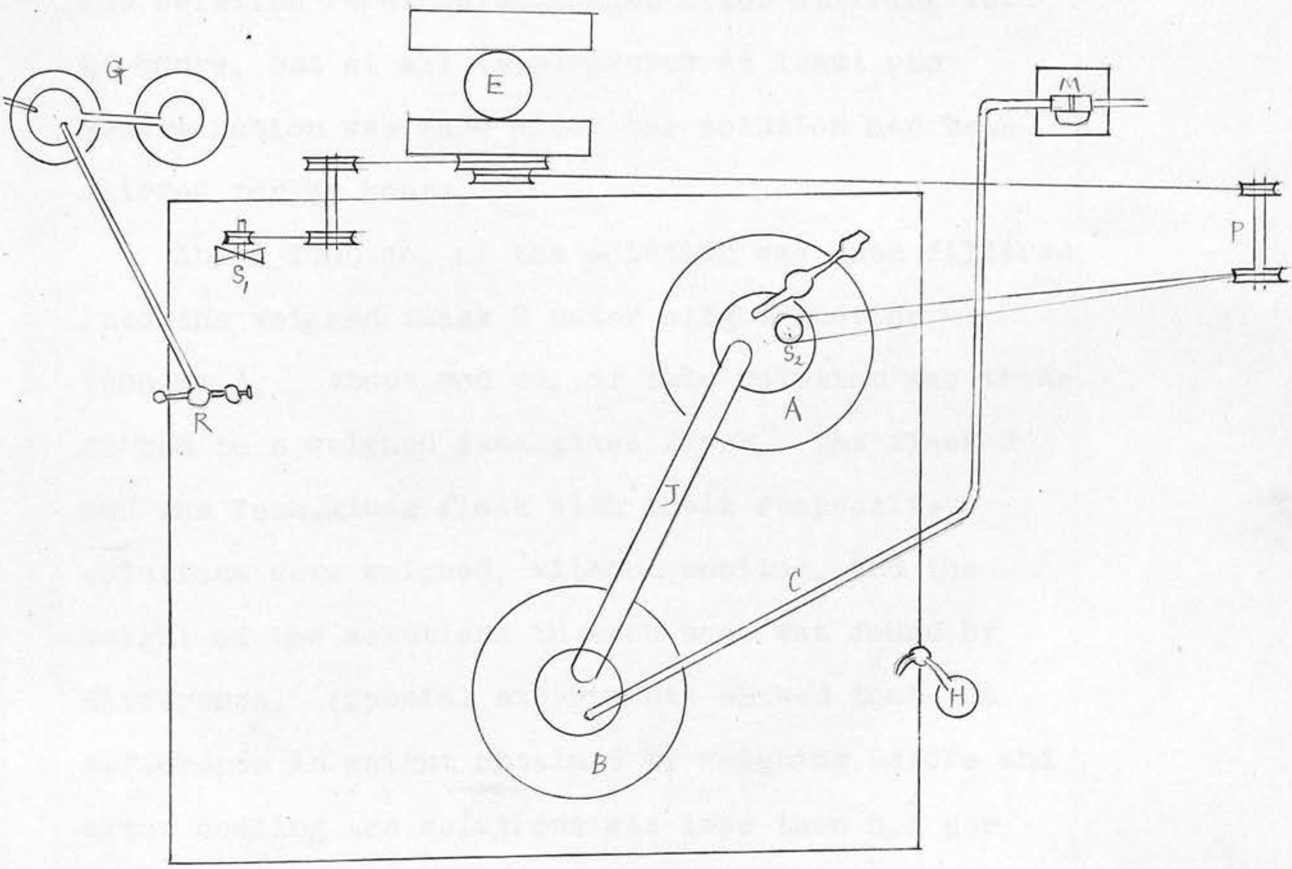
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This thermostat was used for the determinations from 25° to 80°. For the determinations at 100°, another thermostat was employed, consisting of a copper vessel in which water was kept at the boiling point.

The general procedure was as follows:- A sufficient quantity of strontium sulphate and two litres of water (conductivity = 1.5×10^{-6} mhos) were placed in the flask A. The solution was vigorously stirred at constant temperature until equilibrium between the solid and the solution was attained. It was found that the concentration of the solution remained unchanged after stirring for 24 hours, but at all temperatures at least one determination was made after the solution had been stirred for 36 hours.

About 1700 cc. of the solution was then filtered into the weighed flask B under slight suction (300 mm.). About 600 cc. of this solution was transferred to a weighed Jena-glass flask. The flask B and the Jena-glass flask with their respective solutions were weighed, without cooling, and the weight of the solutions in each case was found by difference. (Special experiments showed that the difference in weight obtained by weighing before and after cooling the solutions was less than 0.1 per cent. even at the higher temperatures. To each portion/

portion of the solution 10 cc. of redistilled 3N hydrochloric acid was added in order to prevent the separation of strontium sulphate from solution during subsequent evaporation. These two portions of the solution were treated as follows:-

Solution in flask B. The flask was placed over wire gauze and the solution (about 1 litre) was evaporated at the boiling-point, two boiling-rods of Pyrex-glass being placed in the solution to prevent bumping. When the volume was reduced to 100 cc. - 50 cc. the solution was transferred to a weighed platinum basin. The flask was rinsed very carefully with 50 cc. of water, using 10 cc. at a time, and the rinsings were combined with the solution in the platinum basin. (Special experiments showed that no acid could be detected in a flask of this size after it had been carefully rinsed five times with, in all, 50 cc. of water.)

The solution was now evaporated over an electric heater. Just before complete evaporation, a few drops of dilute sulphuric acid were added and the residue was finally heated to barely visible redness for fifteen minutes. After cooling, the basin with contents was weighed. Heating and weighing were repeated until the weight was constant.

Solution in Jena flask. This portion of the solution (about 600 cc.) was transferred to a large platinum basin,/

basin, and was evaporated on the steam-bath, precautions being taken to protect it from dust. When the volume was reduced to about 50 cc., the solution was transferred to a weighed platinum basin. Further evaporation and the final weighing were done in the same manner as before.

The details of the experiments and the results obtained at each temperature are given below. At each temperature, four distinct saturated solutions were prepared, the duration of stirring being varied from 24 to 36 hours. In the first column of the tabulations, the experiments numbered 1a to 4a refer to experiments in which the initial evaporations were made in a glass flask, and those numbered 1b to 4b to evaporations in a platinum basin. In addition, the numbers 1a and 1b refer to two portions of the <u>same</u> saturated solution, 2a and 2b to two portions of <u>another</u> saturated solution, and so on. A correction, amounting to 0.3 mgrm., has been applied to the results obtained in experiments 1a to 4a at each temperature.

Temperature 25°

Number of Experiment.	Weight of Solution. (grams)	Weight of $SrSO_4$ obtained. (gram)		Solubility. Gram. $SrSO_4$ per 1000 grams water.
1a	1158.8	0.1330		0.1148
2a	1027.3	0.1185		0.1151
3a	1129.4	0.1301		0.1149
4a	1156.3	0.1333		0.1150
			Mean	0.1150
1b	666.5	0.0767		0.1151
2b	609.4	0.0669		0.1147
3b	618.0	0.0713		0.1154
4b	716.5	0.0882		0.1147
			Mean	0.1150

Tmeperature 30°

Number of Experiment.	Weight of Solution (grams)	Weight of $SrSO_4$ obtained. (gram)		Solubility, Gram. $SrSO_4$ per 1000 grams water.
1a	1160.1	0.1346		0.1157
2a	1309.4	0.1518		0.1156
3a	1132.1	0.1310		0.1154
4a	1069.6	0.1242		0.1158
			Mean	0.1156
1b	730.4	0.0846		0.1158
2b	652.9	0.0753		0.1153
3b	699.8	0.0809		0.1156
4b	711.4	0.0824		0.1158
			Mean	0.1156

Temperature 35°

Number of Experiment.	Weight of Solution. (grams)	Weight of $SrSO_4$ obtained. (gram)		Solubility. Gram $SrSO_4$ per 1000 grams water.
1a	1105.5	0.1316		0.1188
2a	1135.6	0.1352		0.1188
3a	1288.2	0.1535		0.1190
4a	1117.2	0.1330		0.1188
			Mean	0.1188
1b	691.6	0.0823		0.1190
2b	764.1	0.0908		0.1188
3b	751.0	0.0893		0.1189
4b	800.2	0.0952		0.1190
			Mean	0.1189

Temperature 40°.

Number of Experiment.	Weight of Solution. (grms)	Weight of Sr SO_4 obtained. (gram)	Solubility. Gram $SrSO_4$ per 1000 grams water.
1a	1097.0	0.1310	0.1191
2a	1134.3	0.1356	0.1193
3a	1117.7	0.1326	(0.1184)
4a	1092.3	0.1304	0.1191
			Mean 0.1192
1b	714.5	0.0852	0.1192
2b	730.6	0.0871	0.1192
3b	705.6	0.0843	0.1195
4b	736.1	0.0877	0.1192
			Mean 0.1193

Temperature 50°.

Number of Experiment	Weight of Solution. (grams)	Weight of $SrSO_4$ obtained. (gram)	Solubility. Gram $SrSO_4$ per 1000 gram water.
1a	1176.5	0.1418	0.1202
2a	1100.7	0.1324	0.1200
3a	956.2	0.1156	0.1206
4a	969.9	0.1171	0.1205
			Mean 0.1203
1b	754.6	0.0909	0.1205
2b	725.7	0.0873	0.1203
3b	698.1	0.0840	0.1203
4b	744.5	0.0897	0.1206
			Mean 0.1204

Temperature 60°

Number of Experiment.	Weight of Solution. (grams)	Weight of $SrSO_4$ obtained. (grams)	Solubility. Gram $SrSO_4$ per 1000 gram water.
1a	1050.1	0.1328	0.1262
2a (lost)	----	----	----
3a	1112.9	0.1404	0.1259
4a	994.8	0.1245	0.1249
			Mean 0.1257
1b	718.6	0.0908	0.1264
2b	730.9	0.0919	0.1258
3b	700.6	0.0882	0.1259
4b	748.0	0.0937	0.1253
			Mean 0.1258

Temperature 70°.

