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**THE EFFECT OF SALTS UPON THE SOLUBILITY OF OTHER SALTS,  
V. THE SOLUBILITY OF UNIBIVALENT SALTS IN SOLUTIONS OF SALTS OF DIFFERENT TYPES.**

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### 1. Introduction.

There has been a marked tendency among chemists to apply the solubility-product principle, usually together with the principle of the constancy of the concentration of the unionized part, to univalent salts, even though there are several cases in the literature in which it is clearly shown that the addition of certain salts with a common ion may cause only a slight lowering, or even an increase in the solubility. Even the investigators who have obtained the data which show this fact regard the solubility-product principle as true, and seek to harmonize their data with the theory by the assumption of a *specific* double salt or intermediate ion. In no case has there been a suggestion that the effect is a general one, or that double salts or intermediate ions occur other than with certain specific salts, which are therefore supposed to be abnormal in their behavior. A comparison of the meager existing data<sup>1</sup> suggested that the peculiar effect of the bivalent common ion upon the total solubility may be general instead of specific, and that the deviations may be regular, and therefore due to some common cause or causes. It was the purpose of this research to investigate this point in as general a way as possible, in order to discover if such a regularity exists, and if so, to endeavor to give some explanation of the great apparent deviations from the solubility-product principle.

This investigation was undertaken at the suggestion of Prof. A. A. Noyes, and was carried out at the Mass. Institute of Technology with the aid of a grant made to him by the Carnegie Institution of Washington.

The substances used for the solubility determinations were silver sulfate, barium bromate, and lead chloride; and their solubilities were determined at 25° in water, and in solutions of salts of as many different types as possible, both of those with no common ion and of those with a common ion. The conductances and densities of all of the simple solutions and of the mixtures were measured. In the calculations the atomic weights for 1910 were used, and all weighings were corrected for air-buoyancy.

### 2. Preparation of Salts and Solutions.

All of the salts used in this investigation were finally purified by recrystallization from conductivity water, with a maximum specific conductance, in the bottles in which it was stored, of  $0.8 \times 10^{-8}$ .

*Silver Sulfate.*—This salt was made by three methods, and all of these methods gave a salt of the same solubility, except where the salt had turned dark during recrystallization. This darkening always resulted in an increase in solubility. All of the silver sulfate was recrystallized and kept in the dark, both before and during the solubility determinations, in order to prevent darkening by the action of light.

<sup>1</sup> See the first article of this series, Noyes and Bray, *THIS JOURNAL*, 33, 1647-9.

(1) A sample of Eimer and Amend's silver sulfate was recrystallized once from conductivity water.

(2) The salt was obtained from Merck & Co., and was dissolved at 300° in an excess of concentrated sulfuric acid. The silver acid sulfate<sup>1</sup> which separated out on cooling was washed with water until the washings were neutral to litmus, and the silver sulfate thus obtained was recrystallized from conductivity water.

(3) The silver sulfate was first reduced by an alkaline saccharose solution, the silver dissolved in dilute nitric acid, evaporated and silver nitrate precipitated by concentrated nitric acid. The silver nitrate was washed, dissolved in water, and silver sulfate precipitated by adding sulfuric acid. The silver sulfate thus formed was purified by recrystallization from water until the solution of the salt was alkaline to litmus and acid to rosolic acid.

*Potassium Nitrate.*—This salt was purified by seven crystallizations from water and was dried at 160° in a current of dry air.

*Silver Nitrate.*—Kahlbaum's silver nitrate was recrystallized from water. A stock solution was made up and analyzed by precipitation with dilute hydrochloric acid.

*Magnesium Nitrate.*—This salt was purified by two methods as follows: (1) Kahlbaum's magnesium nitrate was dissolved in water, and boiled with magnesium carbonate formed by precipitating a magnesium nitrate solution by pure dilute sodium carbonate solution, the solution was filtered, the filtrate made acid with nitric acid and partly evaporated, and the salt separated by cooling and filtration. This salt was then recrystallized from water until it was alkaline to litmus and acid to rosolic acid. A stock solution was made up, and its concentration determined by adding sulfuric acid to a portion of the solution and evaporating in a platinum crucible. The precipitate was ignited and weighed as anhydrous magnesium sulfate.

(2) Merck's magnesium nitrate was dissolved in concentrated nitric acid, the residue filtered off, and the salt crystallized by evaporation and cooling. This salt was recrystallized from water until it was alkaline to litmus and acid to rosolic acid. A stock solution was made up, and analyzed by evaporation with sulfuric acid.

‡ : *Potassium Sulfate.*—This was obtained by recrystallizing from water a sample of the salt obtained from Kahlbaum, and by drying at low redness.

*Magnesium Sulfate.*—Kahlbaum's magnesium sulfate was recrystallized twice from water. A stock solution was made up, and analyzed by evaporation and weighing as magnesium sulfate.

*Barium Bromate.*—This salt was made by a double decomposition of Kahlbaum's barium chloride and potassium bromate in dilute solution. It was recrystallized from water until it was entirely free from chloride.

*Potassium Bromate.*—A sample of Kahlbaum's potassium bromate was recrystallized twice from water. The salt was dried at 130° and the solutions made by weighing out the salt. The solutions were also analyzed by precipitation as silver bromide after a reduction by hydrazine, according to the method described later.

*Barium Nitrate.*—A sample of Kahlbaum's barium nitrate was recrystallized twice from water and dried for 24 hours in a current of dry air at 135°. The solutions were made by weighing out the dry salt.

*Lead Nitrate.*—Kahlbaum's lead nitrate was recrystallized from water containing a slight amount of nitric acid. The salt was heated at 100° for 6 hours, and at 130° for 12 hours in a current of dry air. The salt when dissolved gave a solution acid to rosolic acid and alkaline to litmus.

*Lead Chloride.*—This salt was precipitated by pure hydrochloric acid from a dilute

<sup>1</sup> Schultz, *Pogg. Ann.*, 133, 143 (1868).

solution of Eimer and Amend's lead nitrate. It was recrystallized from water until the salt became neutral. Stock solutions were made and analyzed by precipitation as silver chloride.

### 3. Methods of Analysis.

*Silver.*—The concentration of solutions of silver salts was determined in every case by precipitation as silver chloride. Enough solution was taken to give a precipitate of more than 1 gram in weight, and then diluted to approximately 0.05 normal. This solution was then added to a sufficient excess of 0.05 normal hydrochloric acid solution to give a final solution about 0.005 normal with respect to hydrochloric acid. The solution was allowed to stand cold, and in the dark, for 24 hours. It was then filtered through a weighed Gooch crucible, made of platinum, which had an asbestos mat protected by a perforated plate of platinum. The crucibles were previously brought to a constant weight by gradually heating up to 160°, and then heating at this temperature over night. The precipitate was washed with about a liter of 0.005 normal hydrochloric acid and then dried for 4 hours at 100° and for 12 hours at 160°. According to Richards<sup>1</sup> the solubility of silver chloride in a solution containing an excess of hydrochloric acid with some sodium nitrate amounts to about 0.03 mg. per liter. The concentration of the excess of hydrochloric acid is not given, but it is certain from an application of solubility-product principle that the solubility of silver chloride had no influence upon the results.

