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THE SOLUBILITY OF SILVER CHLORIDE, BARIUM SULPHATE, AND CALCIUM SULPHATE AT HIGH TEMPERATURES.

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Contents.

1. Outline of the Investigation.

The solubility of many difficultly soluble salts at room temperatures has already been determined by several investigators[1] by means of measurements of the electrical conductance of the saturated solutions. At the higher temperature of 100° Böttger,[2] working in this laboratory with the platinum-lined steel bomb used for conductivity measurements, determined the conductance of the saturated solutions of three silver salts.

The purpose of the present investigation was to apply this method to other salts at the high temperatures. The solubilities of silver chloride and barium sulphate, which are of great importance in analytical chemistry, were determined at 18, 50 and 100°. In addition, conductance measurements of saturated solutions of calcium sulphate were made at the temperatures 18, 50, 100, 156 and 218°, and the solubility and existence of its three forms, gypsum, soluble anhydrite, and ordinary anhydrite, were studied by this method. This substance was chosen for investigation partly because of the great importance of a knowledge of its solubility relations from the standpoint of geological and industrial chemical processes.

2. Previous Investigations upon These Substances.

Kohlrausch and Rose, Holleman, and Böttger[3] measured the conductance of saturated solutions of silver chloride, barium sulphate, and gypsum at temperatures between 2 and 42°. After subtracting the measured conductance of the water, they calculated the corresponding solubility by means of approximate values of the equivalent conductance

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[1] F. Kohlrausch and Rose, *Z. physik. Chem.*, **12**, 234 (1893); Holleman, *Ibid.*, **12**, 125 (1893); F. Kohlrausch, *Ibid.*, **44**, 197 (1903); **64**, 129 (1908); W. Böttger, *Ibid.*, **46**, 521 (1903).

[2] *Z. physik. Chem.*, **56**, 83 (1906).

[3] *Loc. cit.*

at zero concentration. Two later articles of Kohlrausch give new values of the solubility, based upon more recent determinations of the equivalent conductances.

Goodwin[1] calculated the solubility of silver chloride at 25° from measurements of the potential difference of two silver electrodes, one of which was placed in a silver nitrate solution and the other in a potassium chloride solution saturated with silver chloride.

Böttger, as above stated, made preliminary experiments on the solubility of silver chloride at 100° in the platinum-lined bomb.

The solubility of gypsum between 0 and 100° has been determined by numerous investigators by evaporating a known volume of its saturated solution and weighing the residue. The literature relating thereto has been discussed by Hulett and Allen[2] in connection with their own careful determinations.

At higher temperatures Tilden and Shenstone[3] made rough measurements by heating an excess of solid salt with water in a silver-plated gun-metal tube, decanting while still hot through a platinum gauze partition into another part of the tube, cooling in the air, and analyzing the decanted solution. Boyer-Guillon[4] determined the solubility of calcium sulphate by heating a solution of it in a bronze autoclave for some hours at the temperature in question and then withdrawing portions through an asbestos filter.

3. Apparatus and Method.

The conductance measurements were made in a bomb such as is described by Noyes and Coolidge.[5] The electrode was of platinum-iridium, a cylinder dome-capped in shape, and polished so that none of the solid salt in suspension would adhere to it. The bomb carriage[6] was connected by means of gearing to an electric motor so that the bomb could be turned over and over continuously about twelve times per minute. The measurements from 18–156° were made in this way within an electrically heated bath of liquid pseudocumene. Those at 218° were made in a naphthalene-vapor bath, the bomb being rotated occasionally by hand.

The conductance capacity of the bomb was determined by measuring in it the conductances of 0.002 normal potassium and sodium chloride solutions at 18°, and was thus found to be 0.1224 and 0.1225.

It was proved that the conductance of a 0.01 normal potassium chloride solution in the bomb was not measurably changed by the addition

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[1] *Z. physik. Chem.*, **13**, 645 (1894).

[2] THIS JOURNAL, **24**, 676–9 (1902).

[3] *Phil. Trans. Royal Soc.*, **175** *A*, 31 (1884).

[4] *Ann. Conservatoire Arts et Metiers* [3], **2**, 207 (1900).

[5] *Publ. Carnegie Inst., Washington*, **63**, 59.

[6] *Loc. cit.*, p. 64.

of some solid silver chloride, showing that the presence of the solid in suspension would make no appreciable error in the conductance measurements.

The solubility determinations were made in the following manner, except in the cases noted in a later section: About one cubic centimeter of the moist well-washed salt was placed in the bomb and further washed by decantation. Water whose conductance had been determined in a glass cell was introduced into the bomb, and the bomb was closed. The bomb was next rotated at each successive temperature until the conductance was constant for fifteen minutes. The bomb was then carefully opened and the solution decanted off, a quantity of fresh water was added to the same salt, and the process was repeated until the conductances of the successive solutions at each temperature were practically identical.

Conductance measurements with water alone were made in the bomb under the same conditions, so as to determine the water correction. In these cases, the same method of treatment and the same time of heating were followed. The results are given in Table I:

TABLE I.—VALUES OF THE SPECIFIC CONDUCTANCE × 10^6 OF WATER.

