

TABLE XIII (*continued*).

Temperature.	Salt.	Conc. salt.	Solubility of CaSO ₄ .
25	NH ₄ Cl ¹	201.86	57.28
		456.1	79.02
		873.0	103.85
	NH ₄ NO ₃ ¹	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

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

salt became more nearly what would be expected from this principle as the solubility of the "saturating salt" decreased. It is therefore of interest to determine such solubility curves for salts which are very difficultly soluble.

The salts best suited for such an investigation seemed to be the iodates of barium and lead, whose solubilities in pure water at 25° are 0.001578 and 0.0001101 equivalents per liter, respectively. The molal solubility of lead iodate is only three and one-half times the solubility of silver chloride, and it seems to be the most difficultly soluble univalent salt of such a character as to permit of analytical determinations of its concentration of sufficient accuracy. The solubility of this salt was determined in solutions of lead nitrate, potassium nitrate, and in very dilute solutions of potassium iodate. The solubility of barium iodate was determined in solutions of barium nitrate, potassium nitrate, and potassium iodate.

This investigation was carried out with the aid of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

The barium and lead iodates used for the solubility determinations were made by precipitating the respective nitrates with potassium iodate, in a very dilute solution in which the nitrate was kept constantly in excess. The salt was washed with conductivity water until its solubility became constant.

The barium nitrate and potassium nitrate were purified by recrystallization in the same way as was described in the fifth paper of this series. The potassium iodate was recrystallized twice from conductivity water, and the strength of the solutions was determined by analysis.

TABLE I.—THE SOLUBILITY OF BARIUM IODATE IN WATER AT 25°.
(Concentrations in equivalents per liter.)

No.	Solubility.	Mean solubility.	Specific conductance.	Equivalent conductance.	Gram per liter.
1	0.001579		0.00016820	106.5	
2	0.001578		0.00016834		
3	0.001581				
4	0.001581(s)				
5	0.001581(s)				
6	0.001577(s)				
7	0.001575(s)	0.001579			0.3845

The concentration of the "saturating salt" was determined by adding potassium iodide to the solution of the iodate, and liberating iodine by adding hydrochloric acid. The iodine was determined by titration with a 0.01 or a 0.005 normal solution of sodium thiosulfate. These dilute thiosulfate solutions were made up as needed by diluting a standard tenth-normal solution. This latter was standardized against iodine, and against a solution of pure copper sulfate. The dilute solutions were constantly checked by titrating against a 0.01 normal potassium iodate

solution, which was made by weighing out the pure salt which had been dried at 120°. The concentration of this potassium iodate solution was checked by titrating with one of the standard thiosulfate solutions. The thiosulfate solutions were made up with water of a conductivity of about 0.80×10^{-8} , and were kept in a black bottle, which was fitted with soda lime tubes to protect the solution from the action of carbon dioxide. Even the most dilute solutions kept perfectly for a week or more when

TABLE II.—THE SOLUBILITY OF BARIUM IODATE IN SOLUTIONS OF BARIUM NITRATE, POTASSIUM NITRATE AND POTASSIUM IODATE AT 25°.

No.	Added salt.	Conc. added salt.	Solubility Ba(IO ₃) ₂ .	Mean sol.	Fractional conc. added salt.	Fractional solubility.	
8	Ba(NO ₃) ₂	0.001	0.001361				
9			0.001364(<i>s</i>)				
10			0.001363				
11			0.001360(<i>s</i>)	0.001362	0.634	0.862	
12		0.002		0.001214			
13			0.001213(<i>s</i>)				
14				0.001211			
15				0.001211(<i>s</i>)	0.001212	1.268	0.768
16		0.005		0.0009740			
17			0.0009757(<i>s</i>)				
18			0.0009747				
19			0.0009770(<i>s</i>)	0.0009753	3.170	0.619	
20	0.020		0.0006739				
21		0.0006752					
22			0.0006749(<i>s</i>)				
23			0.0006737(<i>s</i>)	0.0006744	12.68	0.427	
24	0.050		0.0006128				
25		0.0006133					
26			0.0006137(<i>s</i>)				
27			0.0006127(<i>s</i>)	0.0006131	31.70	0.388	
28	0.100		0.0005663				
29		0.0005655(<i>s</i>)	0.0005659	63.4	0.358		
30	0.200		0.0005573				
31		0.0005587(<i>s</i>)	0.0005580	126.8	0.353		
32	KNO ₃	0.002	0.001624				
33			0.001625(<i>s</i>)	0.001624	1.268	1.029	
34		0.010	0.001826				
35			0.001827(<i>s</i>)	0.00182	6.34	1.155	
36	0.050		0.002640				
37		0.002641(<i>s</i>)	0.002640	31.70	1.671		
38	0.200		0.003192				
39		0.003189(<i>s</i>)	0.003190	126.8	2.021		
40	KIO	0.00010608	0.001509				
41			0.001512(<i>s</i>)	0.001510	0.0673	0.908	
42		0.0005304	0.001240				
43			0.001244(<i>s</i>)	0.001242	0.336	0.748	
44	0.0010608		0.0009416				
		0.0009421	0.0009418	0.673	0.596		