### 4. The Analysis of Bromates.

*Bromate.*—The concentration of barium bromate and potassium bromate solutions was determined by precipitation as silver bromide after a reduction by hydrazine. The solution was reduced in a half-liter bottle of the form devised by Baxter<sup>2</sup> and by a method somewhat similar to that used by him for the reduction of iodic acid. To the solution nearly twice the theoretical quantity of hydrazine hydroxide was added, and then nitric acid was dropped in slowly through a thistle tube which extended to the bottom of the bottle. This acid solution was heated to 60° for some time and then allowed to cool, and the determination completed by adding the diluted bromide solution to a dilute silver nitrate solution.

The results of this method were checked by analyzing solutions of potassium bromate made by weighing out the dry salt. The salt used was dried at 130°, but its weight was corrected by the amount of moisture given off by a part of the sample on heating for 19 hours at 165°, and 13 hours at 230°. The concentration of the potassium bromate solutions

<sup>1</sup> "Revision of the Atomic Weights of Sodium and Chlorine," Richards and Wells, *Carnegie Publications*, 1905.

<sup>2</sup> *THIS JOURNAL*, 31, 209 (1909).

was also determined by titration against a thiosulfate solution which was standardized by Prof. W. C. Bray against pure iodine, pure copper sulfate, and pure potassium iodide. The latter solution was standardized by precipitation as silver iodide. In all cases the agreement was satisfactory. The analysis of the potassium bromate solutions by reduction with hydrazine and precipitation as silver bromide gave results from 0.02 to 0.03 per cent. lower than those obtained from the weight of the potassium bromate. The method is undoubtedly by far the most accurate one yet devised for the analysis of bromates.

*Chloride or Bromide.*—Chloride and bromide were determined by adding to solutions containing these radicals an equivalent quantity of very dilute silver nitrate solution, allowing to stand over night, and adding a slight excess of silver nitrate the next day.<sup>1</sup> The precipitates were washed with very dilute silver nitrate solution and then with 100 cc. water made slightly acid by nitric acid. No correction was made for the amount of silver chloride dissolved by the wash water, but this was small, and in the case of the bromide it was practically negligible.

### 5. Experimental Methods.

The solubility was determined by rotating, for about 24 hours, about 20 grams of the salt with water or the solution of a salt in a 250 cc. glass-stoppered "resistenz" glass bottle, the stopper of which was sealed in with paraffin. The temperature of the thermostat was measured by a thermometer, which was frequently compared with a Baudin thermometer which had been certified by the Bureau of Standards at Washington, and was kept at  $25^{\circ} \pm 0.01$  by means of a large regulator filled with mercury. For each determination, saturation was approached both from under-saturation and supersaturation. In order to supersaturate the solution it was first saturated at a temperature of about  $40^{\circ}$  and then allowed to cool to the temperature of the thermostat.

The solutions were filtered in the thermostat by forcing them by means of air pressure through a thin inverted submerged asbestos filter which was held in a glass tube between two perforated platinum disks. The first 50 cc. of solution which was passed slowly through the filter, was rejected, in order to prevent errors from adsorption, and the remainder of the filtrate was used for analyses, conductivity measurements and density determinations.

The conductivity measurements were made in the usual way with a Kohlrausch slide-wire bridge carefully standardized. The apparatus was that used in this laboratory by Franklin L. Hunt<sup>2</sup> for the determination of the conductance of certain aqueous solutions.

<sup>1</sup> Richards, "Researches Concerning Atomic Weights," *Carnegie Publication*, page 17 (1907).

<sup>2</sup> THIS JOURNAL, 33, 796 and 783 (1911).

## 6. Solubility of Silver Sulfate in Water.

Ten determinations were made of the solubility in water, and the results of the measurements are given in Table I. In making up the average, measurements one to four were rejected because the salt darkened slightly, and nine and ten, because the salt was slightly acid with sulfuric acid. All of the bottles were protected from the action of light by being enclosed in covers of black rubber, but there seemed to be a slight darkening and a resultant increase of solubility whenever the salt had been only very slightly darkened during the recrystallization from hot water. It was found that even when recrystallized in the dark after a previous heating to  $300^{\circ}$  with concentrated sulfuric acid to insure the absence of organic matter the salt darkened if it was heated in water for any considerable time after it had become perfectly neutral. This darkening seemed to proceed much more rapidly as soon as darkening once began, but a slight amount of sulfuric acid served to prevent this action even in the hot solution. The salt used in all of this work was perfectly white except that used in the first four experiments. To prevent darkening the solution was heated as short a time as possible during the recrystallization from water.

Conductivity measurements were made upon three of the solutions, but it was considered better to take the results obtained from solutions which had not been rotated in the thermostat. A complete series of conductivity measurements upon the silver sulfate used in this work was made by Franklin L. Hunt. However, the two sets of results show that the equivalent conductance was practically the same for the two series of measurements, and therefore the darkening seems to have had no appreciable effect upon the conductivity of the solution.<sup>1</sup>

TABLE I.—SOLUBILITY OF SILVER SULFATE IN WATER AT  $25^{\circ}$ .

	(Concentrations in milliequivalents per liter.)			
	Conc. $\text{Ag}_2\text{SO}_4$ .	Spec. cond. $\times 10^3$ .	Equiv. cond.	Density $25^{\circ}4^{\circ}$ .
1.....	53.58	5.232	97.65 <sup>1</sup>	1.0052
2.....	53.74(s) <sup>2</sup>	5.247	97.64	
3.....	53.74(s)	5.257	97.83	
4.....	53.62			
5.....	53.50			
6.....	53.48			
7.....	53.58(s)			
8.....	53.52(s)			
9.....	53.62(s)			
10.....	53.58(s)			

Mean of best determinations (5, 6, 7, and 8) = 53.52 milliequivalents per liter = 8.344 grams per liter.

<sup>1</sup> The average value of the equivalent conductance of the saturated solution obtained by Hunt was 97.7.

<sup>2</sup> (s) denotes that equilibrium was approached from the side of supersaturation.

The final value for the solubility at 25°, 0.02676 moles per liter, is 4.1 per cent. higher than that obtained by Drucker,<sup>1</sup> 0.0257 moles per liter, and 0.86 per cent. lower than that obtained by Swan,<sup>2</sup> 0.02699 moles per liter.

7. The Solubility of Silver Sulfate in Solutions of Magnesium Nitrate, Potassium Nitrate, Magnesium Sulfate, Potassium Sulfate, Silver Nitrate, Potassium Acid Sulfate, Sulfuric Acid and Nitric Acid.

The results of the solubility determinations in solutions of potassium nitrate, magnesium nitrate, potassium sulfate, magnesium sulfate, and silver nitrate are given in Table II. In this table columns one to three refer to the salt solution which was used in the solubility determination,

TABLE II.—SOLUBILITY OF SILVER SULFATE IN SALT SOLUTIONS AT 25°. (Concentrations in milliequivalents per liter.)