Number of Experiment.	Weight of Solution. (grams)	Weight of $SrSO_4$ obtained. (gram)	Solubility. Gram $SrSO_4$ per 1000 grams water.
1a	1040.9	0.1258	0.1206
2a	1098.5	0.1334	0.1212
			Mean 0.1209
1b	757.2	0.0917	0.1211
2b	714.9	0.0866	0.1212
			Mean 0.1211

Temperature 80°.

Number of Experiment.	Weight of Solution. (grams)	Weight of $SrSO_4$ obtained (gram)	Solubility. Gram $SrSO_4$ per 1000 grams water.
1a	1168.7	0.1376	0.1175
2a	1104.1	0.1302	0.1176
3a	1092.9	0.1277	0.1166
4a	1099.7	0.1288	0.1168
			Mean 0.1171
1b	693.2	0.0814	0.1174
2b	743.8	0.0874	0.1175
3b	699.0	0.0818	0.1170
4b	688.2	0.0804	0.1168
			Mean 0.1172

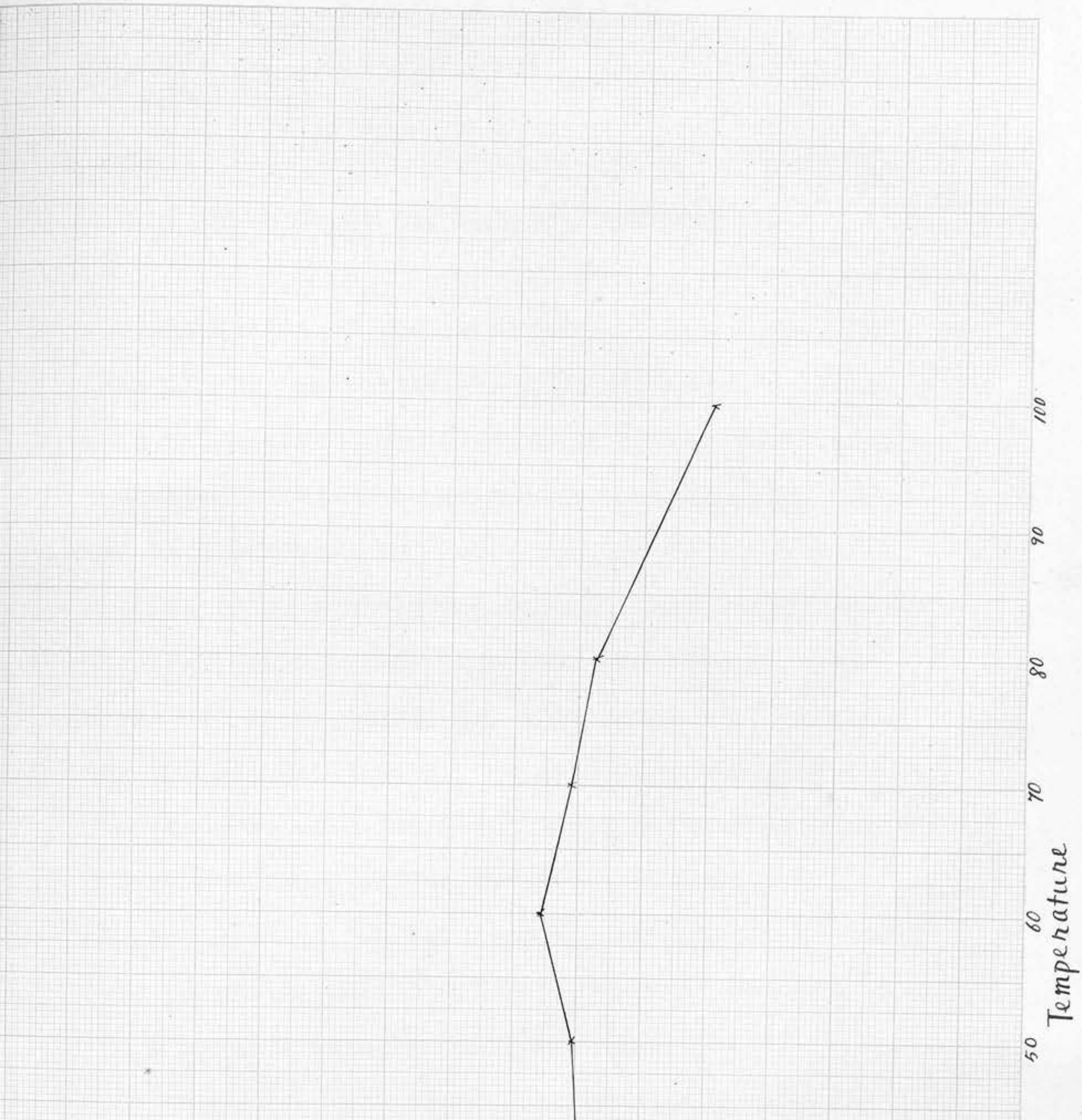
Temperature 99.8°.

Number of Experiment.	Weight of Solution. (grams)	Weight of $SrSO_4$ obtained. (gram)	Solubility. Gram $SrSO_4$ per 1000 grams water.
1a	1294.9	0.1292	0.0995
2a	1170.5	0.1175	0.1001
3a	1018.7	0.1009	0.0988
			Mean 0.0995

The following table gives a summary of the results obtained for the solubility of strontium sulphate in water between 25° and 100° by the gravimetric method.

Temperature.	Solubility. (grams per 1000 grams water)
25°	0.1150
30°	0.1156
35°	0.1189
40°	0.1193
50°	0.1204
60°	0.1258
70°	0.1210
80°	0.1172
99.8°	0.0995

The solubility has been found to increase somewhat slowly between 25° and 60° and to fall again between 60° and 100°. The accompanying graph shows the path of the "curve" obtained by joining the experimentally determined points, without making any attempt to smooth the curve.


Solubility (Gram per Litre)
.13
.12
.11
.10
.09
.08
.07
.06
.05
10
20
30
40
50
60
70
80
90
100
Temperature

Chem. /

DETERMINATION OF THE SOLUBILITY OF STRONTIUM SULPHATE IN WATER BY THE CONDUCTIVITY METHOD.

As stated in the introduction, the method of determining the solubility of a sparingly soluble salt by measuring the electrical conductivity of its saturated solution - originally devised by Hollemann and by Kohlrausch and Rose (loc. cit.) - has been studied by several investigators. Kohlrausch (Zeit. physikal. Chem., 1903, 44, 197) and Böttger (Zeit. physikal. Chem., 1903, 46, 521) determined in this way the solubilities at, or near, the ordinary temperature, of a large number of salts such as silver chloride, silver bromide, silver iodate, silver chromate, silver oxalate, calcium fluoride, lead sulphate, barium sulphate, barium chromate, and the much more soluble calcium sulphate.

The method has been less frequently used for solubility determinations at higher temperatures. Apart from experimental difficulties, the necessary data for calculating the solubility of a salt from the conductivity of its saturated solution are sometimes uncertain and cannot always be directly ascertained. Böttger (Zeit. physikal. Chem., 1906, 56, 83) however, determined the solubilities of silver chloride, silver bromide, and silver thiocyanate at 100° in this way; and Melcher (J. Amer. Chem./

Chem. Soc., 1910, 32, 50) found the solubilities of silver chloride and barium sulphate at 18°, 50°, and 100°, and of calcium sulphate at the same temperatures and also at 156° and 218°

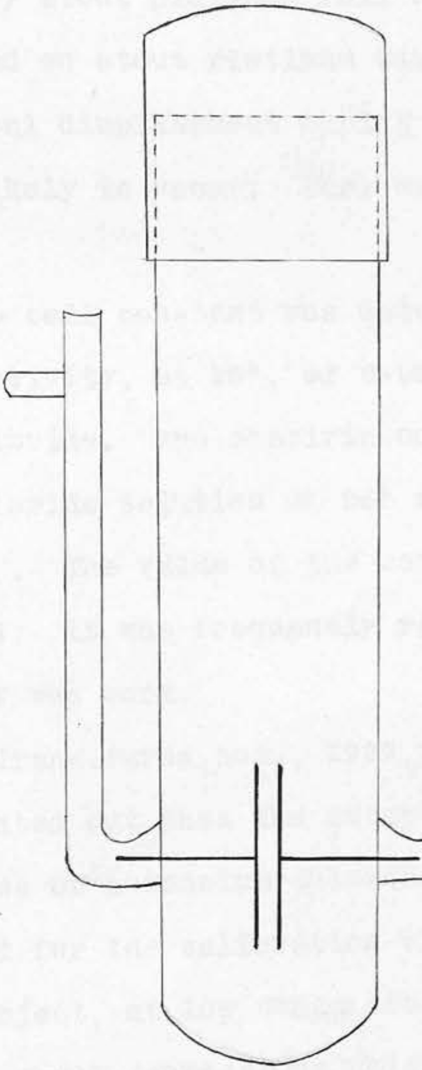
The only determinations of the solubility of strontium sulphate based on conductivity measurements appear to be those obtained at, or near, the ordinary temperature by Hollemann and by Kohlrausch and Rose.

Apparatus and Experimental Method.

For the purpose of measuring the resistance of the strontium sulphate solutions, the author used the ordinary Wheatstone bridge method. A straight measuring bridge was used. The bridge wire was one metre long and was carefully calibrated.

As a source of alternating current, a valve oscillator was used in place of the more usual rotating commutator or induction coil. The valve oscillator has a constant frequency of sine wave form, so that any polarisation that may be produced by the swing of the current in one direction is completely reversed on the opposite swing - a property that cannot be claimed for a current obtained by any form of make and break.

The Conductivity Cell. The type of conductivity cell used for the work is shown in the accompanying diagram. It/



Conductivity Cell
(Full Size)

It was made from Pyrex-glass and was provided with a well-fitting, ground-on, glass cap. The dimensions of the electrodes (25 mm. diameter) and their distances apart (3 mm.) were in accordance with the principles recommended by Washburn (J.Amer.Chem.Soc., 1916, 38, 2431), and were suitable for conductivities ranging from about 10^{-4} to 10^{-6} mho. The electrodes were made from very stout platinum foil (0·25 mm.) and were supported on stout platinum wire (1.25 mm.) so that accidental displacement during the course of the work was unlikely to occur. They were lightly platinised.

The cell constant was determined by measuring it in the conductivity, at 25°, of 0·02N solution of potassium chloride. The specific conductivity of the potassium chloride solution at 25° was taken as $2{\cdot}768 \times 10^{-3}$. The value of the constant was found to be 0·05193; it was frequently re-determined during the course of the work.