Date. 1908.	Glass cell (18°).	Bomb at 18°. Initial.	Bomb at 18°. Final.	Bomb at 50°. Initial.	Bomb at 50°. Final.	Bomb at 100°.
Feb. 5	0.49	0.65	0.68	1.29	1.34	2.66
Feb. 7	0.47	0.58	0.67	1.15	1.24	2.25
Feb. 11	0.55	0.72	0.79	1.28	1.42	2.42
Mean,	0.50	0.65	0.71	1.24	1.34	2.45

4. Preparation of the Materials.

Two samples of silver chloride were prepared in a photographic darkroom illuminated only by red light. Sample I was prepared as follows: A solution, approximately 0.1 normal, of silver nitrate was heated to 100° in a water bath. A solution of 0.1 normal hydrochloric acid was dropped slowly into the hot silver nitrate solution with constant stirring. The silver chloride was washed by decantation, the chloride settling out very quickly. Sample II was prepared in the same way from silver nitrate and potassium chloride solutions. The washed chloride was, however, in this case further washed by shaking with a dilute ammonia solution in a bottle. The remaining chloride was treated with cold ammonia, 0.96, until about three-fourths of it had dissolved, and the solution was separated by decantation. This solution was heated slowly with vigorous stirring, and the precipitated chloride was washed by decantation. Both samples were kept under water in the dark.

Barium sulphate was prepared by dropping a 0.1 normal barium chloride solution into a hot 0.1 normal sulphuric acid solution which was constantly agitated by a revolving stirrer. The salt was washed by decantation and rotated for hours in hot water. The smaller particles were then washed away by decantation.

Calcium sulphate was prepared both in the form of gypsum and of anhydrite. A quantity of Kahlbaum's C. P. calcium sulphate was washed by long agitation with several portions of water. Conductivity water was then saturated with this salt at the temperature of its maximum solubility (35–40°), and the solution was then partially evaporated at a temperature below 60°; yielding the sample of gypsum. The anhydrite was obtained by dehydrating the salt so obtained by heating at 200° for twelve hours, when a constant weight had resulted.

The water used in the solubility determinations was prepared by redistilling ordinary distilled water to which alkaline permanganate solution was added, from a copper still with a tin condenser. This water was used directly in the work with calcium sulphate. For the solubility experiments with silver chloride and barium sulphate, this water was again redistilled from a special tin-lined still with a block-tin condenser. Only those portions from either distillation which had a specific conductance less than 0.8 × 10^{-6} were used in the investigation.

5. Conductance of Solutions Saturated with Silver Chloride and Barium Sulphate.

The specific conductances of the saturated solutions of silver chloride and barium sulphate are given in Table II. The column headings are for the most part self-explanatory. All the conductance values are expressed in reciprocal ohms and multiplied by 10^6. The specific conductance value given for the water employed are those measured in the glass cell at 18 or 25°:

TABLE II.—SPECIFIC CONDUCTANCE DATA FOR SATURATED SOLUTIONS OF SILVER CHLORIDE AND BARIUM SULPHATE.

Date. 1908.	Salt and sample. AgCl.	Water at 18 or 25°.	18 or 25°.[1]		50°.		100°.		
			Init.	Fin.	Init.	Fin.	Init.	Fin.	156°.
Feb. 19	I	0.61	2.08	2.94	9.39	10.75	61.8	....	....
Feb. 20		0.54	2.06	3.04	9.46	10.75	61.6	....	....
Feb. 26		0.54	2.05	2.91	9.32	10.60	61.6	....	....
Feb. 27		0.49	1.89	2.48	9.10	9.96	61.2	....	....
Feb. 28	II	0.49	2.00	3.52	9.75	11.78	63.3	....	....
Mar. 2		0.65	1.99	2.73	9.25	10.40	62.0	....	....
Mar. 3		0.56	2.00	2.52	9.32	10.03	61.6	....	....
	$BaSO_4$.								
July 27	I	0.80	3.90[2]	8.82	7.85	...	16.93	....	24.1
July 28		0.60	3.75[2]	6.42	7.79	11.60	16.54	21.2	20.2[3]
July 29		0.65	3.81	3.99	7.73	7.93	16.45	....	....
			(3.99)	6.60	....	...	...	....	19.8[4]

[1] 18° in the experiments with AgCl, 25° in those with $BaSO_4$.

[2] The values at 18° were 3.01 and 2.94 in these two experiments.

[3] This increased to 24.6 in 45 minutes.

[4] This increased to 25.0 in 30 minutes.

The conductance of the saturated silver chloride solutions became constant in about twenty minutes. Preliminary experiments carried to the higher temperature 156° showed the impracticability of making any determinations above 100°. The large increase of conductance with the time in the case of barium sulphate at 156° is shown in the footnotes of the table. When, as in the third experiment, the solution was not heated above 100°, the final value at 25° is seen to be only slightly larger than the initial value; but when heated to 156°, as in the first two experiments, it was nearly doubled in less than an hour. The last row in the table shows directly the effect of heating to 156° the solution (represented by the row above) which had been previously heated to 100°.

6. The Solubility Values for Silver Chloride and Barium Sulphate.

From the specific conductances of the saturated solutions given in Table II, the conductance of the water was first subtracted, this being derived from Table I by multiplying the mean "bomb" values there given by the ratio to 0.50 of the specific conductance shown by the water in question when measured in the glass cell. As final values for barium sulphate were adopted the so-called initial values obtained in the last experiment (on July 29th) when the salt had been most fully leached out. As final values for silver chloride at 18 and 50° the mean of the initial values obtained in the last experiment with each sample (on Feb. 27th and March 3rd) were adopted. The value for silver chloride at 100° was corrected by determining the temperature coefficient of the contamination from the difference of the initial and final values at 18 and 50° and subtracting the proportionate value at 100°. The following specific conductances × 10^6 were thus derived:

TABLE III.—SPECIFIC CONDUCTANCE OF SATURATED SOLUTIONS OF SILVER CHLORIDE AND BARIUM SULPHATE.