No.	Salt solution.			Mixture.					
	Salt.	Conc. salt.	d. 25°/4°.	Solubility Ag <sub>2</sub> SO <sub>4</sub> .	Mean solubility.	Solubility grams per liter.	Sp. cond. × 10 <sup>3</sup> .	d. 25°/4°.	Conc. added salt in mix.
	None	0.00							
11	KNO <sub>3</sub>	24.914	0.9986	57.64		8.344	8.344		
12				57.68(s)			8.402		
13				57.76(s)					
14				57.72	57.70	8.996			
15		49.774	1.0002	61.06			11.403	1.0092	49.749
16				61.12(s)					
17				61.20(s)					
18				61.18					
19				61.14(s)					
20				61.08(s)	61.13	9.531			
21		99.87	1.0034	66.92			17.204	1.0034	99.81
22				66.90			17.251		
23				66.88(s)					
24				66.94					
25				67.00(s)	67.93	10.435			
26	Mg(NO <sub>3</sub> ) <sub>2</sub>	24.764	0.9985	59.44			7.373	1.0073	24.750
27				59.44					
28				59.44(s)					
29				59.44(s)	59.44	9.267			
30		49.595	0.9999	64.28			9.522	1.0094	49.569
31				64.38(s)			9.529		
32				64.34(s)	64.32	10.029			
33		99.46	1.0026	72.70			13.750	1.0133	99.40
34				72.68(s)					
35				72.70(s)	72.70	11.334			
36	AgNO <sub>3</sub>	24.961	1.0007	39.08			6.497	1.0065	24.96
37				39.10(s)	39.09	6.095			
38		49.86	1.0044	28.44			8.125	1.0084	49.84

<sup>1</sup> *Z. anorg. Chem.*, 28, 362 (1901).

<sup>2</sup> "Chemistry Thesis," Mass. Institute of Technology (1899).

TABLE II (continued).

No.	Salt solution.		Mixture.						
	Salt.	Conc. salt.	<i>d.</i> 25°/4°.	Solubility. Ag <sub>2</sub> SO <sub>4</sub> .	Mean solubility.	Solubility grams per liter.	Sp. cond. × 10 <sup>3</sup> .	<i>d.</i> 25°/4°.	Conc. added salt in mix.
39				28.46(s)	28.45	4.487	8.123		
40		99.61	1.0112	16.94			12.122	1.0137	99.60
41				16.98(s)	16.96	2.644	12.125		
42	K <sub>2</sub> SO <sub>4</sub>	25.024	(0.9989)	(50.80) <sup>1</sup>			7.517	1.0064	25.015
43				(51.20) <sup>1</sup>			7.535		
44				50.66					
45				50.66(s)	50.66	7.899			
46		50.044	1.0006	49.34			9.806	1.0079	50.025
47				49.36(s)	49.35	7.694	9.807		
48		100.00	(1.0041)	(48.26) <sup>1</sup>			14.396	1.0112	99.96
49				(48.06) <sup>1</sup>			14.383		
50				48.04					
51				48.04(s)	48.04	7.490			
52		200.03	1.0110	48.26			23.187	1.0180	199.96
53				48.34(s)	48.30	7.531	23.190		
54	MgSO <sub>4</sub>	20.022	0.9984	52.18			6.118	1.0061	20.014
55				52.24(s)	52.21	8.140	6.119		
56		50.069	1.0002	50.92			7.371	1.0079	50.059
57				50.94(s)	50.93	7.941	7.370		
58		100.04	1.0032	49.96			9.410	1.0105	99.96
59				49.94(s)	49.95	7.740	9.409		
60		200.05	1.0092	49.60			13.242	1.0164	199.87
61				49.60(s)	49.60	7.733	13.241		

TABLE II B.—THE SOLUBILITY OF SILVER SULFATE IN SOLUTIONS OF ACIDS AND SALTS ACCORDING TO SWAN.<sup>2</sup>

Acid or salt added.	Conc. in milliequivalents.	Solubility (milliequivalents).	Fractional conc. added acid or salt	Fractional solubility.
HNO <sub>3</sub>	0.0	53.98	0.0	1.0
	15.89	59.86	0.294	1.110
	31.78	65.32	0.588	1.211
	63.57	75.90	1.177	1.406
H <sub>2</sub> SO <sub>4</sub>	0.0	53.98	0.0	1.0
	29.02	54.88	0.538	1.017
	58.02	55.64	1.075	1.031
	105.26	56.82	1.951	1.057
KHSO <sub>4</sub>	0.0	53.98	0.0	1.0
	52.64	52.18	0.976	0.967
	105.26	51.76	1.951	0.959
K <sub>2</sub> SO <sub>4</sub>	0.0	53.98	0.0	1.0
	27.18	50.90	0.504	0.943
	54.34	49.30	1.006	0.914

<sup>1</sup> The numbers in parentheses were not used in determining the average since they are the results obtained in experiments where the silver sulfate darkened perceptibly.

<sup>2</sup> Clifford M. Swan, "Chemistry Thesis," Mass. Inst. Tech., 1899.



and columns 4 to 9 give data concerning the mixture after equilibrium has been established. Column nine gives the concentration of the added salt corrected for the change of volume which takes place during the dissolving of the silver sulfate.

In Table II B are given the results of measurements upon the solubility of silver sulfate in solutions of nitric acid, sulfuric acid, potassium acid sulfate and potassium sulfate. The data are taken from an unpublished thesis by Clifford M. Swan.

### 8. The Solubility of Barium Bromate in Water and in Solutions of Potassium Nitrate, Magnesium Nitrate, Barium Nitrate and Potassium Bromate.

The solubility of barium bromate in milliequivalents per liter is given in Table III.

TABLE III.—SOLUBILITY OF BARIUM BROMATE IN WATER AT 25°.

Solubility.	Conductance $\times 10^3$ .	Equivalent cond.	Density 25°/4°.
40.20(s)	3.664	91.1	1.0038
40.14			
40.18			
40.18(s)			

Mean = 40.18 = 0.793 gram to 100 grams solution.

TABLE IV.—SOLUBILITY OF BARIUM BROMATE IN SOLUTIONS OF SALTS AT 25°.  
(Concentrations in milliequivalents per liter.)

Salt solution.		Mixture.							
No.	Salt.	Milli-equiv. conc.	d. 25°/4°.	Solubility $\text{Ag}_2\text{SO}_4$ in milli-mols.	Mean.	Solubility, grams per liter.	Sp. cond. $\times 10^3$ .	d. 25°/4°.	Conc. salt.
	None	0.00		40.18	40.18		1.0038		0.00
100	$\text{KNO}_3$	25.018	0.9985	43.88	43.86	8.62	6.783	1.0059	24.988
101				43.84(s)			6.784		
102		50.032	(1.003)	47.02			9.756	1.0081	50.02
103				47.04(s)	47.03	9.91	9.737		
104		99.97	1.0033	52.12			15.452	1.0120	99.77
105				52.14(s)	52.13	10.25	15.451		
106	$\text{Ba}(\text{NO}_3)_2$	25.018	1.0003	36.70			5.643	1.0059	24.978
107				36.84(s)	36.77	7.221			
108		50.039	1.0025	34.72			7.597	1.0083	49.990
109				34.76(s)	34.74	6.83	7.596		
110		99.97	1.0073	32.60					
111				32.66(s)	32.63	6.415	11.325	1.0132	99.92
112		199.95	1.0183	30.96			18.100		
113				30.94(s)	30.95	7.085	18.097	1.0233	199.54
114	$\text{KBrO}_3$	24.988	(1.0001)	26.52				1.0046	24.970
115				26.54(s)	26.53	5.216			
116		49.971	(1.0031)	17.38			6.974	1.0062	49.956
117				17.36(s)	17.37	3.415	6.973		
118		99.85	1.0093	8.82			11.309	1.0109	99.84
119				8.70(s)	8.76	1.72	11.308		
120	$\text{Mg}(\text{NO}_3)_2$	100.00		52.54				1.0114	
121				52.60(s)	52.57	8.196			

The solubility was determined by precipitating as silver bromide, after reducing with hydrazine, and is 0.63 per cent. higher than that found by Trautz and Anschütz<sup>1</sup> (0.788 gram). According to the analyses given in their article the solid phase has the composition  $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ .<sup>1</sup>

The solubility of barium bromate in salt solutions is given in Table IV.