(*s*) after a number denotes that the value was obtained by approaching equilibrium from the side of supersaturation.

treated in this way. A weight buret was used for all of the titrations. Iodates have a special advantage when it is necessary to make analytical determinations in extremely dilute solutions, since each mol. of barium or lead iodate releases twelve equivalents of iodine from potassium iodide in acid solution.

The results of the solubility determinations, together with the densities of the solutions, are given in Tables I-IV.

17. The Solubility of Lead Iodate in Water and in Solution of Lead Nitrate, Potassium Nitrate and Potassium Iodate.

TABLE III.—SOLUBILITY OF* LEAD IODATE IN WATER AT 25°. (Concentrations in equivalents per liter.)

No.	Solubility of lead iodate.	Mean.	Gram per liter.
46	0.0001105		
47	0.0001102		
48	0.0001107		
49	0.0001101(s)		
50	0.0001097(s)		
51	0.0001194(s)		
52	0.0001097(s)	0.0001102	0.0307

TABLE IV.—SOLUBILITY OF LEAD IODATE IN SOLUTIONS OF LEAD NITRATE, POTASSIUM NITRATE AND POTASSIUM IODATE.

No.	Salt added	Conc. added salt.	Solubility Pb(IO ₃) ₂ .	Mean solubility.	Fractional conc. salt.	Fractional solubility.	
53	Pb(NO ₃) ₂	0.0001	0.0000870				
54			0.0000870(s)	0.0000870	0.908	0.790	
55		0.001	0.0000408			9.08	0.373
56			0.0000414(s)	0.0000411	
57		0.010	0.0000185				
58			0.0000186(s)	0.0000185	90.8	0.169	
59		0.100	0.000016				
60			0.000016(s)	0.000016	908.0	0.145	
61		0.500	(0.000030)				
62			(0.000027)(s)	(0.000028)	4590.0	(0.259)	
63	3.0	(0.00015)					
64		(0.00015)(s)	(0.00015)	27240.0	...		
65	KNO ₃	0.002	0.0001145				
66			0.0001138(s)	0.0001141	18.16	1.039	
67		0.010	0.0001334				
68			0.0001334(s)	0.0001334	90.8	1.211	
69		0.050	0.0002037				
70			0.0002037(s)	0.0002037	454.0	1.848	
71		0.200	0.0002548				
72			0.0002540(s)	0.0002544	1816.0	2.311	
73		KIO ₃	0.00005304	0.0000717			
74				0.0000697	0.0000697		
75			0.0000714(s)				
76			0.0000734(s)	0.0000715	0.482	0.65	
77	0.0001061		0.0000432				
		0.0000442(s)	0.0000437	0.963	0.493		