Substance.	18°.	25°.	50°.	100°.
Silver chloride	1.26	....	7.90	57.9
Barium sulphate	2.30	3.00	6.45	14.0

By dividing the values given in Table III by the sum of the equivalent conductances of the separate ions, as given by Johnston,[1] the ion-concentrations in the saturated solutions were calculated. The results expressed in milli-equivalents per liter are given in Table IV:

TABLE IV.—ION CONCENTRATION IN THE SATURATED SOLUTIONS OF SILVER CHLORIDE AND BARIUM SULPHATE.

Substance.	18°.	25°.	50°.	100°.
Silver chloride	0.0105	....	0.0363	0.146
Barium sulphate	0.0187	0.0208	0.0281	0.0322

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[1] THIS JOURNAL, **31**, 1015 (1909). The values of Λ_0 which were employed are:

	18°.	25°.	50°.	100°.
AgCl	119.8	...	217	395
$BaSO_4$	123	144	229	434

These values of the ion-concentration differ somewhat from those of the total concentration of the salt in the saturated solutions. The extent of the difference may be determined by estimating the degree of ionization in these very dilute saturated solutions by means of the ionization formula $(1 - \gamma) = K\ C^{0.5}$, which corresponds to the conductance formula employed by Kohlrausch. The constant K for barium sulphate was assumed to be the same as for calcium and magnesium sulphates, and was derived for these salts from the ionization data at 2 millinormal given in Table VIII. That for silver chloride was assumed to be the same as for silver nitrate, the ionization value for the latter at 2 millinormal given by Noyes and Melcher being employed. By dividing the ion concentration given in Table IV by the ionization values so determined, the total concentrations (in milli-equivalents per liter) in the saturated solutions, given in Table V, were obtained:

TABLE V.—SOLUBILITY OF SILVER CHLORIDE AND BARIUM SULPHATE.

Substance.	18°.	25°.	50°.	100°.
Silver chloride..............	0.0105	....	0.0365	0.147
Barium sulphate............	0.0190	0.0212	0.0288	0.0334

These results at 18° may be compared with those previously found by Kohlrausch and Böttger. Kohlrausch's[1] values are 0.0094 for silver chloride and 0.0197 for precipitated barium sulphate. It seems probable that the lower values are more accurate in each case. Böttger's[2] values for silver chloride at 19.95° were 3 per cent. larger than Kohlrausch's. His value[3] for the specific conductance of that salt at 100° is 56.7×10^{-6}, which is nearly identical with that given in Table III. When divided with the same Λ_0 value as that used by me, it gives a solubility of 0.0143 milli-equivalents per liter. At the time of his measurements the agitation of the bomb was done by hand instead of by a mechanical rotating arrangement, which made the securing of saturation at exactly 100° more difficult.

From the solubilities of these salts at 18, 50, and 100°, the heat absorbed by the solution of one formula weight of the salt was calculated by solving the two simultaneous equations:

$$\log_e \frac{S_{50}}{S_{18}} = \frac{L_0}{2R}\left(\frac{1}{291} - \frac{1}{323}\right) + \frac{\alpha}{2R}\ \log_e \frac{323}{291}\ .$$

$$\log_e \frac{S_{100}}{S_{50}} = \frac{L_0}{2R}\left(\frac{1}{323} - \frac{1}{373}\right) + \frac{\alpha}{2R}\ \log_e \frac{373}{323}\ .$$

These are the forms obtained by integrating the fundamental thermodynamic equation

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[1] *Z. physik. Chem.*, **64**, 148, 152 (1908).

[2] *Ibid.*, **46**, 602 (1903).

[3] *Ibid.*, **56**, 93 (1906).

$$d \log S = \frac{L}{2RT^2}\, dT$$

for the case that $L = L_0 + \alpha T$, and by substituting the appropriate values of T.

By these calculations the value in calories of L, the heat absorbed by the solution of one formula weight of the salt at the absolute temperature T was found to be:

$$L = 34200 - 60.5\ T \text{ for silver chloride;}$$

and $$L = 30800 - 85.2\ T \text{ for barium sulphate.}$$

For $T = 273 + 18$, this expression yields:

$$L = 16600 \text{ cal. for AgCl; and } L = 6000 \text{ cal. for } BaSO_4.$$

The heat evolved by the precipitation of these salts when produced by the metathesis of silver nitrate and hydrochloric acid or of soluble barium salts and sodium sulphate was found by Thomsen to be 15800 calories for silver chloride[1] and to be 4970 calories for barium sulphate.[2] Considering the inaccuracy of the very small solubility values at 18°, the agreement is perhaps as close as could have been expected.

7. Conductance of Calcium Sulphate Solutions of Known Concentration.

A stock solution of calcium sulphate was made by dissolving some of the salt in conductivity water. The concentration was determined by precipitating the calcium as oxalate, filtering, and washing the precipitated calcium oxalate, and then titrating it in hot acid solution with potassium permanganate solution, which had been standardized against sodium oxalate ("nach Sörensen"). It contained 23.50 milli-equivalents per liter. More dilute solutions were made by weighing out some of the stock solution and making up to a known volume.