Davis (Trans.Farad.Soc., 1929, 25, 129) has recently pointed out that the accepted value for the conductivities of potassium chloride solutions commonly used for the calibration of conductivity cells are subject, at low concentrations (less than 0·001 N), to small corrections which depend on interionic forces, viz. the mutual influence of the solvent and the solute ions upon one another. At the/

the concentration here employed, these corrections are negligible.

Conductivity Water. This was obtained from a still similar to that described by Bourdillon (J. Chem. Soc., 1913, 103, 791). As a rule the freshly distilled water had a conductivity of slightly less than 1×10^{-6} mho at 25°. This water was regarded as suitable for the purpose, seeing that it would be unavoidably exposed to the air during the course of work and that the conductivity of pure water in equilibrium with normal air is 0.8×10^{-6} mho at 25°. Freshly distilled conductivity water was used for each series of experiments at different temperatures, and the conductivity of the water at each temperature was determined by direct measurement.

Preparation of the Saturated Strontium Sulphate Solutions and Determination of their Conductivities.

These solutions were prepared from the actual strontium sulphate that had been already used for the solubility determinations by the gravimetric method, and the salt had therefore been washed in the course of the earlier work with many litres of conductivity water. A suitable portion of this strontium sulphate was placed in a 250 cc. Jena-glass bottle/

bottle together with 150 cc. of conductivity water, and a piece of sheet rubber was very tightly tied over the stopper and neck of the bottle. The bottle was then rotated in the thermostat for six hours.

A portion of the clear solution was transferred to the conductivity cell by using a pipette which was filled by means of a rubber bulb, and the conductivity of the solution was determined at the temperature of saturation. The remainder of the solution was decanted from the bottle, more conductivity water was added, and the bottle was rotated in the thermostat for twelve hours. The conductivity of the solution was again determined. Although six hours contact between the salt and its solution appeared to be sufficient to secure saturation equilibrium, the final conductivity measurements were made after intimate contact had been maintained for not less than twelve hours and sometimes for twenty hours. The conductivities of the saturated solutions, at temperatures ranging from 25° to 92.8°, are shown in the following table.

t^{o} = temperature.
k = observed conductivity of the saturated solution at t^{o}.
k' = conductivity of the water at t^{o}.
$k_t = k - k'$ specific conductivity of the saturated Solution at t^{o}.

t^{o}	$k.10^{6}$	$k'.10^{6}$	$k_t.10^{6}$
25°	154.2 154.2	1.0 1.0	153.2 153.2
30°	168.8 169.2	1.1 1.3	167.7 167.9
40°	196.3 196.3	1.9 1.4	194.4 194.9
49.5° 49.7°	216.7 216.7	1.9 2.0	214.8 214.7
60°	233.7 233.7	2.1 2.2	231.6 231.5
69.5° 69.6°	235.8 234.8	2.1 2.1	233.7 232.7
79.7° 79.8°	233.2 233.2	1.8 2.0	231.4 231.2
92.5° 92.8°	233.7 234.3	2.6 2.5	231.1 231.8

The results quoted in the table for duplicate determinations at each temperature are not merely duplicate measurements of the conductivity of the <u>same</u> saturated solution, but were obtained with distinct solutions prepared by shaking the salt with water for different periods of time. It may be seen that the agreement between these duplicate determinations is very good. It is also noteworthy that whereas the conductivity of the saturated solutions increases with rise of temperature up to 50°, it is very nearly constant between 60° and 93°.

The only values for the conductivities of saturated strontium sulphate solutions with which the above results may be compared are those determined by Kohlrausch and Rose (Zeit. physikal. Chem., 1908, <u>64</u>, 129). Their results are as follows:-

<u>t^o</u>	<u>$k.10^6$</u>
2.85°	85.8
10.18°	105.5
17.38°	126.7
32.26°	173.1

Graphic interpolation from the above figures shows that the conductivity would be 150 at 25° and 166 at 30° - values that are, respectively, about 2 per cent. and 1 per cent. lower than those found by the author.

A possible error in the results of the conductivity measurements might arise through contamination of the solutions with impurities derived from the /

the glass with which they were in prolonged contact. The following experiments show that neither water nor a strontium sulphate solution appear to derive any measurable amount of conducting impurity from the glass, even at high temperature.

(1) The conductivity of a sample of water was measured at 25°. The water, contained in a closed Jena-glass bottle, was then placed in an electrically heated oven for 24 hours at 90°. After cooling, the conductivity of the water was again measured at 25°. The following results were obtained:-

	Sample I.	Sample II.
Conductivity at 25° before heating	0.98×10^{-6}	0.93×10^{-6}
Conductivity at 25° after heating.	0.96×10^{-6}	0.89×10^{-6}

It is remarkable that the water in each experiment showed a slightly lower conductivity at 25° after having been in contact with glass for 24 hours at 90°. The lower value may perhaps be due to a lower concentration of carbon dioxide in the water after heating.

(2) A saturated solution of strontium sulphate was prepared at 25° by shaking excess of the salt with water in a Jena-glass bottle and its conductivity was measured at the same temperature. The bottle with its contents was then shaken for 16 hours in a water-bath/

water-bath at 80°. It was next cooled and shaken for 12 hours in a thermostat at 25°, after which its conductivity was again measured at 25°. The following results were obtained:-

Conductivity at 25° before heating	154.8×10^{-6}
Conductivity at 25° after heating.	153.1×10^{-6}

The above experiment shows that no marked change in conductivity results from prolonged contact of the solution with glass at 90°; it affords proof, also, that saturation equilibrium at 25° may be approached from either a lower or a higher temperature.

CALCULATION OF THE SOLUBILITY OF STRONTIUM SULPHATE FROM THE CONDUCTIVITY OF THE SATURATED SOLUTION.

The specific conductivity of a solution, k, multiplied by the volume, ϕ , in cubic centimetres, containing 1 gram-equivalent of the dissolved substance, gives the equivalent conductivity of the solution, Λ . Accordingly, for any solution,

$$\phi = \frac{\Lambda}{k},$$

and the concentration of the solution, expressed in gram-equivalents per cc. is given by

$$c = \frac{k}{\Lambda}.$$

If a saturated solution of a salt, at t°, has a specific conductivity of k_t at the same temperature, the concentration of the saturated solution, expressed in gram-equivalents per cc. is therefore given by

$$c = \frac{k_t}{\Lambda}.$$

If the salt is a very sparingly soluble one, for which the concentration of the saturated solution is of the order of 10^{-5} N, the assumption may be made, without very serious error, that the equivalent conductivity, Λ at this very low concentration, is identical with Λ_0 , the equivalent conductivity at/

at zero concentration, and the concentration of the saturated solution at t° may be obtained from

$$c = \frac{k_t}{\Lambda_0}.$$

It is seldom, however, that this assumption is permissible.

If we adhere to the conductivity method of calculating ionic concentrations and if, following Arrhenius, we put α, the degree of ionisation, equal to Λ/Λ_0, the concentration of the saturated solution is also given by

$$c = \frac{k_t}{\alpha\Lambda_0},$$

where α is the degree of ionisation of the salt in its saturated solution. In what follows, two methods of calculating the concentration of the saturated solutions are attempted. In the first method, the specific conductivities at t° are reduced to the values corresponding to 18°, and the value of Λ, at 18°, for each saturated solution is obtained. The concentration of the solution is then calculated from $c = k_{18}/\Lambda$.

In the second method, the value of Λ_0 for strontium sulphate at t°, and the degree of ionisation of strontium sulphate in its saturated solution at t° are obtained, and the concentration of the solution is calculated from $c = k_t/\alpha\Lambda_0$.

First Method of Calculation.

Having determined the conductivities of the saturated strontium sulphate solutions at the temperature of saturation, the next step was to reduce these conductivities to the values corresponding to 18° -assuming that the concentrations remain unchanged. This involves a knowledge of the influence of temperature on the conductivity of the solutions.

The conductivity of salt solutions increases with rise in temperature, the increase for 1° varying somewhat widely with the nature of the salt, with the concentration of the solution, and (often somewhat irregularly) with the temperature interval considered. The ratio of the change in conductivity for 1° to the total conductivity is the temperature coefficient. If k_{18} and k_t are the conductivities at 18° and t°, the temperature coefficient, c, referred to the conductivity at 18°, is given by

$$c = \frac{k_t - k_{18}}{k_{18}(t^\circ - 18^\circ)}.$$

The increase in conductivity is not, as a rule, proportional to the rise in temperature, and the change in conductivity with temperature is commonly put in the following form:-

$$k_t = k_{18}\left[1 + c(t^\circ - 18^\circ) + c'(t - 18^\circ)^2\right].$$

The temperature coefficients for salt solutions determined by Kohlrausch and others are valid over a restricted range of temperature - usually between 0° and 30° - and no temperature coefficients over a wider temperature interval are available for strontium sulphate solutions. Accordingly it was considered advisable to attempt the direct determination of the influence of temperature on the conductivity of a strontium sulphate solution over the whole range of temperature covered by the solubility determinations.

A solution of strontium sulphate was prepared by shaking excess of the salt with water at 25°, and a portion of the absolutely clear solution was transferred to the conductivity cell. Filtration was avoided, because many experiments had shown that the solution had invariably a higher conductivity after filtration, even when a very carefully washed filter was used.

The conductivity of this solution was determined at 18°, 25°, 50°, and 75° - automatic thermostatic control being used at each temperature as usual. At higher temperatures, the upper part of the conductivity cell was kept warm, and any water vapour that condensed there was restored to the solution by appropriate tilting of the vessel.

In/

In most of the older determinations of temperature coefficients by Kohlrausch and others, the change in concentration due to the expansion of the solution with rise of temperature was apparently ignored and for this reason alone the direct results obtained in such measurements are subject to correction, seeing that the change in specific volume of a dilute solution between 4° and 100° is about 4%.