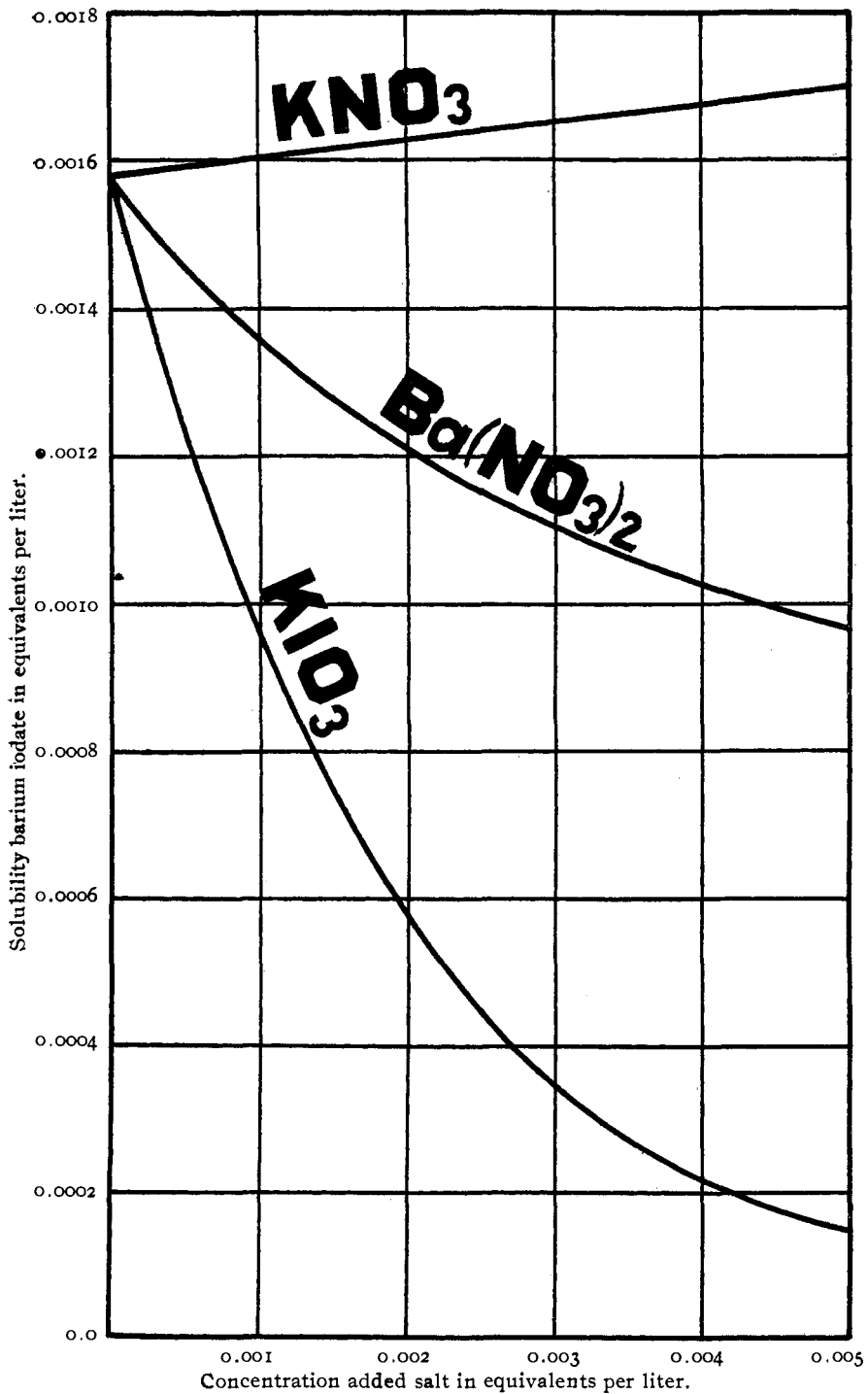


Fig. 1.

The results of these tables, with other results used for purposes of comparison, are plotted in Figs. 1-3, where the abscissas represent the equivalent concentration of the added salt. In Figs. 1 and 2 the ordinates represent the equivalent solubility, while in Fig. 3 they represent the fraction of the solubility in water, or the ratio of the solubility of dissolved salt in salt solution to its solubility in water. The curves for barium iodate presented in Fig. 1 have, at least qualitatively, the form which would be expected from the solubility-product principle. The curve representing the addition of a salt with a common univalent ion falls with extreme rapidity, and much more rapidly than the similar