The conductivity data are given in Table VI. The first two columns are self-explanatory. The third column gives the concentration at the temperature of the measurement expressed in milli-equivalents per liter. The fourth column gives the specific conductance of the solution corrected for all instrumental errors. The fifth column gives the calculated equivalent conductance after correcting for the conductance of the water.

Using as a means of interpolation the formula $C(\Lambda_0 - \Lambda) = K(C\Lambda)^{1.5}$, the values at round concentrations given in Table VII were obtained. The values at zero concentration are the sums of those derived for the calcium and sulphate ions by Johnston[3] from measurements with other substances.

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[1] Ostwald's *Lehrbuch d. allgemeinen Chem.*, **2**, I, 335.

[2] Thomsen's "Thermochemistry," Ramsay's Series, p. 118. Mean of the results with barium chloride, nitrate, and chlorate.

[3] THIS JOURNAL, **31**, 1015 (1909).

TABLE VI.—CONDUCTANCE OF CALCIUM SULPHATE SOLUTIONS.

Date. 1908.	Concentration at 4°.	Temperature t°.	Concentration at t°.	Specific conductance x 10^6.	Equivalent conductance.
May 11	1.976[1]	18	1.973	193.7	97.8
		50	1.952	346.7	176.7
		100	1.894	568.0	299.0
		156	1.799	637.0	352.0
May 5	3.951	18	3.946	354.7	89.7
		50	3.904	629.0	160.8
		100	3.788	990.0	261.0
		156	3.598	1044.0	289.0
		18.	3.946	355.1	89.8
May 6	7.988	18	7.978	645.0	80.7
		50	7.894	1127.0	142.7
		100	7.658	1706.0	222.0
May 7	23.53	18	23.50	1558.0	66.2
		50	23.25	2640.0	113.5
		100	22.55	3800.0	168.5

The value of the exponent n in the expression $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ that best corresponds to these results at 18° was found to be 1.50. It is therefore of about the same magnitude as in the case of the uni-univalent and uni-bivalent salts previously studied. In the case of the values of Hulett, which extend over a wider range of concentration, the double curvature[2] due to a change in the value of the exponent n was clearly evident.

TABLE VII.—EQUIVALENT CONDUCTANCE OF CALCIUM SULPHATE AT ROUND CONCENTRATIONS.

Concentration.	18°.	50°.	100°.	156°.
0	119.0	223.0	425.0	682
2.0	97.7	176.0	295.0	341
4.0	89.6	160.0	258.0	280
8.0	80.7	142.4	220.5	...
10.0	77.7	136.5	209.0	...
20.0	68.5	118.0	174.0	...

Plotting the data of Hulett[3] in the same way, so as to get the values of the equivalent conductance for corresponding concentrations, the following results were obtained. The two series are seen to be in excellent agreement:

Concentration.	Melcher.	Hulett.
2.00	97.7	97.4
4.00	89.6	89.6
8.00	80.7	80.7
10.00	77.7	77.7
20.00	68.5	68.6

[1] This solution was heated to 218°, but even this dilute solution was so supersaturated that the salt began to precipitate out before the temperature was reached.

[2] See THIS JOURNAL, **31**, 746, 1000 (1909).

[3] *Z. physik. Chem.*, **42**, 577 (1902).

From the equivalent conductance values given in Table VII, the ratio 100 Λ/Λ_0 corresponding to the percentage ionization of the calcium sulphate was calculated. The resulting values are given in Table VIII beside those previously obtained[1] for magnesium sulphate. The degree of ionization of calcium sulphate is seen to be substantially the same as that of magnesium sulphate at 18°, but distinctly less at 100 and 156°.

TABLE VIII.—PERCENTAGE IONIZATION OF CALCIUM SULPHATE.

Temperature.	Concentration.	$CaSO_4$.	$MgSO_4$.
18°	2	82.0	82.6
	10	65.2	66.7
	20	57.5	59.2
50°	2	79.0	....
	10	61.0	....
	20	53.0	....
100°	2	69.0	71.0
	10	49.0	52.0
	20	41.0	45.0
156°	2	50.0	55.0

8. The Specific Conductance of Solutions Saturated with Calcium Sulphate.

The data obtained with the saturated solutions of calcium sulphate are contained in Table IX. The first column contains the number of the experiment, each series of measurements made with a new charging of the bomb with fresh water being indicated by a letter attached to the preceding number and each series where both salt and water were renewed being given a separate number. The second column contains the date. The third shows the form of solid salt which had been originally introduced, G representing gypsum and A anhydrite. The fourth column contains the (corrected) temperature. The fifth and sixth columns show the values of the specific conductance in reciprocal ohms multiplied by 10^6, those under "first value" being measured as soon as the temperature of the bath had presumably been attained and those under "last value" being measured after the interval of time in minutes shown in the seventh column. The last column shows the change in specific conductance per minute which was still taking place during the last ten minutes of that interval; where dots are inserted, the reading was constant. Whether saturation was approached from a higher or lower temperature is indicated by the temperature given in the row next above, except that in passing from 218 to 156° the bomb was always cooled *below* the latter temperature before introducing it into the bath.

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[1] *Publ. Carnegie Inst., Washington* **63**, 108.

TABLE IX.—CONDUCTANCE DATA FOR THE SATURATED SOLUTIONS OF CALCIUM SULPHATE.