Noyes and his collaborators (Zeit.physik. Chem.,1903,46,323 and 1910,70,335) have made very careful determinations of the conductivities of solutions between 18° and 306° in which the correction for the change in specific volume with temperature has been introduced. For the purpose of the present investigation, this correction was found indirectly by measuring the resistance at 18°, 25°, 50°, and 75° of a solution of potassium chloride the concentration of which was 0·01N at 25°, and the value of the cell constant that would give the correct (Noyes) specific conductivity of 0·01N potassium chloride at each of the above temperatures was calculated, i.e. the apparent change with rise of temperature in the value of the cell constant was ascertained. The specific conductivities of the potassium chloride solution - the concentration of which was 0·01N at each experimental temperature - as given by Noyes, and the values of/

of the cell constant that would give those specific conductivities at each experimental temperature with a solution that was 0·01N at 25° are shown in the following table:-

t°	$k \cdot 10^5$	Cell Constant
18°	122.4	0·05100
25°	141·5	0·05100
50°	215·2	0·05166
75°	295·2	0·05331

By using the value of the cell constant corresponding to each temperature, the corrected conductivities of the strontium sulphate solution at 18°, 25°, 50°, and 75° were obtained. The values at intermediate temperatures were obtained by graphic interpolation, and as the graph (shown on a separate page) is very nearly a straight line, the extrapolated values for 80° and 90° involve no serious error. In the following table are shown the conductivities (k) of the strontium sulphate solution at temperatures between 18° and 90°, and also the temperature coefficients (c) referred to the conductivity at 18°, for each temperature interval ($t° - 18°$), c being given by

$$\frac{k_t - k_{18}}{k_{18}\,(t^\circ - 18^\circ)}.$$

The experimentally determined values of k are underlined in red.

t°	$k \cdot 10^6$	c
18	131·6	---
25	154·0	0·0243
30	171·0	0·0250
40	206·0	0·0257
50	241·0	0·0260
60	276·0	0·0262
70	312·0	0·0264
75	330·7	0·0265
80	349·0	0·0266
90	385·0	0·0267

If k_t is the conductivity of a strontium sulphate solution at t°, the conductivity of the solution at 18° is given by

$$k_{18} = \frac{k_t}{1 + c(t^\circ - 18^\circ)} ,$$

in which c has the value, shown in the table above, corresponding to t°.

The temperature coefficients obtained for strontium sulphate may be compared with those for potassium chloride and magnesium sulphate which have been calculated from the conductivities given by Noyes and are shown below.

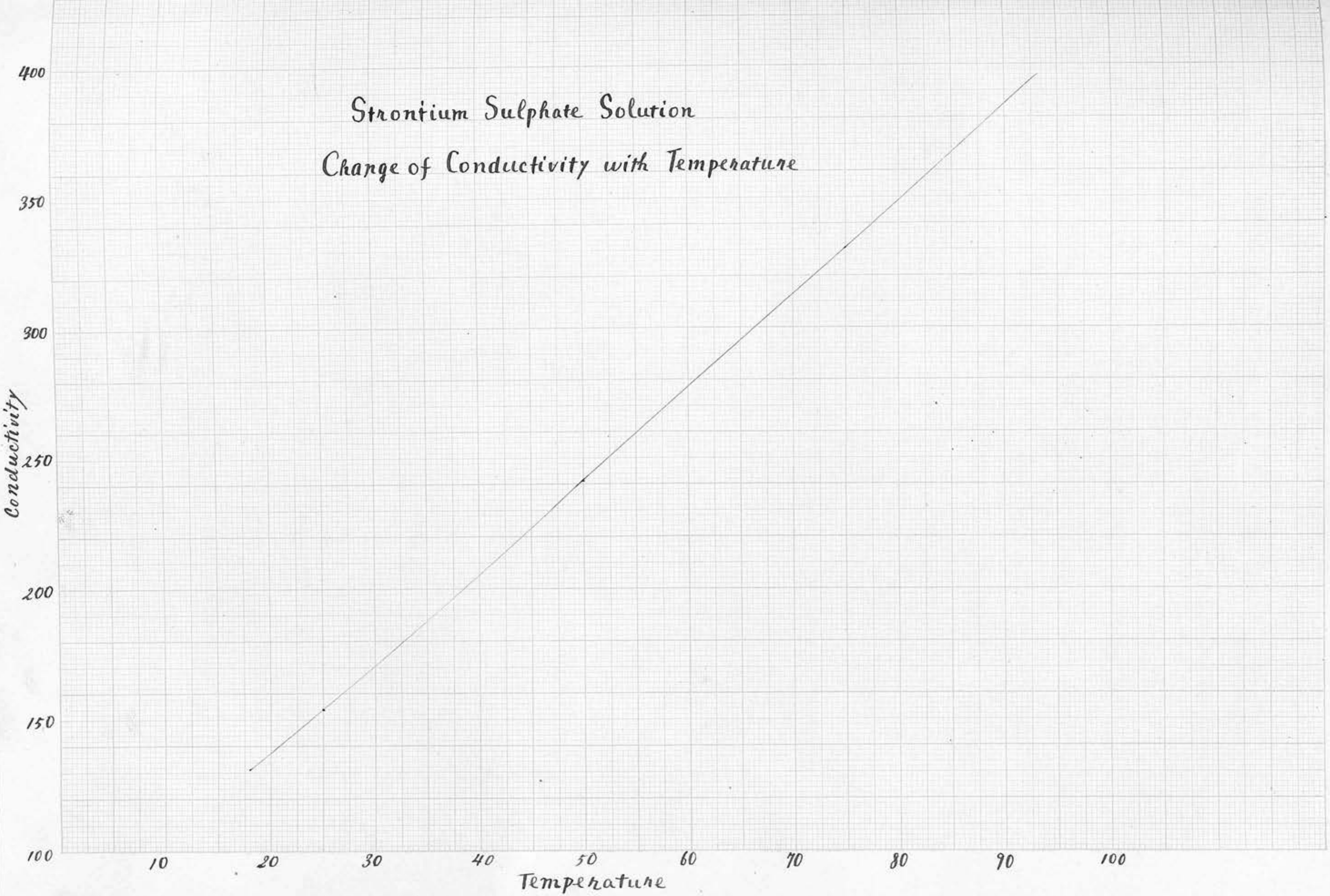
0·01N KCl

t°	$k \times 10^5$	c
18°	122.4	---
25°	141.5	0·0242
50°	215·2	0·0246
75°	295·2	0·0258
100°	377	0·0264

0·002N $MgSO_4$

t°	$k \times 10^6$	c
18°	188·6	---
100°	604	0·0269

It may be seen that the coefficient for 0·002N magnesium sulphate between 18° and 100° agrees closely with that obtained for strontium sulphate for the same temperature interval.



Strontium Sulphate Solution

Change of Conductivity with Temperature

The conductivities, at 18°, of the strontium sulphate solutions, saturated at t°, calculated from the observed conductivities at t° by means of the above formula, are shown in the third column of the following table. In the fourth column, for comparison, are shown the values of k_{18} for the same solutions calculated from k_t by means of Kohlrausch's temperature coefficients for strontium sulphate and the formula

$$k_{18} = \frac{k_t}{1 + 0.0228(t^\circ - 18) + 0.000084(t^\circ - 18)^2}$$

t°	$k_t.10^6$	$k_{18}.10^6$	$k_{18}.10^6$ (Kohlrausch)
25	153.2	130.9	131.6
30	167.8	129.1	130.4
40	194.6	124.3	(126.1)
49.7	214.7	117.7	(118.8)
60	231.6	110.3	(110.0)
69.6	232.7	98.6	(97.1)
79.7	231.4	87.5	(84.8)
92.8	231.8	77.3	(73.0)

The Kohlrausch temperature coefficients and formula were obtained for temperature ranging from 0° — 30° and the extrapolated values of $k_{18}.10^6$ (Kohlrausch) are shown within brackets.

The/

The Value of Λ at 18° This may be obtained on the basis of the law, discovered empirically by Kohlrausch (cf. Zeit. physikal. Chem., 1908, 64, 135), that the decrease in Λ with increasing concentration is proportional to the square root of the concentration. This is known as the square root rule which may be put in the form

$$\Lambda = \Lambda_0 - N\sqrt{c}$$

where c is the concentration expressed in gram-equivalents per litre, and N (the "Gefällefaktor", according to Kohlrausch) is a constant for salts of similar type but varies widely for salts of different types. Kohlrausch obtained the values of N from actual conductivity measurements, and for bi-bivalent salts like strontium sulphate the mean value is 520.

The same law has recently been obtained theoretically on the basis of the Debye-Hückel theory of interionic attraction in solutions of electrolytes (Debye, Trans. Farad. Soc., 1927, 23, 334; Onsager, ibid., 341). The theoretical equation of Onsager agrees well with the experimental data for uni-univalent and uni-bivalent salts, but not for bi-bivalent salts, e.g. $MgSO_4$.

In order to find Λ for a saturated solution of a sparingly soluble salt, an approximate estimate of the concentration, c_1 , is first obtained from

$$c_1 = \frac{k}{\Lambda_0}.$$

The value of Λ (corresponding to c_1) is obtained from

$$\Lambda = \Lambda_0 - N\sqrt{c_1}$$

A more accurate value, C_2 , for the concentration is then obtained from

$$c_2 = \frac{k}{\Lambda}.$$

If Λ differs much from Λ_0 , the process of successive approximation is repeated until the appropriate value of Λ is obtained. The procedure is suitable for <u>very</u> sparingly soluble salts where Λ does not differ much from Λ_0 .

Instead of using the rule in the above form in order to find Λ for saturated solutions of strontium sulphate, we may take advantage of the fact that the ionic mobilities of calcium and strontium are the same. For both sulphates Λ_0 is 119 at 18°. According to the Kohlrausch rule (that the decrease in Λ with increasing concentration is the same for similar salts), the conductivities of dilute solutions of these salts will be equal at equal concentrations. This is true, for example, for dilute solutions of calcium and strontium nitrates up to, at least, 0.002N.

Accordingly, if we know the specific conductivity of a solution of strontium sulphate, we can obtain the approximate concentration of the solution by interpolation from the curve obtained by plotting k against/

against c for calcium sulphate solutions. This interpolation is, however, not very accurate, since c changes in the same proportion, roughly, as k. If, now, the <u>equivalent</u> conductivities of calcium sulphate solutions are plotted against the square roots of the concentrations, an approximate straight line is obtained in accordance with the square root rule, and, since Λ changes very slowly with the concentration, an accurate interpolation for the value of Λ corresponding to the rough value of c is possible.

The data for calcium sulphate solutions are given below.