### g. The Solubility of Lead Chloride in Water and in Solutions of Salts.

The solubility of lead chloride in water and in solutions of lead nitrate is given in Table V.

TABLE V.—SOLUBILITY OF LEAD CHLORIDE IN WATER AND IN SOLUTIONS OF LEAD NITRATE.

Salt solution.				Mixture.			
No.	Salt.	Equiv. conc.	d. 25°/4°.	Solubility $\text{PbCl}_2$ .	Solubility, grams per liter.	Sp. cond. $\times 10^2$ .	Conc. salt.
118	Water			77.76			
119				77.76	77.76		1.0069
120	$\text{Pb}(\text{NO}_3)_2$	20.020	(1.0008)	76.74			
121				76.76	76.75	10.67	1.0095
122		50.063	(1.0045)	76.64			19.980
123				76.64	76.64	10.65	1.0139
124		99.66	1.0119	77.98		13.124	50.003
125				77.98	77.98	10.84	99.49
126		200.0		83.20 <sup>2</sup>		13.124	1.0210

In Table VI are given the mean results on the solubility of lead chloride as obtained by A. A. Noyes.<sup>3</sup>

TABLE VI.—SOLUBILITY OF LEAD CHLORIDE AT 25° ACCORDING TO A. A. NOYES.  
(Concentrations in milliequivalents per liter.)

Salt added.		50.	100.	200.
HCl.....	77.70	47.86	32.43	19.27
KCl.....	...	48.2	34.1	21.9
$\text{MgCl}_2$ .....	...	50.3	35.0	...
$\text{CaCl}_2$ .....	...	50.3	35.5	21.9
$\text{MnCl}_2$ .....	...	50.1	34.9	21.7
$\text{ZnCl}_2$ .....	...	...	...	22.0
$\text{CdCl}_2$ .....	...	60.1	48.1	35.5
$\text{HgCl}_2$ .....	...	...	99.2	...
$\text{Pb}(\text{NO}_3)_2$ .....	...	...	...	83.2

The mean values for the solubility of silver sulfate, barium bromate, and lead chloride, together with the results of A. A. Noyes upon the solubility of lead chloride,<sup>4</sup> and of Abegg and Spencer on the solubility

<sup>1</sup> *Z. physik. Chem.*, 56, 240 (1906).

<sup>2</sup> No. 126 is the mean of two results obtained by A. A. Noyes, *Z. physik. Chem.*, 9, 629 (1892).

<sup>3</sup> *Loc. cit.*, 623-9.

<sup>4</sup> *Z. physik. Chem.*, 9, 629 (1892).

of thallium oxalate,<sup>1</sup> have been brought together in Table VII. The column headed "Fractional conc. salt" gives the values of the ratio.<sup>2</sup>

Equivalent concentration of added salt

Equivalent solubility of "saturating salt in water,

while the column headed "Fractional solubility" gives the values of the ratio

Solubility of salt in salt solution

Solubility of salt in water.

These ratios will be used for the plotting of curves, which will be given in the seventh paper of this series.

TABLE VII.—MEAN VALUES FOR THE SOLUBILITY OF SALTS IN SOLUTIONS OF SALTS.

Salt added.	Milli-normal conc. salt solution.	Solubility in milli-moles.	Fractional conc. added salt.	Fractional conc. solubility.	Solubility in grams per liter.	Density solution 25°/4°.
Solubility of Silver Sulfate.						
KNO <sub>3</sub>	0.0	26.76	0.0	1.0	8.344	1.0052
	24.903	28.85	0.466	1.078	8.996	1.0072
	49.749	30.56	0.930	1.142	9.531	1.0092
	99.81	33.96	1.866	1.250	10.435	1.0034
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.0	26.76	0.0	1.0	8.344	1.0052
	24.750	29.72	0.463	1.112	9.267	1.0073
	49.569	32.16	0.926	1.202	10.029	1.0094
	99.40	36.35	1.857	1.358	11.334	1.0133
AgNO <sub>3</sub>	0.0	26.76	0.0	1.0	8.344	1.0052
	24.96	19.55	0.466	0.7075	6.095	1.0065
	49.84	14.22	0.932	0.528	4.428	1.0084
	99.60	8.48	1.861	0.313	2.644	1.0137
K <sub>2</sub> SO <sub>4</sub>	0.0	26.76	0.0	1.0	8.344	1.0052
	25.015	25.33	0.468	0.9475	7.899	1.0064
	50.025	24.67	0.936	0.922	7.694	1.0079
	99.96	24.02	1.878	0.898	7.490	1.0112
	199.96	24.15	3.740	0.9025	7.521	1.0180
MgSO <sub>4</sub>	0.0	26.76	0.0	1.0	8.344	1.0052
	20.014	26.10	0.375	0.976	8.140	1.0061
	50.059	25.46	0.936	0.952	7.941	1.0079
	99.96	24.97	1.868	0.934	7.788	1.0105
	199.87	24.80	3.713	0.927	7.733	1.0164

<sup>1</sup> *Z. anorg. Chem.*, 46, 406 (1905).

<sup>2</sup> Throughout these papers certain terms will be used which are not accurate except as defined here. The term "added salt" will be used to denote the salt originally present in the standard solutions in which other salts were dissolved later. By the "saturating salt" is meant the salt which is present in a solution in contact with the solid phase, and also in equilibrium with it. These short terms are much more convenient than the accurate explanation, and the effect is the same as if the "saturating salt" were first dissolved to form its saturated solution, and then the "added salt" added in the solid form in the correct proportions and the whole rotated until equilibrium is reached. Of course this latter method could not be recommended as a method for accurate work, but it is often of use in obtaining approximate results quickly—for example in teaching solubility principles to students of qualitative analysis.

TABLE VII (continued).