Expt. No.	Date. 1908.	Substance added.	Temperature.	Specific conductance × 10^6		Time interval.	Change per minute.
				First value.	Last value.		
1	Mar. 26	G	18	1785	1860	60	....
			50	3200	3225	35	....
	Mar. 27		100	3940	3880	40	....
			156	1605	1600	30	
			218	460	375	50	—3.1
	Mar. 30		18	1820	1920	30	+3.0
2	Mar. 30	G	18	1805	1865	60	....
			50	3220	3225	30	....
	Mar. 31		100	3890	3885	20	....
			156	1600	1580	30	....
3	Apr. 2	G	18	1860	1870	30	....
			50	3230	3230	25	....
			100	3925	3880	30	....
			156	1600	1590	30	....
	Apr. 3		218	463	299	120	....
	Apr. 6		156	1600	1040	400	—0.25
	Apr. 7		218	358	315	60	....
4	Apr. 9[1]	A	100	4210	4045	50	....
			156	1545	955	220	—0.25
			218	225	235	140	....
			156	930	870	75	....
			100	1950	2035	75	+0.4
4*a*	Apr. 13		100	2970	2690	60	—1.4
			156	1200	915	60	—1.0
			218	230	210	60	....
			156	935	835	40	....
			161[2]	....	(755)	...	....
			156	810	830	30	....
			100	1860	1975	30	....
			95[2]	....	(2055)	...	....
			100	2050	2030	30	—0.4
4*b*	Apr. 14		218	232	202	70	....
			161[2]	....	(795)	..	....
			156	795	840	45	....
			100	1845	1965	30	....
			95[2]	....	(2020)	..	....
			100	2015	1990	45	—0.2
5	May 21	G	50	3230	3225	30	....
5*a*	May 21		18	1865	1870	20	....
			50	3230	3225	20	....
			100	3880	3880	20	....

[1] From April 9th to 14th, inclusive, the substance was always in contact with a solution whose temperature was above the transition point of gypsum and anhydrite.

[2] The bomb was rotated in the neighborhood of these temperatures until the conductance was practically constant. The values of the latter (enclosed within parenthesis) are very rough ones.

TABLE IX.—CONDUCTANCE DATA FOR THE SATURATED SOLUTIONS OF CALCIUM SULPHATE—(*Continued*).

				Specific conductance × 10^6			
Expt. No.	Date. 1908.	Substance added.	Temperature.	First value.	Last value.	Time interval.	Change per minute.
			110[1]	....	(3750)	..	....
			100	3870	3885	20	...
			135[1]	....	(2510)	..	....
			100	3820	3825	25	....
			156	1625	1560	30	....
			100	3810	3825	15	....
			50	5250	5850	40	+1.1
	May 22		100	4520	3830	85	....
			67[1]	....	(3675)	..	....
			100	4135	3825	70	....
			50	3275	3185	30	....
	May 25		156	1565	1560	240	....
			100	3825	3825	60	....
			50	....	5660	90	+1.1
	May 26		50	....	3225	180	....
	May 27		218	....	216	450	....
	May 28		218	222	215	90	....
			156	820	830	60	....
			100	1740	1950	110	....
			50	2300	2635	35	+3.0

In deriving final values of the conductance and solubility at the different temperatures it is necessary to take into consideration the character of the solid phase in contact with the solution, for this may be present in different forms under the different conditions. To make clear the relations here involved, the results of two of the most complete experiments (No. 5*a* and the latter part of No. 4*a*) are represented graphically in Figure 1, in which the abscissae denote somewhat arbitrary intervals of time. The upper graph shows the behavior of a solution made by introducing gypsum as the solid substance. This is the solid phase still present in the first measurement at 100°, and the figure shows that heating to 110° for a short time does not transform it, since on returning to 100° the conductance has the same value as before. After heating to 135°, however, the conductance is seen to return to an appreciably lower value at 100°, and this same value is again obtained after heating to 156°. Considering now the lower graph, which represents the behavior of a solution made by adding anhydrite to hot water (above 70°), it will be seen that upon coming down from 218 to 156° and later to 100° much lower values of the conductance are obtained at both temperatures

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[1] The bomb was rotated in the neighborhood of these temperatures until the conductance was practically constant. The values of the latter (enclosed within parenthesis) are very rough ones.

(whether approached from above or a little below) than in the other experiment where gypsum was the added substance. These facts make