<u>Conductivity of Calcium Sulphate Solutions at 18°.</u>

Concentration. (gram-equivalents per litre) C	$\sqrt{C}$	Λ	$k \cdot 10^3$
0	0	119.0	0
0.0001	0.0100	114.9	11.49
0.0002	0.0141	113.8	22.76
0.0005	0.0224	109.3	54.65
0.001	0.0316	104.3	104.3
0.002	0.0447	97.0	194.0
0.005	0.0707	85.9	429.5

From these data, two curves were plotted, viz., k against c, and Λ against $\sqrt{C}$. Corresponding to the observed values of k_{18} for the saturated solutions of strontium sulphate, the approximate value of c is obtained from curve I, and then from curve/

curve II the value of Λ corresponding to each value of c is obtained.

The observed values of k_{18} for the saturated strontium sulphate solutions, and the values of c, $\sqrt{c}$, and Λ obtained in the manner described above, are shown in the following Table:-

$k_{18} \cdot 10^6$	c	$\sqrt{c}$	Λ
130.9	0.00129	0.0359	101.9
129.1	0.00126	0.0355	102.1
124.3	0.00121	0.0348	102.4
117.7	0.00114	0.0338	103.0
110.3	0.00106	0.0326	103.8
98.6	0.00094	0.0307	104.7
87.5	0.00083	0.0288	105.7
77.3	0.00073	0.0270	106.8

The values of Λ for calcium sulphate solutions obtained in this way may be used for strontium sulphate solutions having the same specific conductivities, and therefore the concentrations of the strontium sulphate solutions are given by

$$c = \frac{k_{18}}{\Lambda} \cdot 10^3 \quad \text{gram-equivalents per litre.}$$

The solubility, expressed in grams $SrSO_4$ per litre is given by

$$c \times 91.8 \ .$$

The results are shown in the following Table.

Temperature	$k_{18} \cdot 10^6$	Λ	Concentration (gram-equivalents per litre)	Solubility (grams $SrSO_4$ per litre)
25°	130·9	101·9	0·00128	0·118
30°	129·1	102·1	0·00124	0·116
40°	124·3	102·4	0·00121	0·111
49·7°	117·7	103·0	0·00114	0·105
60°	110·3	103·8	0·00106	0·098
69·6°	98·6	104·7	0·00094	0·087
79·7°	87·5	105·7	0·00083	0·076
92·8°	77·3	106·8	0·00073	0·067

Second Method of Calculation.

The concentrations of the saturated solutions of strontium sulphate may also be calculated from their specific conductivities in the following manner.

If k_t is the specific conductivity at t^o and Λ_o the equivalent conductivity at zero concentration at t^o, the ion-concentration at t^o, expressed in gram-equivalents per litre is given by

$$\frac{k_t}{\Lambda_o} \cdot 10^3 .$$

If the degree of ionisation in the saturated solution at t^o is α, the total salt concentration is equal to

$$\frac{k_t}{\alpha \Lambda_o} \cdot 10^3 .$$

Johnston (J. Amer. Chem. Soc., 1909, 31, 1015) has computed the values of Λ_o for calcium sulphate at temperatures ranging from 18° to 156°. By graphic interpolation the following values for Λ_o at t^o are obtained:-

t^o	Λ_o
25	140
30	156
40	188
49.7	222
60	260
69.6	298
79.7	338
92.8	395

Melcher (J. Amer. Chem. Soc., 1910, 32, 50) has measured the conductivities of calcium sulphate solutions at 18°, 50°, 100°, and 156°, and the degree of ionisation at these temperatures may be calculated from his results. The lowest concentration for which the conductivity, at 50° and 100°, was determined by Melcher is 0.002N, but as α decreases somewhat slowly with rise of temperature, it is possible to estimate the value of α for lower concentrations at high temperatures by assuming the same percentage decrease with rise of temperature at all concentrations. In the following table the values of α are given, the figures within brackets being extrapolated values.

Percentage Ionisation of Calcium Sulphate at different temperatures and concentrations.

concentration (gram-equivalents per litre)	100α at 18°	50°	100°
0.002	82	79	69
0.001	88	(85)	(74)
0.0005	92	(89)	(77)

With the help of the above table, it is possible to compute with considerable accuracy the value of α for any temperature between 18° and 100° and for concentrations between 0.002N and 0.0005N.

Having obtained the values of Λ_0 and α in the manner indicated, the concentrations of the saturated/

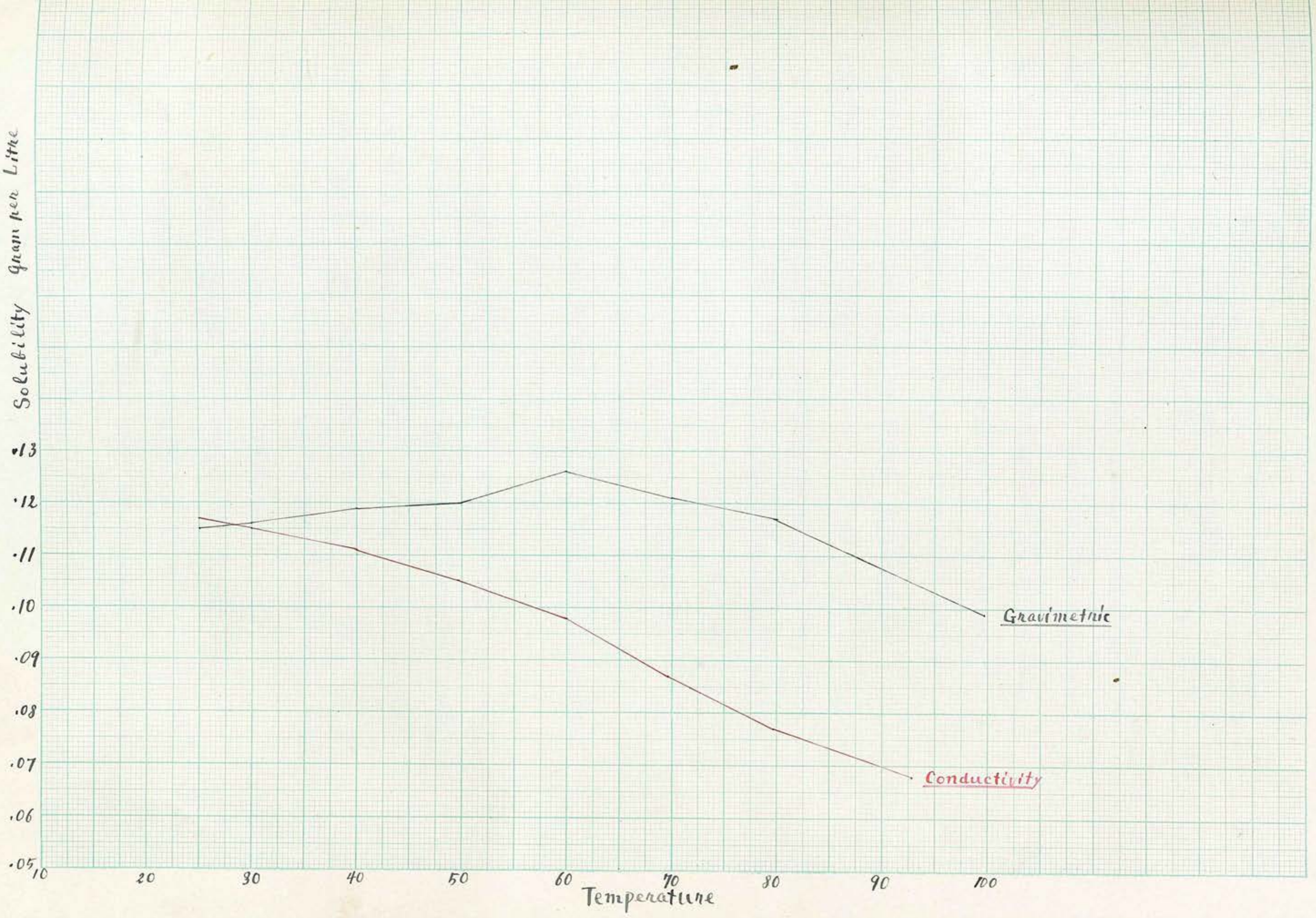
saturated solutions of strontium sulphate may be calculated. The results are shown in the following table, together with those obtained by the first method of calculation.

Temperature	Concentration of Saturated Solution. (gram-equivalents per litre).	
	$\frac{k_{18}}{\alpha \Lambda}.10^3$	$\frac{k_{18}}{\Lambda}.10^3$
25°	0.00127	0.00128
30°	0.00125	0.00126
40°	0.00121	0.00121
49.7°	0.00114	0.00114
60°	0.00107	0.00106
69.6°	0.00096	0.00094
79.7°	0.00085	0.00083
92.8°	0.00075	0.00073

The results obtained by the two methods of calculation, based on essentially independent data, are in fair agreement. From the mean value of the above concentrations at each temperature the solubility of strontium sulphate, expressed in grams $SrSO_4$ per litre, was calculated. The results are shown in the following table, together with the solubilities determined by the gravimetric method.

Temperature	Solubility (grams $SrSO_4$ per litre). Conductivity method.	Gravimetric method.
25°	0.117	0.115
30°	0.115	0.116
40°	0.111	0.119
49.7°	0.105	0.120 (at 50°)
60°	0.098	0.126
69.6°	0.087	0.121 (at 70°)
79.7°	0.077	0.117 (at 80°)
92.8°	0.068	(0.105)
99.8°	----	0.099

The change in solubility with rise of temperature is shown graphically in the accopanying diagram. The results obtained by the conductivity method are shown in red, and those obtained by the gravimetric method in black.


Solubility gram per Litre
·13
·12
·11
·10
·09
·08
·07
·06
·05
10
20
30
40
50
60
70
80
90
100
Temperature
Gravimetric
Conductivity

DISCUSSION OF RESULTS.

A glance at the figures in the preceding table and at the graphs shows that the results obtained by the two methods of determination do not agree, except at the lower temperatures of 25° and 30°. At these temperatures, also, the results are in substantial agreement with those obtained by Kohlrausch (loc. cit.).

According to the gravimetric method, the solubility increases with temperature between 25° and 60° and falls again between 60° and 100°. At 60° the solubility is about 10 per cent. greater than at 25°, and at 100° about 15 per cent. less than at 25°. The solubility therefore reaches a maximum at about 60°.

The results obtained by the conductivity method, on the other hand, show a steadily diminishing solubility with rise of temperature. The solubility at 93° is about 60 per cent. of the value at 25°, and at all temperatures above 30° it is much lower than that obtained by the gravimetric method.