Salt added.	Milli-normal conc. salt. solution.	Solubility in milli-moles.	Fractional conc. added salt.	Fractional conc. solubility.	Solubility in grams per liter.	Density solution 25°/4°.
Solubility of Barium Bromate.						
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.0	20.09	0.0	1.0	7.93	..
	100.0	26.28	2.490	1.308	8.196	1.0114
KNO <sub>3</sub>	0.0	20.09	0.0	1.0	7.93	1.0038
	24.988	21.93	0.622	1.092	8.62	1.0059
	50.02	23.01	1.246	1.146	9.91	1.0081
	99.77	26.06	2.482	1.297	10.25	1.0120
Ba(NO <sub>3</sub> ) <sub>2</sub>	0.0	20.09	0.0	1.0	7.93	1.0038
	24.978	18.38	0.623	0.915	7.22	1.0059
	49.99	17.37	1.246	0.865	6.683	1.0083
	99.92	16.31	2.486	0.812	6.415	1.0132
	199.54	15.47	4.978	0.770	7.085	1.0233
KBrO <sub>3</sub>	0.0	20.09	0.0	1.0	7.93	1.0038
	24.970	13.26	0.624	0.662	5.216	1.0046
	49.956	8.68	1.248	0.433	3.415	1.0062
	99.84	4.38	2.488	0.218	1.72	1.0109
	Solubility of Lead Chloride.					
Pb(NO <sub>3</sub> ) <sub>2</sub>	0.0	38.88	0.0	1.0	10.81	1.0069
	19.98	38.37	0.258	0.987	10.67	1.0095
	50.003	38.32	0.644	0.986	10.65	1.0139
	99.49	38.99	1.282	1.003	10.84	1.021
	200.0	41.60	2.572	1.070	11.566	..
KCl <sup>1</sup>	0.0	38.85	0.0	1.0	10.801	..
	50.0	24.10	0.643	0.620	6.70	..
	100.0	17.05	1.286	0.439	4.74	..
	200.0	10.95	2.571	0.282	3.04	..
HCl <sup>1</sup>	0.0	38.85	0.0	1.0	10.801	..
	50.0	23.93	0.643	0.616	6.653	..
	100.0	16.21	1.286	0.417	4.507	..
	200.0	9.63	2.571	0.248	2.677	..

10. The Solubility of Thallium Oxalate<sup>2</sup> in Solution of Salts.

Salt added.	Conc. salt.	Solubility Tl <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	Fractional conc. salt.	Fractional solubility Tl <sub>2</sub> C <sub>2</sub> O <sub>4</sub> /2.
None	0	75.36	0.0	1.0
TlNO <sub>3</sub>	41.14	52.8	0.546	0.701
	79.90	39.0	1.062	0.518
	159.7	25.7	2.120	0.328
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	0	75.36	0.0	1.00
	99.6	70.2	1.322	0.932
	199.2	71.3	2.645	0.946
	493.4	78.0	6.55	1.036
	977.2	90.12	12.97	1.196
	1957.0	110.72	26.0	1.47

## 11. Conductance and Ionization of the Salts at 25°.

Conductance measurements upon a number of salts used in this in-

<sup>1</sup> A. A. Noyes, *Z. physik. Chem.*, **9**, 629 (1892).

<sup>2</sup> Abegg and Spencer, *Z. anorg. Chem.*, **46**, 406 (1905).

investigation were made by Mr. F. L. Hunt and the writer, and are given in Tables VIII–XI together with the results of other investigators.<sup>1</sup>

TABLE VIII.—CONDUCTANCE AND IONIZATION OF THE SALTS AT 25°.

Salt.	C × 10 <sup>3</sup> .	Equivalent conductance.					100 <sub>r</sub> .	Σi × 10 <sup>3</sup> .
		Measured.	H. M. or J.	B. & W.	Final.	100 <sub>r</sub> .		
KNO <sub>3</sub>	0.0	...	..	..	(145.4) <sup>2</sup>	100.0	0.0	
	12.5	...	134.9	..	134.9	92.8	11.60	
	20.0	...	..	132.5	132.5	91.1	18.24	
	25.0	131.1	..	..	131.1	90.2	22.55	
	50.0	126.3	126.3	126.1	126.3	86.85	43.43	
	100.0	120.4	120.3	120.3	120.4	82.8	82.8	
	200.0	113.5	..	..	113.5	78.0	156.0	
K <sub>2</sub> SO <sub>4</sub>	300.0	...	..	108.3	108.6	74.5	223.6	
	0.0	...	..	..	(154.8)	100.0	0	
	20.0	...	128.1	127.9	128.0	82.5	16.5	
	25.0	125.6	..	..	125.6	81.1	20.3	
	50.0	118.1	118.15	117.95	118.1	76.3	38.15	
	100.0	109.9	109.9	109.8	109.9	71.0	71.0	
	200.0	101.4	101.4	..	101.4	65.5	131.0	
300.0	...	..	96.15	96.15	62.1	186.4		

TABLE IX.—CONDUCTANCE AND IONIZATION OF THE SALTS.

Salt.	Conc. × 10 <sup>3</sup> .	Δ <sub>25</sub> measured.	100 <sub>r</sub> .	Σi × 10 <sup>3</sup> .	Δ <sub>18</sub> Kohlrausch.	100 <sub>r</sub> .
AgNO <sub>3</sub>	0.0	(134.0)	...	..	(115.8)	100.0
	10.0	..	...	..	107.8	93.2
	25.0	120.0	89.6	22.4	..	..
	50.0	115.1	85.9	42.95	99.5	85.9
	100.0	109.1	81.5	81.5	94.33	81.4
	200.0	101.8	75.97	151.94	..	..
MgSO <sub>4</sub>	0.0	(135)	...	..	(114.4)	100.0
	20.0	78.6	58.2	11.64	67.7	59.2
	50.0	66.0	48.9	24.45	56.9	49.75
	100.0	57.6	42.65	42.65	49.7	43.4
	200.0	50.0	37.05	74.10	43.2	37.8
Ba(NO <sub>3</sub> ) <sub>2</sub>	0.0	135.8	...	..	(117.2)	100.0
	20.0	..	...	..	95.7	81.65
	25.0	108.6	80.0	20.0	..	..
	50.0	100.8	74.25	37.12	86.8	74.06
	100.0	91.8	67.6	67.6	78.9	67.3
	200.0	81.8	60.2	120.4	70.2	59.9
Pb(NO <sub>3</sub> ) <sub>2</sub>	0.0	141.8	...	..	(122.6)	100.0
	20.0	112.9	79.6	15.9	97.0	79.04
	50.0	101.0	71.2	35.6	86.4	70.4
	100.0	90.5	63.8	63.8	77.3	63.0
	200.0	79.0	55.75	111.5	67.4	54.9

<sup>1</sup> Potassium nitrate, Noyes and Johnston, THIS JOURNAL, 31, 979 (1909). Potassium sulfate, preliminary values obtained by Mr. A. C. Melcher, of this laboratory. Potassium nitrate and potassium sulfate, Bray and Winninghoff, THIS JOURNAL, 33, 1667 (1911).

<sup>2</sup> Values in parenthesis were obtained by extrapolation.

$\Lambda$  is the equivalent conductance,  $100\gamma$  the conductance ratio ( $=100 \Lambda/\Lambda_0$ )  $C \times 10^0$  the concentration in milliequivalents, and  $1000\sum i = 1000 C\gamma$ , the ion concentrations.

Table X gives the results of conductance measurements made by Mr. F. L. Hunt upon a number of the salts used in this investigation.<sup>1</sup> The values of the conductance ratio ( $100\gamma$ ) are given in the table, together with extrapolated values enclosed in parentheses.

TABLE X.—PERCENTAGE IONIZATION OF THE SALTS AT 25°.