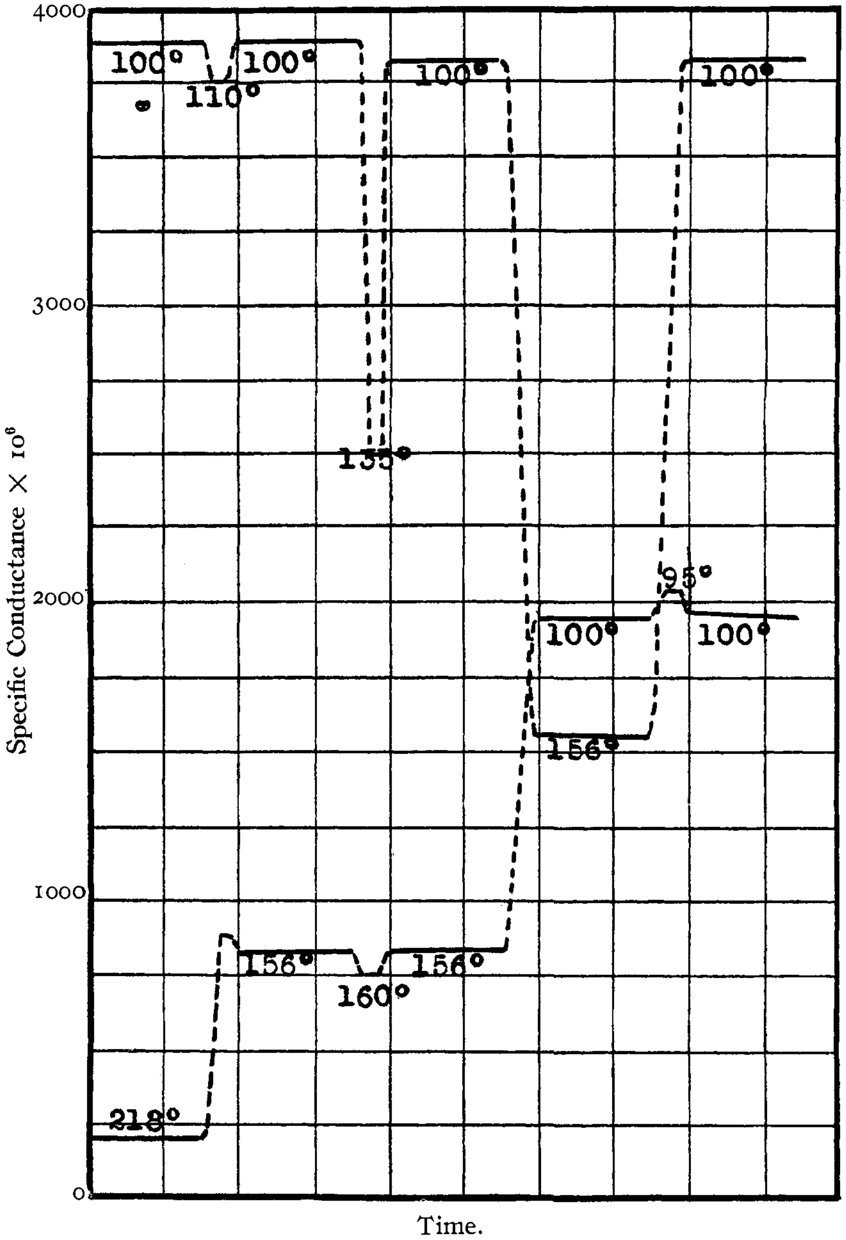

Fig. 1.

it clear that there are in the different cases three different solid phases involved. That corresponding to the highest conductance value at 100° is doubtless gypsum, and that corresponding to the lowest conductance values at 100° and at 156° is doubtless ordinary anhydrite. The intermediate value at 100° and the higher one at 156° must correspond to a third solid phase. This might be either another hydrate or another form of the anhydrous salt. Its solubility relations, namely, the temperature at which its solubility curve intersects that of gypsum and the constancy (at 100 and 156°) of the ratio of its solubility to that of the anhydrite, prove, as will be seen below, that it is the latter and that it is undoubtedly identical with the "soluble anhydrite" of van't Hoff.[1]

Table X contains final values of the conductance of the solutions saturated with these three different forms:[2]

TABLE X.—SPECIFIC CONDUCTANCE × 10^6 OF THE SATURATED SOLUTIONS OF CALCIUM SULPHATE.

	18°.	50°.	100°.	156°.	218°.
Gypsum	1867	3226	3882	....	...
Soluble anhydrite	....	....	3825	1560	...
Anhydrite	....	....	1963	834	211

9. The Solubility Values for Calcium Sulphate.

To determine the corresponding solubility values, the concentrations of calcium sulphate, which would give at the various temperatures the specific conductances recorded in Table X, were calculated as follows: With the data given in Table V for solutions of known concentration plots of $1/\Lambda$ against $(C\Lambda)^{0.5}$ were made, Λ representing as usual the equivalent conductance, C the equivalent concentration, and $C\Lambda$ therefore the specific conductance × 10^3. From these plots the values of Λ corresponding to the values of the specific conductance of the saturated solution were taken off, and by dividing the latter by the former values, the concentrations of the saturated solutions were obtained. The result at 218°, however, is only an estimate obtained by dividing the fairly accurate value of the ion concentration in the saturated solution given below in Table XIII, by the degree of ionization, this latter being estimated to be about 30 per cent. through a consideration of the ionization values at 218° obtained for magnesium sulphate by Noyes and Melcher.[3]

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[1] *Z. phys. Chem.*, 45, 273 (1903).

[2] For the solutions saturated with gypsum at the various temperatures these values are means of all the "last values." For the solutions saturated with anhydrite the mean of the last four values at 156 and 218° given in the table was taken, and at 100° for both forms of anhydrite the mean of all the constant values was taken. For the soluble anhydrite at 156° the mean of the last two measurements was taken.

[3] By plotting their values of the ionization γ against $(C\gamma)^{0.5}$ and extrapolating, it is found that $\gamma = 0.36$ for $C\gamma = 0.2$ millinormal; and we have assumed that for calcium sulphate the value is 15 per cent. less than this, upon the basis of the results at 156°.

This solubility value at 218° is almost certainly correct within 0.1 milli-equivalent.

Table XI contains the solubility values expressed in milli-equivalents per liter:

TABLE XI.—SOLUBILITY VALUES FOR CALCIUM SULPHATE.