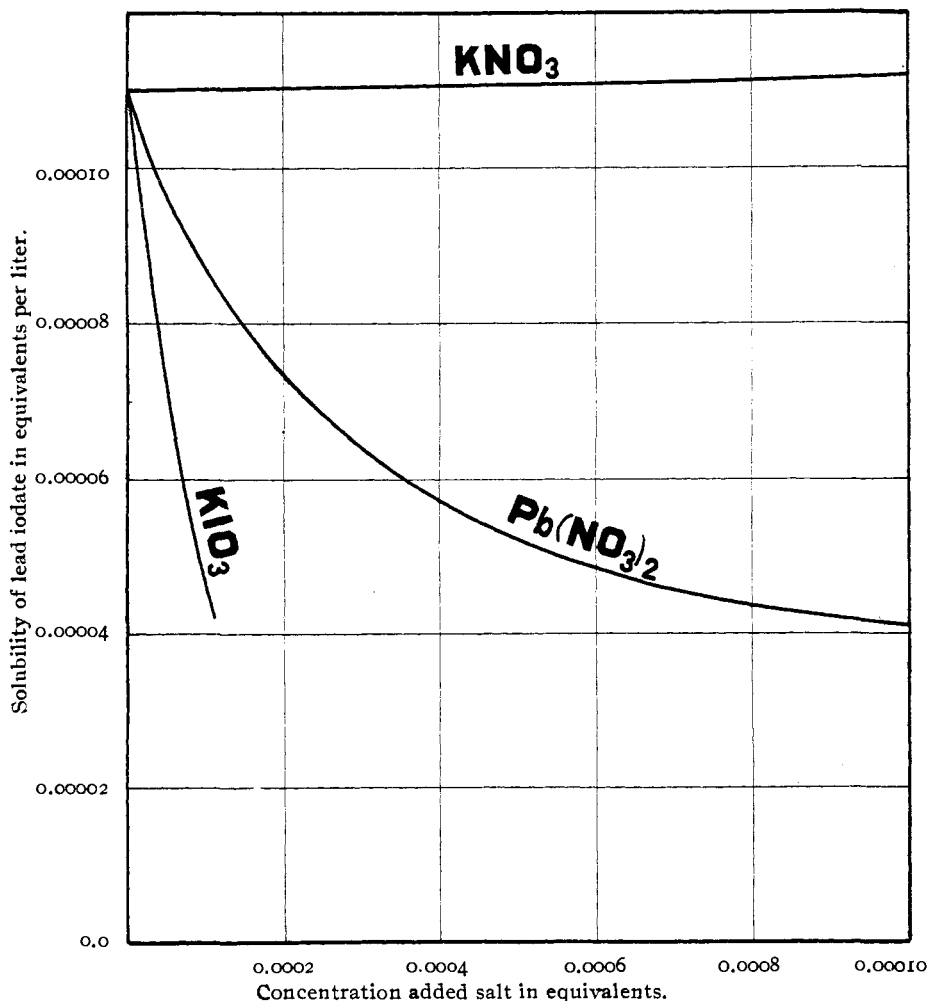


Fig. 2.

curves for the more soluble salts considered in the fifth paper of this series. The corresponding curve for lead iodate drops very much more rapidly than that for barium iodate.

The curves representing the addition of a salt with a common bivalent ion also drop very rapidly, which is contrary to what was found for the more soluble salts.