In comparing the two methods of determination, we may note that the gravimetric method is a direct one in which the dissolved salt is actually separated and/

and weighed; whereas the conductivity method is indirect and the final result depends on a calculation involving a knowledge of other factors, partly experimental and partly theoretical.

In the gravimetric method the sources of error are mainly two:-

(1) Failure to secure saturation equilibrium would lead to low or to high results according to the manner in which saturation was approached. But the fact that duplicate determinations, in which the time factor was varied, agree remarkably well appears to justify the belief that saturation equilibrium was, in fact, attained.

(2) The solvent action of the solutions on the glass vessels employed would lead to high results. That this source of error appears to be negligible is shown by the various "blank" experiments carried out in the course of the investigation.

In the conductivity method the sources of error are of two kinds, viz. experimental errors and errors involved in the calculation.

(1) Probably the most serious possible source of experimental error here is that occasioned by the presence of conducting impurity in the strontium sulphate solutions - impurity either present in the original salt or derived from the glass vessels in which the solutions were prepared. Such impurity would, of course, lead to high results for the solubility/

solubility. It has already been stated that the solutions used for the conductivity measurements were prepared from the actual strontium sulphate that had been washed with many litres of conductivity water in the course of the earlier determinations by the gravimetric method, and it was probably free from any appreciable conductivity impurity. Again, the special experiments described on p.31 show conclusively that neither water nor strontium sulphate solutions appear to dissolve any appreciable amount of conducting material from the glass vessels, even at high temperature.

(2) Errors due to failure to secure saturation equilibrium appear to have been eliminated, seeing that there is good agreement between the observed conductivities of dulpicate solutions in which different periods of time were allowed for saturation.

(3) A possible source of error lies in the calculation of the concentration of the solution corresponding to an observed conductivity, expecially at the higher temperatures. An error in the temperature coefficient, for example, would seriously affect the final result, seeing that the reduction of the conductivity at 93° to the value corresponding to 18° involves a reduction to one-third of the observed value, viz. from 232×10^{-6} at 93° to $77{\cdot}3 \times 10^{-6}$ at 18°. On the other hand, the fact that the two methods of calculating concentrations from conductivities give results that/

that agree (at 93°) to about 2 per cent. suggests that the errors involved in calculation are not large.

According to the results given on p.29, the conductivity, at 75°, of a solution saturated at the same temperature is 232×10^{-6}. The concentration of this solution, as given by either method of calculation, is 0·082 gram per litre (see conductivity/graph facing p.47), and an attempt was made to verify this result experimentally in the following way:- A solution of strontium sulphate containing 0·082 gram per litre was prepared by appropriate dilution of a solution that had been saturated at 25°. (The concentration of a solution saturated at 25° was taken as 0·117 gram per litre -see p.47- and 70 c,c. of this solution was made up to 100 c,c. at75°.). The conductivity of this solution was measured at 75° and was found to be 235×10^{-6}, which is in substantial agreement with the observed value (232×10^{-6}) for a saturated solution at 75°. This experiment affords partial confirmation of the results obtained by the conductivity method or, at least, shows that the relationship between observed conductivity and concentration holds equally at 75° as at 25°.

It may be noted that the conductivities of the saturated solutions are nearly constant between 60° and 93°. It follows that the concentration of the saturated solution must diminish between 60° and 93°, and in this respect the two methods of determination -the conductivity method and the gravimetric method/

method- are in qualitative agreement, as the solubility graphs indicate.

It must be admitted, however, that it is not possible to reconcile the results obtained by the two methods. According to the gravimetric method, the solubility at 75° (0·119 gram per litre) is slightly higher than the solubility at 25° (0·115 gram per litre), whereas according to the conductivity method the solubility at 75° (0·082 gram per litre) is much lower than at 25° (0·117 gram per litre). The following <u>experimental</u> evidence appears definitely to support the results obtained by the latter method:- A solution that was brought into equilibrium with the solid salt at 25° was found to have a conductivity, in absence of the solid phase, of $330 \cdot 7 \times 10^{-6}$ at 75° (p.37a), whereas the conductivity, at 75°, of a solution saturated at that temperature was only 232×10^{-6} (p.29). It follows that the concentration corresponding to saturation equilibrium must be lower at 75° than at25°.

A matter of first importance in connexion with solubility in general is the composition of the solid phase. In this respect strontium sulphate is simple, for the only solid phase stable in contact with the saturated solution appears to be the anhydrous salt. Lambert and Hume-Rothery it is true, in their "Studies of Pecipitated Solids" (J.C.S., 1926,2637), observed that, when moderately concentrated solutions of/

of strontium sulphate and sulphuric acid were mixed, the initial precipitate formed at all temperatures between 0° and 100° consists of fine needle-shaped crystals which were identified as a hydrated form of strontium sulphate. These needles are however unstable in contact with the mother liquid and are quickly transformed into stable rhombic crystals of the anhydrous salt. The rate of transformation of needle to rhomb is markedly increased by rise of temperature and at 100° is complete in ten seconds. The rhombic crystals themselves vary greatly in size and form according to the temperature of precipitation. At 0° they are strictly rectangular; on raising the temperature, new faces appear on the crystals, and at 35°, 50°, and 75° distinct forms predominate, until at about 100° the pure rhombic form alone is obtained.

It is recognised, of course, that the solubility curve of any substance is continuous so long as the solid phase remains unchanged. Any change in either the composition or the fundamental crystalline form of the solid phase will be accompanied by a "break" or discontinuous change in the path of the solubility curve. At the transition point of the two enantiotropic forms of ammonium nitrate, for example, such a discontinuous change in the solubility curve has been observed (cf. Müller and Kaufmann, Zeit. physikal. Chem., 1903, <u>42</u>, 499; Millican, Joseph, and Lowry, J.C.S., 1922, 959).

It/

It was at first thought possible that there might be some connexion between the changes in crystalline form exhibited by strontium sulphate and the somewhat discontinuous path of the solubility curve as obtained by the gravimetric method, since the discontinuities appear at approximately the same temperatures as those at which the different forms of crystals are predominant. However, it appears that, although the crystals vary in external form, they all belong to the same fundamental crystalline form identical with the mineral celestine.

Strontium sulphate, then, forms no hydrate stable in contact with the saturated solution between 0° and 100° and, since there is only one fundamental crystalline form of the anhydrous salt, the solubility curve should be continuous. The form of the curve obtained by the gravimetric method resembles the similar, and unusual, type of curve, concave to the temperature axis, given by gypsum. The solubility of gypsum, first carefully determined by Raupenstrauch (Monatsh., 1885, <u>6</u>, 563), and of the other forms of calcium sulphate - anhydrite and the hemihydrate - (cf. Partridge and White, J.A.C.S., 1929, <u>51</u>, 360) has been the subject of many investigations which afford a good illustration of the complexity of the problem of solubility determinations in general. For example, Hulett (Zeit. physikal. Chem., 1901, <u>37</u>, /

37, 385) confirmed with gypsum the old observation of Wollaston (Phil. Trans., 1813, 103, 51) that the solubility of very fine particles was greater than that of coarse-grained powders; and Hulett and Allen (J.A.C.S., 1902, 24, 667) found that the concentration of a solution of calcium sulphate in equilibrium with a plane surface of the solid is different from that in equilibrium with a curved surface. In fact, the solubility of a substance depends on so many superimposed factors that a satisfactory quantitative theory has not yet been arrived at. No explanation, for instance, can be given of the fact that the solubility of gypsum reaches a maximum at about 39°. The continuity of the vapour curves of the salt hydrates excludes the possibility of explaining the downward path of the curve at 39° by the appearance of a new phase, although Davis (J. Soc. Chem. Ind., 1907, 26, 727) suggests that, by analogy with calcium chromate (cf. Mylius and Wrochem., Ber., 1900, 33, 3689), the ascending and descending portions of the gypsum curve may belong to α and β forms of the dihydrate. Further, the temperature of transition from gypsum to anhydrite appears to be about 39°, and although anhydrite is the more stable and less soluble phase above the transition point, no explanation has been given of the fact that gypsum is not converted into anhydrite when in contact with water above/

above that temperature.

According to Lumsden (J.C.S., 1902, 363), the factors that determine the path of a solubility curve are (1) the "thermal energy" of the solid (2) the "affinity" between solid and solvent (3) the osmotic pressure of the dissolved substance. The first and second promote solution and the third opposes it. The solubility curve is the "resultant" of these superimposed forces. Lumsden concludes that the normal path of a solubility curve is either a straight line or a curve convex to the temperature axis and that the existence of solubility curves concave to the temperature axis is improbable. Ignoring the familiar case of gypsum, he states that no well-authenticated case of a solid the solubility of which is expressed by a curve concave to the temperature axis is known.

If we accept the results of the gravimetric method in the present investigation, strontium sulphate affords another example of a salt the solubility of which is represented by a curve concave to the temperature axis.

Thermodynamics connects the path of the solubility curve with the heat of solution of the solid. According to van't Hoff, the relation that exists between the change of solubility (C) with the temperature (T) and the molar heat of solution (Q) is given by the expression

$$\frac{d\log C}{dT} = -\frac{Q}{2T^2}.$$

By the molar heat of solution is here meant the "theoretical" heat of solution of 1 mole of the substance <u>in its saturated solution</u>. The expression shows that the sign (+ or -) of the heat of solution determines whether the solubility will increase or decrease with rising temperature. If Q is negative, i.e. if heat is absorbed when the substance dissolves (in its saturated solution), the solubility increases with rising temperature; if Q is positive, i.e. if heat is evolved when the substance dissolves, the solubility decreases with rising temperature.

This expression was originally obtained for "ideal" solutions, and many attempts have been made to find a formula that would be valid for salts and other electrolytes. By the introduction of the van't Hoff factor i, the expresion becomes

$$\frac{d\log C}{dT} = - \frac{Q}{2iT^2}$$

By integration, assuming Q and i constant within the range of temperature considered, we obtain

$$\log C = \frac{Q}{2iT} + \text{constant.}$$

If the heat of solution and the ionisation do not vary with temperature, log C is a linear function of 1/T, and the graph obtained by plotting log C against 1/T should be a straight line. If we use the solubility results obtained by the gravimetric method, the/

the graph thus obtained is by no means linear. It is shown on a separate page and points to a change in the sign of the heat of solution.