Form.	18°.	50°.	100°.	156°.	218°.
Gypsum	29.5	30.0	23.3	...	...
Soluble anhydrite	....	....	22.8	6.4	...
Anhydrite	....	....	9.2	2.7	0.7

The results obtained by other investigators or interpolated from their values are placed beside mine in Table XII:

TABLE XII.—COMPARISON OF THE SOLUBILITY VALUES WITH THOSE OBTAINED BY OTHER INVESTIGATORS.

Solid phase.	Temperature.	Melcher.	Hulett and Allen.[1]	Boyer-Guillon.[2]	Tilden and Shenstone.[3]
Gypsum	18°	29.5	29.6	....	...
"	50°	30.0	30.1	....	...
"	100°	23.3	23.8	24.2	...
Anhydrite	200°	0.9	....	....	...
Soluble anhydrite	200°	....	....	2.3	3.7

It will be seen that the new values agree almost perfectly with those obtained by Hulett and Allen by an entirely different method. They also agree well with the results of Boyer-Guillon at 100 and 156°. His much higher value at 200° seems clearly to have been due to the fact that the solid phase in contact with the solution was still soluble anhydrite. This conclusion is confirmed by the fact that the ratio (2.3 : 0.9 = 2.5) of the solubility of the two anhydrites at 200° is nearly the same as that (2.4) at 156°—a relationship discussed more fully below. His results therefore supplement those here presented in an important way by showing the solubility of that phase at higher temperatures than those at which it was determined in these experiments. The values of Tilden and Shenstone are probably too high, owing to errors involved in their method.

It seems desirable to give also the values of the equivalent concentrations of the ions in the saturated solutions. These are given in Table XIII. They were obtained by dividing the measured values of the specific conductance given in Table X by the values of $\Lambda_{Ca} + \Lambda_{SO_4}$ (at zero concentration) as computed by Johnston:[4]

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[1] THIS JOURNAL, **24,** 474 (1902).

[2] *Ann. Conservatoire Arts et Metiers* [3], **2,** 209 (1900).

[3] *Trans. Roy. Soc.* (*London*), **175***A*, 31 (1884).

[4] THIS JOURNAL, **31,** 1015 (1909). The values of $\Lambda_{Ca} + \Lambda_{SO_4}$ employed are:

18°.	50°.	100°.	156°.	218°.
119	223	4.25	68.2	1060

The value at 218°, not being given by Johnston, was assumed to be somewhat (2 per cent.) less (as at 156°) than that previously computed for magnesium sulphate by Noyes and Melcher.

TABLE XIII.—EQUIVALENT CONCENTRATION OF IONIZED CALCIUM SULPHATE IN THE SATURATED SOLUTIONS.

Form.	18°.	50°.	100°.	156°.	218°.
Gypsum	15.69	14.47	9.13	....	....
Soluble anhydrite	...	...	9.00	2.29	....
Anhydrite	...	...	4.62	1.22	0.20

A comparison of these values with those given in Table XI shows that the ionization in the solution saturated at 100° with gypsum is 39 per cent. and that that in the solution saturated at 156° with anhydrite is 45 per cent.

10. Discussion of the Solubility Relations of Calcium Sulphate.

In order to make clearer the solubility relations of calcium sulphate, the values given in Table XI are represented graphically in Fig. 2. The curve given for gypsum has been completed with the aid of the data of Hulett and Allen, and that for soluble anhydrite with the aid of those of Boyer-Guillon. An additional point at 60° upon the anhydrite curve has been furnished by van't Hoff's determination[1] of the transition temperature for gypsum and anhydrite.

Attention may be called to the following facts shown by a consideration of the diagram and the values of Table XI:

Anhydrite is the stable form at temperatures above 60°. Its solubility decreases with great rapidity with rising temperature, having at 218° a value only one-fortieth as great as that of gypsum at 18°.

The solubility curve for soluble anhydrite cuts that for gypsum at a point corresponding to a temperature of about 97°. The transition temperature of these two forms was estimated by van't Hoff[2] from vapor-pressure measurements to be 93°, thus a few degrees lower. The agreement is, however, as close as could be expected.

The ratio of the solubility of soluble anhydrite to that of ordinary anhydrite is almost the same at 100 and at 156°, namely 2.48 at 100° and 2.37 at 156°. This fact is significant in showing that the former solid substance is, as assumed, another form of anhydrous calcium sulphate and not a hydrate, for it follows from the thermodynamic equation $d \log \frac{S_{\mathrm{II}}}{S_{\mathrm{I}}} = \frac{Q}{RT^2}\, dT$, that, when $S_{\mathrm{II}}/S_{\mathrm{I}}$, the ratio of the solubilities of the two forms is constant, the heat of transition Q is zero. While this would be highly improbable for the transition of an anhydrous into a hydrated salt, it is to be expected that the value of the heat of transition of two solid anhydrous substances of the same chemical composition would be very small.

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[1] See Landolt-Bornstein-Meyerhoffer Tabellen, p. 529.

[2] *Z. phys. Chem.*, **45**, 279 (1903). Compare, however, the statements of Davis (*J. Soc. Chem. Ind.*, **26**, 732 (1907)) in regard to this equilibrium.