Concentration at $\rho$ .	Mg(NO <sub>3</sub> ) <sub>2</sub> .	KBrO <sub>3</sub> .
0.....	100.0	100.0
1.....	95.2	97.9
2.....	93.5	96.9
5.....	90.5	95.2
10.....	87.6	93.4
20.....	84.1	90.9
50.....	78.8	86.7
100.....	74.4	82.7
200.....	69.4	78.0

Concentration at $\rho$ .	Ag <sub>2</sub> SO <sub>4</sub> 25°.	Ba(BrO <sub>3</sub> ) <sub>2</sub> 25°.	PbCl <sub>2</sub> 25°.
0.....	100.0	100.0	100.0
1.....	94.7	94.7	94.3
2.....	92.5	92.7	91.5
4.....	89.3	...	...
5.....	88.1	89.2	86.3
10.....	83.6	85.6	80.4
20.....	77.9	81.1	73.2
40.....	71.3	75.9	...
50.....	...	...	62.1
53.74.....	68.1	...	...
78.2.....	64.3	...	...
77.54.....	...	...	56.2
100.....	(61.7)	(67.93)	
102.63.....	..	...	
145.4.....	..	(64.77)	
200.....	(54.7)	...	
203.6.....	..	(61.64)	

Through a typographical error four of the equivalent conductances determined for silver sulfate were given incorrectly in the published article. The correct results are as follows, where (*s*) represents a saturated solution, and (*ss*) a supersaturated solution:

Equivalent concentration....	53.74( <i>s</i> )	71.8( <i>ss</i> )	72.0( <i>ss</i> )	78.2( <i>ss</i> )
$\Lambda$ at 25°.....	97.7	94.3	93.5	92.15

Table XI gives unpublished results upon the conductance of potassium chloride as determined in this laboratory by Mr. A. C. Melcher.

<sup>1</sup> THIS JOURNAL, 53, 802 (1911).

TABLE XI.—CONDUCTANCE AND IONIZATION OF POTASSIUM CHLORIDE AT 25°.

Conc.	$\Delta_{25}$ Melcher.	$\Delta$ final.	Per cent. ionization.	$\Sigma v$ .
0.....	..	150.6	100.0	..
10.....	141.4	141.4	93.9	9.39
20.....	138.65	138.55	92.0	18.40
50.....	133.65	133.6	88.7	44.35
100.....	129.0	129.0	85.65	85.65
(146).....	..	(126.4)	83.9	122.6
200.....	124.2	124.2	82.47	164.9

### 12. Classification of Solubility Curves According to Types.

The solubility data presented in Tables I–VII are given in a graphic form in Fig. 1, where the ordinates represent the molal solubility, and the abscissas, the equivalent concentration of the added salts.

An examination of the figure shows that the curves belong to three general types, as follows:

I. These curves represent the change in solubility when a salt with a common univalent ion is added. In this case the solubility decreases very rapidly with increasing concentration of the added salt. All of these curves are of the same form as would be expected from a qualitative application of the solubility-product principle.

II. These curves represent the change in solubility when a salt with a common bivalent ion is added. The solubility of the more soluble salts, lead chloride and thallium oxalates, at first decreases, but quickly passes through a minimum, and then increases as the concentration of the added salt increases. Silver sulfate, a less soluble salt, shows only an extremely slight increase in solubility when the concentration of the added potassium sulfate is increased from 0.1 to 0.2 normal, though it increases much more rapidly at higher concentrations. On the other hand, the least soluble salt investigated, barium bromate, shows a continuous, though slight, decrease of solubility up to a concentration of 0.2 normal for the added salt.

*It is remarkable that in the case of the more soluble salts the form of these curves has no resemblance to what would be expected from an application of the solubility-product principle.*

### 13. Increase in the Solubility of an Easily Soluble Univalent Salt Caused by the Addition of a Salt with a Common Bivalent Ion.

The curves for this case seem to be determined by two opposing influences: one, most apparent in dilute solutions, exerts a depressing effect upon the solubility, and is undoubtedly due to the action of the common ion; the other, most apparent in concentrated solutions, tends to increase the solubility. This latter effect becomes more and more apparent as the solubility of the univalent salt increases, and for very soluble salts masks almost entirely, or even entirely, the effect of the common

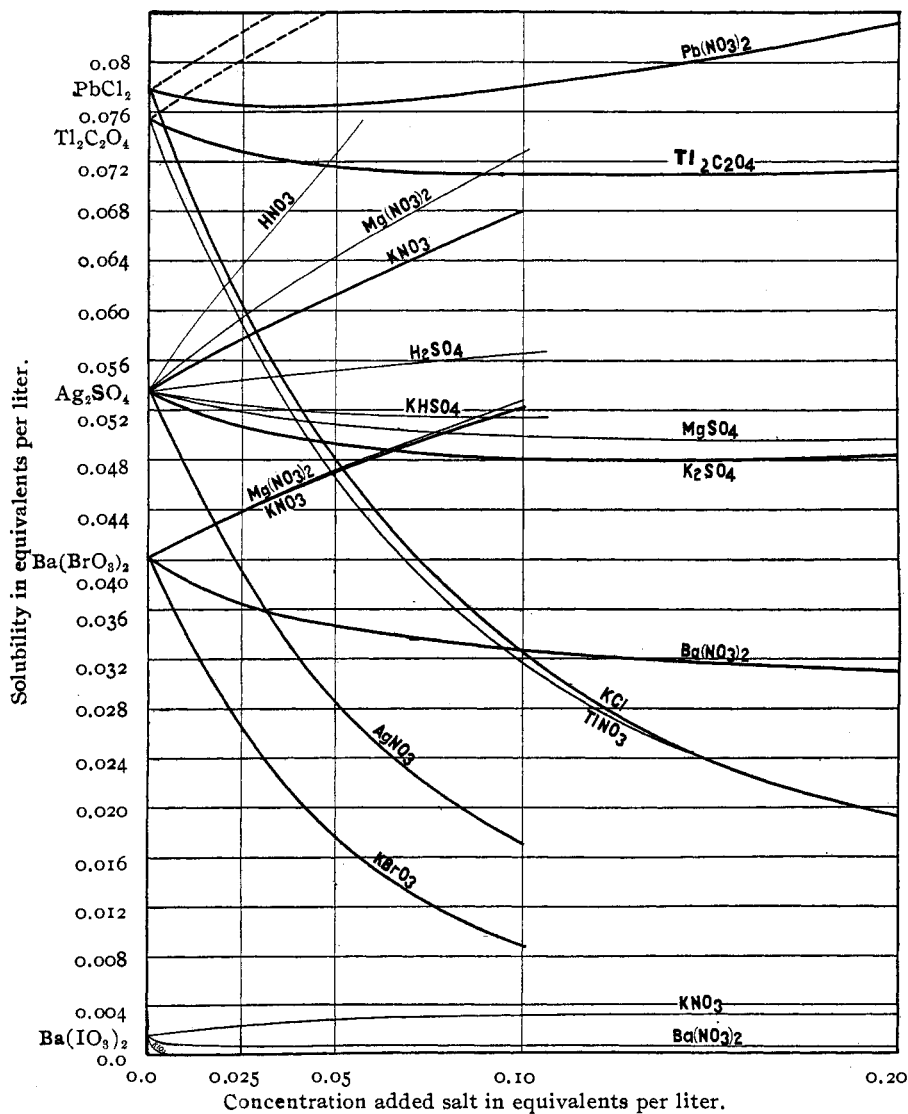


Fig. 1.

ion. This is shown in the case of certain salts investigated by Parsons and Carson<sup>1</sup> and Parsons and Perkins.<sup>2</sup> A much more complete discussion of this case will be found in the seventh article of this series.