The integrated expression may be used to calculate the molar heat of solution if the solubilities at two temperatures and the value of i are known (cf. van't Hoff, Vorlesungen, 1898, Vol.1, p. 153). If C_1 and C_2 are the solubilities at the absolute temperatures T_1 and T_2 , it follows that

$$\log \frac{C_1}{C_2} = \frac{Q}{2i} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right) ,$$

and therefore

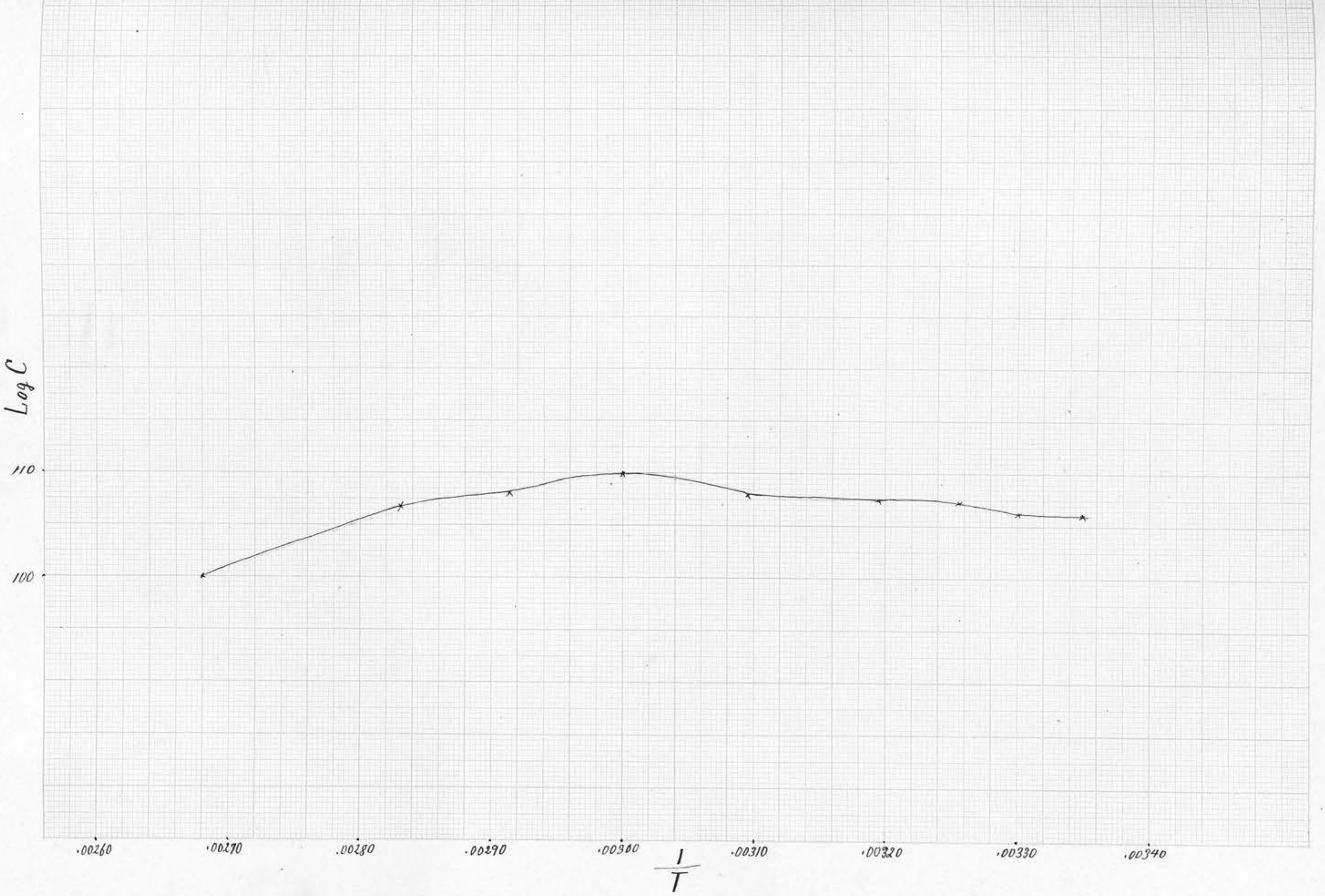
$$Q = 2i . \frac{T_1 \ T_2}{T_2 - T_1} . \log \frac{C_1}{C_2}$$

If we take the degree of ionisation of strontium sulphate in its saturated solution as approximately 0.8, the value of i is 1.8. The values of Q calculated by means of this equation from the solubilities found by the gravimetric method for the temperature intervals 25° - 30° and 25° - 60° are as follows:-

t_1	t_2	C_1	C_2	Q
25°	30°	0.1150	0.1156	-340 calories
25°	60°	0.1150	0.1258	-920 calories

For temperatures above 60°, Q would, of course, be positive.

Now/


Log C
110
100
.00260
.00270
.00280
.00290
.00300
.00310
.00320
.00330
.00340
$\frac{1}{T}$

THE SOLUBILITY OF STRONTIUM SULPHATE IN DILUTE SULPHURIC ACID.

The equilibrium in solutions containing two ionised solutes with a common ion has attracted much attention ever since the theory of ionisation was put forward over forty years ago. Arrhenius himself early examined the problem in his "Theory of Isohydric Solutions (Zeit. physikal. Chem., 1888, 2, 284) and in "Equilibrium between Electrolytes" (ibid., 1890, 5, 1).

An important application of the Arrhenius theory is to the equilibrium in a saturated solution of an electrolyte, and the solubility of salts in dilute solutions of other salts with ions in common with the first has been the subject of many investigations from this point of view. The theory of a "constant ionic solubility product" was first advanced by Nernst (Zeit. physikal. Chem., 1899, 4, 372). According to this theory, the solubility of a sparingly soluble electrolyte is dependent on a constant which is proportional to the product of the concentrations of the ions of the electrolyte, and the "ionic solubility product" remains constant however much the ionic concentrations may be separately varied by the introduction of other electrolytes.

On/

On the basis of the theory it is possible to calculate the "solubility effect" produced by the addition of another electrolyte with a common ion. The principle fails completely to account for the "solubility effect" in concentrated solutions of electrolytes with common ions (cf. Masson, J.C.S., 1911, 99, 1132, and 1912, 101, 103). But when the ionic concentrations are small (as in sparingly soluble salts) and when the ions concerned are univalent, the solubilities calculated by means of the solubility product principle are in fairly good agreement with experiment (cf. Noyes, Zeit. physikal. Chem., 1890, 6, 241, and J.A.C.S., 1911, 33, 1643, and 1807; Stieglitz, J.A.C.S., 1908, 30, 946).

When the ions of the solutes are multivalent, there is no longer accordance between the experimental and the calculated results, and the decrease in solubility produced by the added common ion is much less than would be expected from the solubility product principle (cf. Noyes, J.A.C.S., 1911, 33, 1643 and 1807; Harkins and Paine, ibid, 1919, 41, 1162).

The Debye and Hückel theory of ionised solutes has been applied to the quantitative explanation of the "solubility effect" observed in dilute (saturated) solutions of salts with (or without) common ions. According to the theory, the activity of an ion varies/

varies with its ionic environment: the activity coefficient of a given strong electrolyte is the same in all (dilute) solutions of the same ionic strength; and in very dilute solutions the logarithm of the activity coefficient of an ion is proportional to the square root of the "ionic strength" of the solution. The "ionic strength" of a solution is defined as half the sum of the products of the molar concentrations of each ion into the square of its valency.

Noyes (J.A.C.S., 1924, 46, 1098) finds that the "solubility effect" on a saturating salt produced by the addition of another electrolyte (with or without a common ion) should be given by an equation which, for bi-bivalent saturating salts, may be put in the following form:-

$$\frac{1}{8}\cdot\frac{\log s(s+c)}{s_0^2} = k\left(\sqrt{\sum c' v^2} - \sqrt{8 s_0}\right)$$

where s_0 is the molar solubility of the salt in pure water;

s is the molar solubility of the salt in the solution of the added electrolyte;

c is the molar concentration of the added electrolyte;

$\sum c' v^2$ is the summation of ion concentration (c') x square of valence (v^2) for all the ions present, i.e. it is twice the "ionic strength".

According/

According to the constant ionic solubility product rule, $s(s + c) = s_0^2$, and therefore $\log s(s + c) / s_0^2$ would be zero for all values of c, instead of varying with the ionic strength as in the above expression.

The theoretical value of k for dilute solutions at 25° is 0.357; it should be constant for all solutions, but is found to vary somewhat widely with the valence of the saturating salt and with the concentration. Noyes found that for salts of higher valence (Ag_2SO_4, $Ba(BrO_3)_2$ and $CaSO_4$) the value of k required to satisfy the experimental results was about 0.238.

In what follows, the details are given of the determination of the solubility of strontium sulphate in dilute solutions of sulphuric acid at 25°. The results are examined from the point of view of the above conceptions.

The determinations were carried out in the same manner as already described for the solubility of strontium sulphate in water by the gravimetric method. A mixture of the solid salt and about 2 litres of a solution of sulphuric acid of known concentration was vigorously stirred in a Pyrex-glass flask at 25° until equilibrium was attained (12 to 24 hours). A weighed portion of the filtered solution (about 1 kilogram) was evaporated, first in a Pyrex-glass flask and then in a platinum basin, and the dry residue of strontium sulphate was weighed.

The/

The concentration of the acid was varied from 0.00005 to 0.01 molar normal. Blank experiments were made with each concentration of acid in order to ascertain the error due to the solvent action of the solutions on the glass. The correction due to this action was very small and involved a deduction of from 0.3 to 0.5 milligram from the weight of the strontium sulphate residues. The details of the experiments and the results obtained are given in the following table:-

Molar concentration of H_2SO_4	Weight of Solution (grams)	Weight of $SrSO_4$. (gram)	Solubility.	
			Moles per litre.	Grams per litre.
0	1156	0.1333	0.000626	0.1150
0.0000501	1244	0.1410	0.000615	0.1130
	1327	0.1504	0.000615	0.1130
0.000501	1107	0.0966	0.000473	0.0869
	1237	0.1077	0.000472	0.0867
0.001002	1342	0.0948	0.000382	0.0702
	1490	0.1043	0.000379	0.0696
0.002505	1030	0.0511	0.000268	0.0492
	1100	0.0547	0.0002685	0.0493
0.01002	1129	0.0375	0.000178	0.0327
	878	0.0292	0.0001785	0.0328

The figures in the last column show the progressive decrease in the solubility with increasing concentration of the acid. The solubility in 0.01 molar acid is approximately 30 per cent. of the value in water.