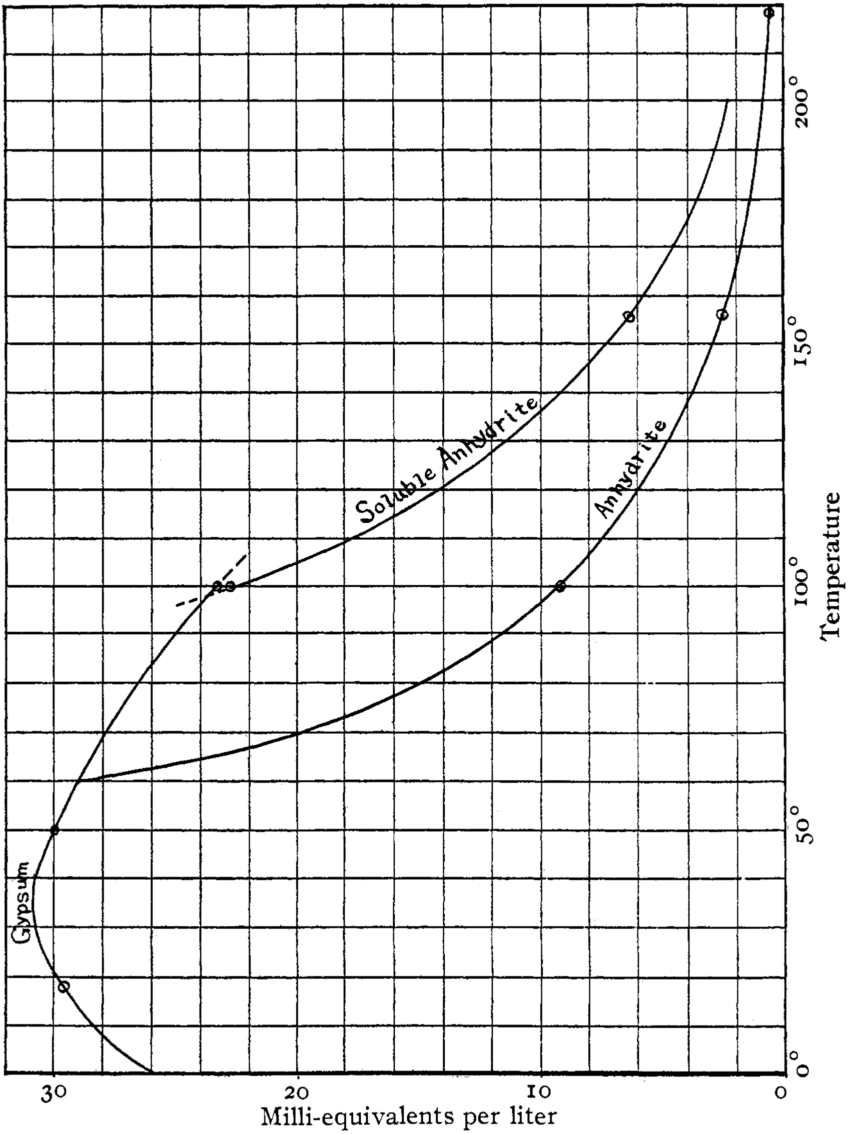

Fig. 2.

11. Summary.

In this article have been presented the results obtained by measuring in a platinum-lined steel bomb provided with a mechanism for rotating it within a liquid bath the conductance of solutions saturated separately with silver chloride and barium sulphate at 18, 50, and 100°, and with calcium sulphate at these temperatures, and also at 156 and 218°. The corresponding solubilities were calculated by dividing the values of the specific conductance so obtained by the appropriate values of the equivalent conductance, which last were derived in the case of the first two salts from the values for the separate ions at zero concentration, and in the case of the calcium sulphate from measurements (also presented above) of the conductance of solutions of it of known concentration. The final solubility values will be found in Tables V and XI, on pages 55 and 63. The heats of solution of silver chloride and barium sulphate were also calculated from these data.

In the case of calcium sulphate, the investigation included the study of the solubility relations of the three forms: gypsum, soluble anhydrite, and ordinary anhydrite. These relations are represented graphically in Fig. 2 on page 65. The transition temperature for the metastable system gypsum, soluble anhydrite, solution, was found, from the point of intersection of the solubility curves, to be about 97°. The solubility of the ordinary anhydrite was shown to decrease enormously with rising temperature, namely from 29.0 milli-equivalents per liter at 60°, where, according to van't Hoff, it is in stable equilibrium with gypsum, to 0.7 milli-equivalents per liter at 218°.

The ion concentrations in the saturated solutions of calcium sulphate have also been calculated and presented in Table XIII, on page 64.

The ionization relations of calcium sulphate have been compared with those for magnesium sulphate previously investigated in this laboratory by Noyes and Melcher. At 18° the degrees of ionization of the two salts are nearly identical; but at 100 and 156° the ionization of the calcium salt is a few per cent. less than that of the magnesium salt at corresponding concentrations.

This investigation has been carried out under the direction of Professor A. A. Noyes with the aid of a grant made to him by the Carnegie Institution of Washington. It is desired to express here grateful acknowledgment of this financial aid, by which this research has been made possible.

BOSTON, October, 1909.

THE PREPARATION OF PERCHLORIC ACID FROM SODIUM PERCHLORATE.[1]

BY FRANK C. MATHERS.

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Most of the methods for the preparation of perchloric acid depend upon the distillation under reduced pressure of a mixture of a perchlorate

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[1] NOTE.—This investigation was the result of a search for a cheap and convenient method for the preparation of perchloric acid, to be used in making perchlorate baths for the electroplating and refining of metals as described in the United States Patent, No. 931,944, issued to the author.