There is thus in dilute solutions an effect, which in its direction is what we would expect from the solubility-product principle as the result of the

<sup>1</sup> Parsons and Carson, *THIS JOURNAL*, 32, 1383 (1910).

<sup>2</sup> Parsons and Perkins, *Ibid.*, 32, 1387.



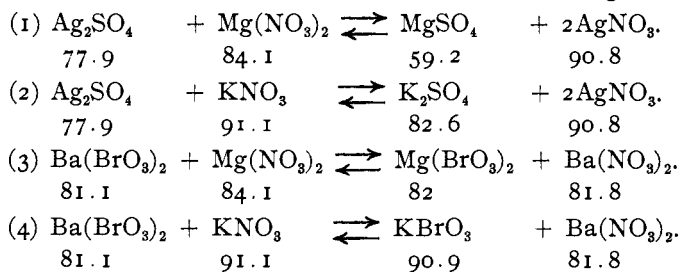
presence of the common ion, but it is of an altogether too small magnitude. In more concentrated solutions this effect becomes quickly imperceptible, though it is doubtless true that the common ion is still exerting an effect which is obscured by the influence, whatever it may be, which causes the increase in solubility.

It is interesting to note that potassium acid sulfate decreases the solubility of silver sulfate less than potassium sulfate, and that sulfuric acid, in spite of its common ion, increases the solubility from the start, thus giving a curve similar in this sense to the curves for no common ion, such as those for potassium nitrate and magnesium nitrate; but it lies much below these curves. In position it seems to be then a cross between the curves for common ions and those for no common ion. This was to have been expected, since the intermediate  $\text{HSO}_4^-$  ion is present in aqueous solutions of potassium acid sulfate and sulfuric acid, but it is remarkable that the curve for potassium sulfate lies so close to the curves for the other two substances in spite of the large amounts of the intermediate ion which solutions of these substances are assumed to contain.<sup>1</sup> The importance of this point will be discussed in the seventh paper of this series.

Incidentally it may be noted that magnesium sulfate does not decrease the solubility of silver sulfate so much as potassium sulfate.

#### 14. Increase of Solubility by Metathesis.

III. These curves represent the change in solubility when salts having no common ion are added. In such cases the solubility increases rapidly with the concentration of the added salt as the result of metathesis. It was found that magnesium nitrate increases the solubility of silver sulfate much more than it is increased by the addition of potassium nitrate. On the other hand magnesium nitrate increases the solubility of barium bromate only very slightly more than it is increased by potassium nitrate. This difference seems peculiar until we consider the metatheses in the different cases. The cause of the difference is largely the different degrees of ionization of the salts in the following metatheses:



<sup>1</sup> This is not an exceptional case, since similar results were obtained by Noyes and Stewart with thallous sulfate in the presence of sodium sulfate, sodium acid sulfate and sulfuric acid, Article II, C of this series. THIS JOURNAL, 33, 1663 (1911).

The figures given under the formulas represent the percentage ionization of the single salts in aqueous solution at a concentration of 20 milliequivalents per liter. These figures show that the ionization of the salts on the two sides of equations (2), (3) and (4) are almost exactly balanced, while in equation (1) the magnesium sulfate, a bi-bivalent salt, has a very much lower ionization than the other salts, and therefore the amount of sulfate ion withdrawn in the form of un-ionized magnesium sulfate is large. For this reason the solubility of the "saturating salt" is much more increased by metathesis number (1) than it is in the remaining three cases.

Nitric acid has a much greater solvent effect upon silver sulfate than either potassium nitrate or magnesium nitrate. This is a result to be expected on account of the formation of the intermediate  $\text{HSO}_4^-$  ion by the metathesis.

### 15. Types of Solubility Curves for Bi-bivalent Salts.

Since diionic salts of either the uni-univalent or the bi-bivalent type are more simple in their constitution than triionic salts, it is to be expected that there will be fewer types of solubility curves. There is, in either of these cases, only one kind of common ion which can be added, so the only types of curves are the one for the addition of a common ion, and that for the addition of no common ion. The characteristic forms of the curves of the two types for the bi-bivalent salt calcium sulfate are presented in Fig. 2. These curves are drawn from the data obtained by different investigators, as presented in Tables XII and XIII. The data are not so complete in dilute as they are in concentrated solutions. They will be discussed from a more quantitative standpoint in a later paper.

TABLE XII.—SOLUBILITY OF CALCIUM SULFATE IN AMMONIUM SULFATE SOLUTIONS ACCORDING TO SULLIVAN.<sup>1</sup>

(Concentrations in milliequivalents per liter.)					
Concentration ( $\text{NH}_4$ ) <sub>2</sub> $\text{SO}_4$ .	Density of ( $\text{NH}_4$ ) <sub>2</sub> $\text{SO}_4$ .	Solubility $\text{CaSO}_4$ .	Density of mixture 25% <sup>4</sup> °.	Sp.cond. ( $\text{NH}_4$ ) <sub>2</sub> $\text{SO}_4$ $\times 10^3$ .	Spec. cond. mixture $\times 10^3$ .
0.00	...	30.60	0.99911	...	2.214
1.9532	0.99711	30.01	0.99911	0.2822	2.394
3.906	0.99721	29.32	0.99920	0.5475	2.546
15.624	0.99765	26.54	0.99946	2.025	3.602
31.26	0.99832	24.36	0.99995	3.801	5.085
62.50	0.99953	22.62	1.00104	7.083	8.106
125.00	1.00201	21.15	1.00341	13.06	13.88
250.00	1.00681	21.37	1.00817	23.91	24.57
500.00	1.01606	23.75	1.01763	43.32	43.89
1500.0	1.05143	34.22	1.05344	109.0	109.1
3000.0	1.10059	48.91	1.10324	185.3	184.6
6000.0	1.18843	66.10	1.19149	268.8	265.2

<sup>1</sup> THIS JOURNAL, 27, 532 (1905).