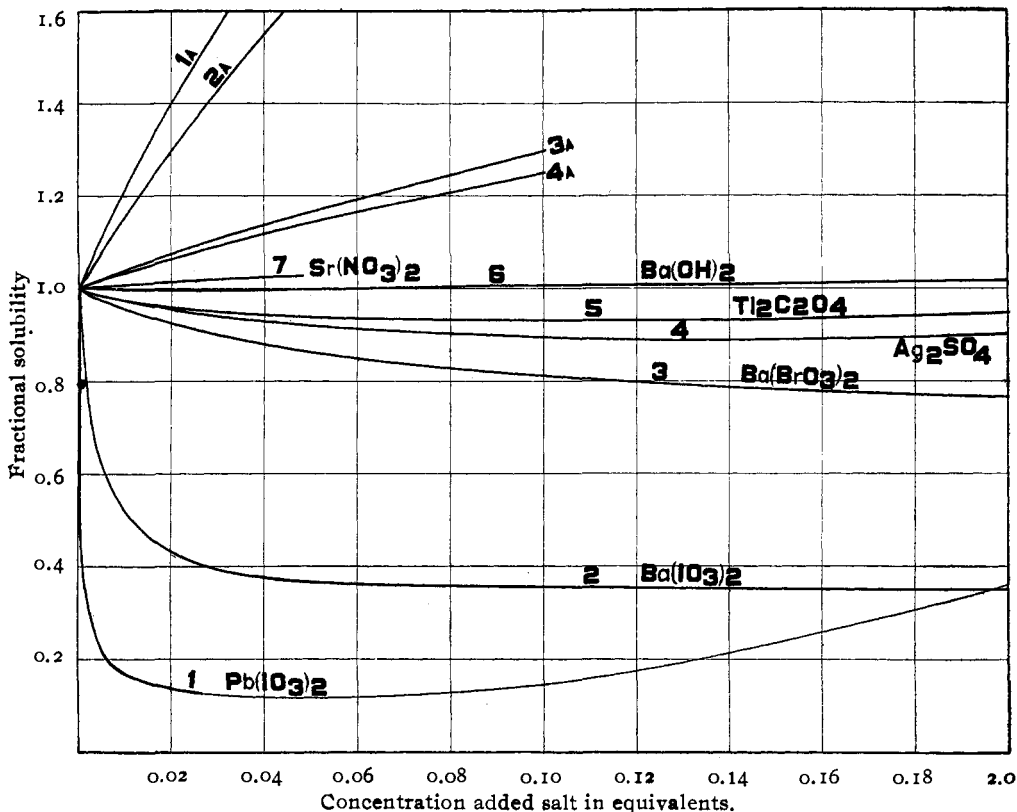


Fig. 3.

No.	"Saturating salt,"	Solubility in water.	Added salt.
1.....	Pb(IO ₃) ₂	0.0001102	Pb(NO ₃) ₂
2.....	Ba(IO ₃) ₂	0.001579	Ba(NO ₃) ₂
3.....	Ba(BrO ₃) ₂	0.04018	Ba(NO ₃) ₂
4.....	Ag ₂ SO ₄	0.05352	K ₂ SO ₄
5.....	Ti ₂ C ₂ O ₄	0.07536	K ₂ C ₂ O ₄
6.....	Ba(OH) ₂	0.562	Ba(NO ₃) ₂
7.....	Sr(NO ₃) ₂	6.176	Sr(OH) ₂
1A.....	Pb(IO ₃) ₂	0.0001102	KNO ₃
2A.....	Ba(IO ₃) ₂	0.001579	KNO ₃
3A.....	Ba(BrO ₃) ₂	0.04018	KNO ₃
4A.....	Ag ₂ SO ₄	0.05352	KNO ₃

The curves for the addition of a salt with no common ion rise very slowly in these figures, but it must be remembered that the concentration of the added salt is given on a very much larger scale than in Fig. 1 of the fifth paper, since the scale is ten times as great for barium iodate, and one hundred times as great for lead iodate.

In Fig. 3 the concentration of the added salt has been plotted on nearly the same scale as that used for Fig. 1 of the fifth article, so that the two figures may be more easily used for purposes of comparison. However, on account of the great differences in solubility it is impossible to plot the curves for barium iodate and lead iodate in the same figure with any degree of accuracy if the equivalent solubilities are plotted on the Y axis, so, instead, all of the curves have been given a common origin. The curves for the addition of the common univalent ion are not represented, since, up to the highest concentrations at which the determinations were made these curves have here become practically coincident with the Y axis, which illustrated the extreme rapidity of the decrease in solubility. The curves presented are those for the common bivalent ion, and for no common ion.

When the curves for the common bivalent ion are considered, it is seen that the solubility of the most difficultly soluble salt, lead iodate (0.0001101 equivalent per liter in water), falls to 0.37 of its original value when the solution contains 0.001 equivalent of lead nitrate per liter,¹ and in 0.01 normal lead nitrate the solubility falls to 16.9 per cent.

As an interesting minor point it should be noted that the curve representing the effect of the addition of lead nitrate to lead iodate in its saturated solutions, turns upward when the concentration of the added salt rises much above 0.05 normal, and the increase in solubility observed is abnormal. It will be remembered that a similar abnormality was observed when lead nitrate was added to dissolved lead chloride. This abnormality would, then, seem to be characteristic of lead salts, and dependent upon the total salt or ion concentration, rather than upon the solubility of the salt itself. This curve for concentrations of the added salt greater than 0.025 *N* has been drawn as a light line in Fig. 3, since the determinations were not very accurate, on account of the very small

¹ Even this decrease is very small when compared with that caused by a salt containing a common univalent ion, since in the latter case the addition of a salt with a concentration of one-ten-thousandth normal decreases the solubility to 39 per cent. of its original value. If such facts as these were better understood by analysts in general they would add a much smaller excess of the salt used for the precipitations, and thereby reduce the amount of adsorbed salt, and decrease the amount of washing necessary. In this case the addition of so small an amount of potassium iodate as to make the solution 0.00044 normal with respect to this salt, would decrease the solubility of $\text{Pb}(\text{IO}_3)_2$ to 0.07 of its value in water, and this decrease would be even more rapid for a less soluble salt.

concentration of the lead iodate present in a solution containing so large an amount of lead nitrate. This latter was precipitated, by the potassium iodide used in the analysis, in the form of lead iodide. This lead iodide oxidizes readily, and the amount oxidized would be added to the concentration of the lead iodate. The determinations in the dilute solutions are not affected by this error.