The solubility in presence of the common ion is much greater than would be predicted by the "constant ionic/

ionic solubility product" principle. In the table given below, s_o is the molar solubility of salt in water, and s (experimental) the solubility in sulphuric acid of concentration c. The third column shows the solubility calculated on the solubility product principle, assuming complete ionisation. If ionic concentrations (obtained from conductivity measurements) are used in the calculation in place of total concentrations, the theoretical solubility (fourth column) still falls below the experimental result. (The method of calculation, in fact, neglects the effect of the total ionic concentration on the activity of the substances concerned.)

$$s_o = 0.000626$$

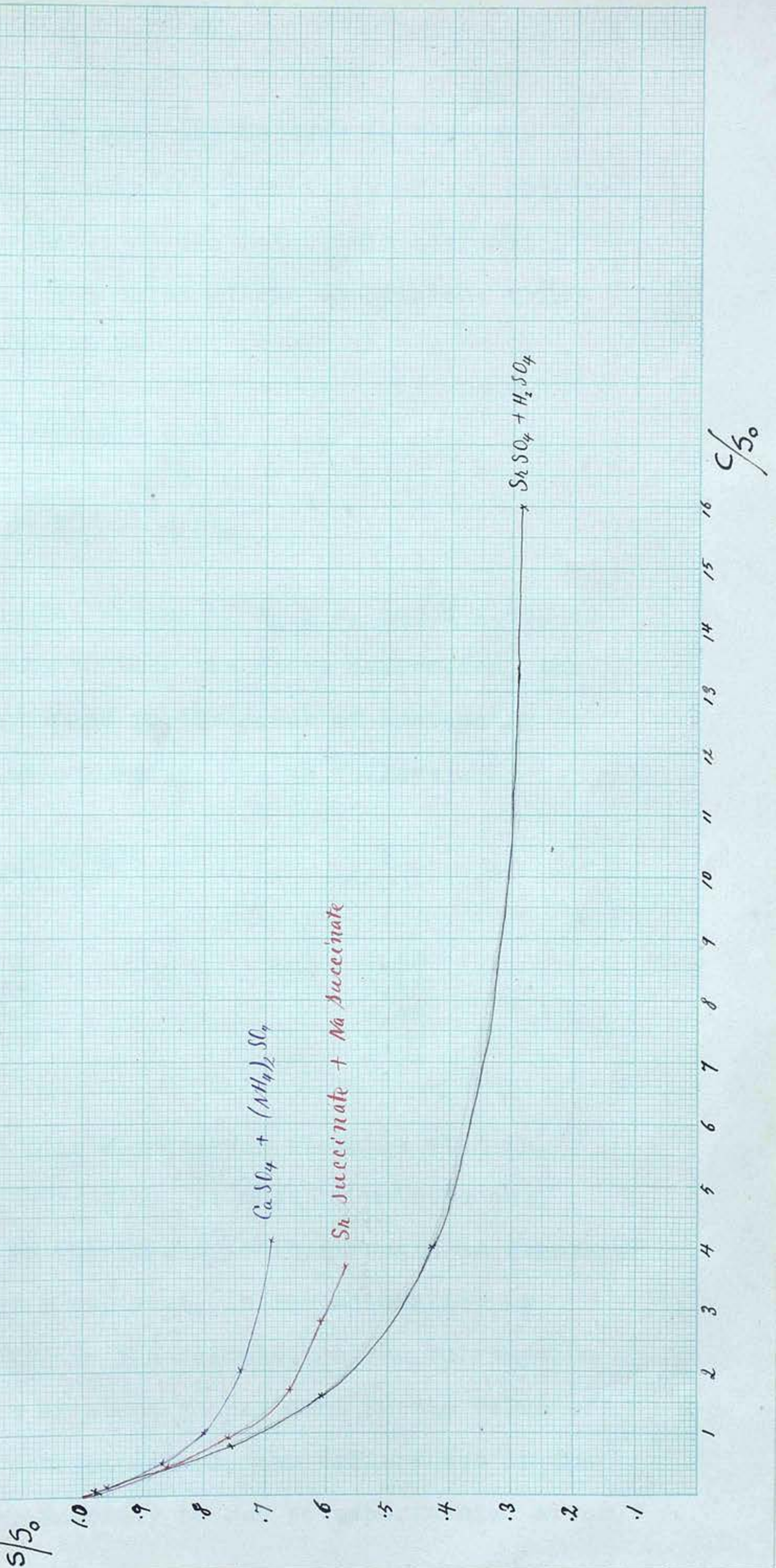
Concentration of acid. c	s (experimental	s^* (theoretical)	$s^\dagger$ (theoretica
0.0000501	0.000615	0.000601	0.000600
0.000501	0.000473	0.000424	0.000435
0.001002	0.000380	0.000301	0.000320
0.002505	0.000268	0.000148	0.000195
0.01002	0.000178	0.000040	0.000070

* Calculated from the equation $s(s + c) = s_o^2$.

† Calculated from the equation $ms(ms + m_{,}c) = (m_o s_o)^2$, where m_o is the degree of ionisation of the salt in its pure saturated solution, and m and $m_{,}$ are the (approximate) ionised fractions of the salt and the acid respectively in presence of one another.

The solubility effect of the sulphuric acid is conveniently shown graphically by plotting the "fractional solubility", s/s_0, against the "fractional concentration", c/s_0. These ratios express respectively the concentrations of the strontium sulphate and of the sulphuric acid in terms of the solubility of the former in pure water.

The graphs obtained in this way are shown on a separate page. On the same diagram are also shown the graphs for the solubility effect of ammonium sulphate on calcium sulphate (solubility data by Sullivan, J.A.C.S., 1905, 27, 532) and of sodium succinate on strontium succinate (Walker, J.C.S., 1925, 61). These bi-bivalent salts are much more soluble than strontium sulphate, their molar solubilities at 25° being respectively 0.0153 and 0.0201, compared with 0.000626 for strontium sulphate. The relative positions of the three curves is in accordance with the observations of Harkins (J.A.C.S. 1911, 33, 1851) and Walker (loc. cit.), who found that the more soluble the saturating salt the less the solubility effect of the common ion.


S/S₀
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
C/S₀
Ca SO₄ + (NH₄)₂ SO₄
Sr Succinate + Na Succinate
Sr SO₄ + H₂ SO₄

The solubility data may be used to test the validity of the formula for solubility effect obtained by Noyes on the basis of the interionic attraction theory (p. 62). The value of the coefficient k in the formula is given by

$$\frac{1/8 \log. \frac{s(s + c)}{s_o^2}}{\sqrt{\sum c' v^2} - \sqrt{8s_o}} .$$

If the experimental values of s_o, s, and c given on p.65 are introduced into the above expression, the values of k, arranged in the order of increasing total solute concentration, are as follows:-

Ionic strength $\frac{1}{2} \sum c' v^2$	k
0.0025	1.55
0.0034	0.75
0.0045	0.65
0.0085	0.58
0.031	0.47

It may be seen that k decreases steadily with increasing ionic strength. It must be pointed out, however, that at the lowest ionic strength an experimental error of 1 per cent. in the solubility is greatly magnified in the calculation and corresponds to a difference of about 30 per cent in the value of k. At higher concentrations, the differences in the values of k can scarcely be due to experimental error. The/

The maximum difference between duplicate solubility determinations is about 1 per cent., which corresponds to a difference of from 2 to 5 per cent. in the value of k (omitting the first value). The lowest value of k is greater than the theoretical value (0.357) and is about twice the value (0.238) that Noyes found best satisfied the experimental facts for salts of higher valence type. It can hardly be said, therefore, that the results obtained here for strontium sulphate show more than a very rough qualitative agreement with the theory.

The decrease of k with increasing ionic strength is noteworthy and is in accordance with the observations of Walker (loc. cit.) who examined the succinates of calcium, strontium, and barium (+ sodium succinate) and magnesium oxalate (+ magnesium sulphate). The value of k, for salts of a given type, appears to depend on and to vary inversely with the solubility of the saturating salt, as the following rounded-off figures show:-

	solubility	k
Calcium succinate (+ $Na_2\overline{Succ}$.)	0.08	0.10
Strontium succinate "	0.02	0.17
Barium succinate "	0.016	0.17
Calcium sulphate (+ $MgSO_4$)	0.015	0.2
Magnesium oxalate "	0.003	0.3
Strontium sulphate (+H_2SO_4)	0.0006	0.6

In conclusion, it may be remarked that the decrease in the solubility of strontium sulphate produced/

produced by the addition of sulphuric acid is of practical interest in analytical chemistry. In precipitating strontium sulphate from 200 cc. of a dilute solution, the addition of an excess of 1 cc. of ordinary dilute (2-molar) sulphuric acid will reduce the solubility of the precipitate to about one-fourth of its solubility in water.

SUMMARY.

(1) The solubility of strontium sulphate in water at temperature ranging from 25° to 100° has been determined by a direct gravimetric method and by a conductivity method. At 30° the results obtained by the two methods agree closely, the solubility at this temperature being 115 to 116 milligrams per litre.

According to the gravimetric method of determination, the solubility increases with rising temperature, reaches a maximum at about 60°, and falls again between 60° and 100°, whereas according to the conductivity method the solubility decreases steadily with rising temperature, and at all temperature~~s~~ above 30° the results are lower than those obtained by the gravimetric method. The fact that the heat of solution of strontium sulphate at ordinary temperature is negative is in accordance with the gravimetric results.

(2) The solubility of strontium sulphate in solutions of sulphuric acid of varying concentration has been determined. The "solubility effect" of the common ion is less than would be predicted by the "constant ionic solubility product rule", but is greater than has been observed with more soluble/

soluble saturating salts.

The solubility data were examined from the point of view of the interionic attraction theory as applied by Noyes to the solubility effect of one electrolyte on another. The experimental results show only a very rough qualitative agreement with the requirements of the theory.

I have pleasure in recording my thanks to Dr Sydney A. Kay for his assistance and advice, and to Sir James Walker for the interest he has taken in my work in Edinburgh.