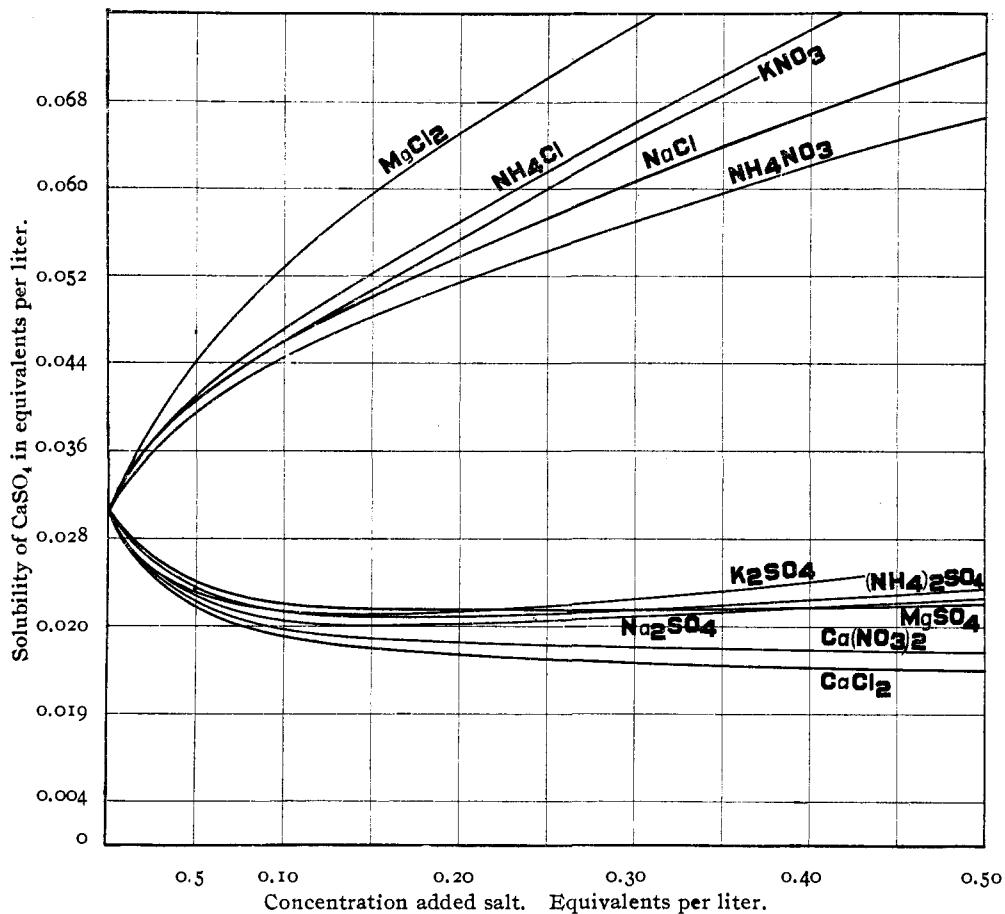


Fig. 2.

TABLE XIII.—SOLUBILITY OF CALCIUM SULFATE IN SOLUTIONS OF SALTS.  
(Concentrations in milliequivalents per liter.)

Temperature.	Salt.	Conc. salt.	Solubility of CaSO <sub>4</sub> .	Density of mixture.
25° C.	CaCl <sub>2</sub> <sup>1</sup>	0.0	30.42	
		136.0	18.42	
		217.2	17.48	
		468.0	16.22	
		582.0	15.98	
	Ca(NO <sub>3</sub> ) <sub>2</sub> <sup>2</sup>	0.0	30.7	0.998
		306.0	18.2	1.014
		612.0	17.6	1.032
	Ca(OH) <sub>2</sub> <sup>3</sup>	0.0	30.55	

<sup>1</sup> Cameron and Seidell, *J. Physic. Chem.*, 5, 643-55 (1901).<sup>2</sup> Seidell and Smith, *Ibid.*, 8, 493 (1904).<sup>3</sup> Cameron and Bell, *THIS JOURNAL*, 28, 1220 (1906).

TABLE XIII (continued).

Temperature.	Salt.	Conc. salt.	Solubility of CaSO <sub>4</sub> .	Density of mixture.
		2.21	29.80	
		6.28	28.17	
		12.45	27.22	
		21.75	25.28	
		33.5	24.00	
	MgSO <sub>4</sub> <sup>1</sup>	0.0	30.04	
		53.2	23.79	
		106.1	22.13	
		176.6	21.60	
		345.8	21.70	
		708.3	22.89	
		1065.0	23.62	
	K <sub>2</sub> SO <sub>4</sub> <sup>2</sup>	58.42	22.96	1.0038
		113.0	21.24	1.0075
		224.6	21.81	1.0151
		325.4	22.84	1.0229
		351.9	23.31	1.0236
	Na <sub>2</sub> SO <sub>4</sub> <sup>2</sup>	33.65	23.68	1.0013
		134.23	21.40	1.0076
		198.95	20.39	1.0114
		343.06	21.61	1.0205
		520.7	22.96	1.0315
		649.8	24.24	1.0391
		1326.3	29.08	1.0795
		1620.0	30.79	1.0965
		2064.0	32.81	1.1427
		2887.0	36.76	1.1765
		3619.0	38.92	1.2120
26°	MgCl <sub>2</sub> <sup>3</sup>	0.0	30.8	
		180.0	63.0	
		406.0	84.2	
		987.6	112.2	
		2570.0	127.6	
		4382.4	97.2	
23	NaCl <sup>4</sup>	0.0	(30.44)	
		17.1	35.2	
		85.2	44.6	
		179.0	52.4	
		520.0	73.6	
		847.1	87.8	
		1301.8	99.8	
		2231.4	111.0	
		33968.0	107.2	

<sup>1</sup> Cameron and Bell, *J. Physic. Chem.*, 10, 212 (1906).<sup>2</sup> Cameron and Brezeale, *Ibid.*, 8, 337-40 (1904).<sup>3</sup> Cameron and Seidell, *Ibid.*, 5, 643-55 (1901).<sup>4</sup> Cameron, *Ibid.*, 5, 560 (1901).

TABLE XIII (*continued*).

Temperature.	Salt.	Conc. salt.	Solubility of CaSO <sub>4</sub> .
25	NH <sub>4</sub> Cl <sup>1</sup>	201.86	57.28
		456.1	79.02
		873.0	103.85
	NH <sub>4</sub> NO <sub>3</sub> <sup>1</sup>	124.9	46.71
		312.3	57.73
		687.05	85.19

It has been shown that the curves representing the change of solubility of a univalent salt, such as silver sulfate, are not at all of the form to be expected from the solubility-product principle, if the salt added contains the common bivalent ion. However, as the solubility of the dissolved univalent salt decreases, the curves of this type rapidly approach what might be considered to be the theoretical curve, although, even in the case of the least soluble salt yet investigated, barium bromate, the actual curve is very far from what would be expected theoretically. The results obtained in this investigation indicate that much less soluble salts would give curves very much nearer the theoretical one; and in order to test this conclusion, the solubilities of the less soluble salts, barium iodate and lead iodate, will be determined. The results are given in the sixth paper of this series. A seventh paper will contain calculations, from the data in this paper, of the ion-concentration product and the un-ionized part of the dissolved salts by the methods outlined in Paper I of this series. It will also contain a discussion of the remarkable abnormalities found in the solubility relations of univalent salts.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 77.]

**THE EFFECT OF SALTS UPON THE SOLUBILITY OF OTHER SALTS.  
VI. THE SOLUBILITY OF DIFFICULTLY SOLUBLE  
UNIVALENT SALTS.**

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**16. The Solubility of Barium Iodate in Water and in Solutions of Barium Nitrate, Potassium Nitrate and Potassium Iodate.**

The results presented in the fifth paper of this series show that, for salts of moderate or of great solubility, there is a very great deviation from the solubility-product principle, when a salt with a common bivalent ion is added to the aqueous solution of a salt in contact with the solid phase and in equilibrium with it. It was observed that the form of the curve representing the change of solubility with the concentration of the added

<sup>1</sup> Cameron and Brown, *J. Physic. Chem.*, 9, 211-13 (1905).