Table V gives the percentage change in the solubility of the univalent salts plotted in Fig. 3, which is caused by making the solution of the salt 0.01 normal with respect to a salt which contains a common bivalent ion or a salt.

TABLE V.—PERCENTAGE CHANGE IN THE SOLUBILITY OF UNIBIVALENT SALTS CAUSED BY MAKING THE SOLUTION 0.01 NORMAL WITH RESPECT TO A, A SALT WITH A COMMON BIVALENT ION, B, A SALT WITH NO COMMON ION (*viz.*, POTASSIUM NITRATE).

Salt.	Equivalent solubility in water.	Percentage decrease in solubility caused by A.	Percentage increase in solubility caused by B.
Pb(IO ₃) ₂	0.000110	83.1	21.1
Ba(BrO ₃) ₂	0.001578	48.0	15.5
Ba(BrO ₂) ₂	0.04018	4.3	3.7
Ag ₂ SO ₄	0.05352	3.3	3.3
Tl ₂ C ₂ O ₄	0.07536	2.7	..
PbCl ₂	0.07776	0.09	..
Ba(OH) ₂	0.562	0.01	..
Sr(NO ₃) ₂	6.18	—0.08 ¹	..

Fig. 3 and Table V deserve careful consideration, as they contain results of great significance. It is unfortunate that no curve has been determined for the solubility of strontium nitrate in a solution of a salt with no common ion, such as potassium chloride; but it may be predicted from the results presented in the figure and the table that this curve will lie practically as low as the curve representing the solubility of strontium nitrate in solutions of strontium hydroxide. In other words, the curves representing the effect of a salt with a common bivalent ion and with no common ion have become practically coincident, at least when the concentration of the added salt is small. This would seem to lead to the interpretation that a 6-normal strontium nitrate solution and a 0.01 normal strontium hydroxide solution have practically no ion in common. The most easily reached explanation of the facts in this case seems to be that presented in the seventh paper of this series, where the assumption is made that very concentrated solutions of a univalent salt, using strontium nitrate for an example, consist most largely of the un-ionized salt and the ions SrNO₃⁺ and NO₃⁻, and only an extremely small amount of the Sr⁺⁺ ion, while the solution of strontium hydroxide would consist in this concentrated salt solution, on the basis of the same hypothesis,

¹ That is, 0.08 per cent. increase.

most largely of SrOH^- and OH^+ ions and un-ionized $\text{Sr}(\text{OH})_2$, with only an extremely small amount of the Sr^{++} ion. Under this assumption the ions present, resulting from the dissociation of the two salts, would be almost altogether non-common ions, and the resulting curve should therefore have the same form as for the addition of a salt with no common ion.

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**THE EFFECTS OF SALTS UPON THE SOLUBILITY OF OTHER SALTS.
VII. DISCUSSION OF THE SOLUBILITY RELATIONS
OF UNIBIVALENT SALTS.**

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18. Introduction.

The data and discussion of the fifth and sixth papers of this series show that the solubility-product principle cannot be even approximately true for moderately soluble salts of the unibivalent type, when a common bivalent ion is added, if the concentration of the un-ionized part remains constant, or varies in the same direction as it always does with uni-univalent salts. In the case of this latter, more simple type of salt the concentration of the un-ionized part of the dissolved salt always decreases with the increase in total ion concentration.¹ If this is true for unibivalent salts, the increase of solubility caused in some cases by the addition of a salt with a common bivalent ion must be accompanied by an enormous increase in the solubility-product. It is therefore of interest to consider these solubility data from a quantitative standpoint, in order to see how much of the variation of the solubility curves from what has been considered the theoretical form may be due to deviations from the solubility-product principle, and how much may be due to irregular behavior on the part of the un-ionized fraction.

With this end in view, calculations of the concentrations of the ionized and un-ionized parts of all of the salts have been made by the methods which have been employed in the study of uni-univalent salts. The method of calculation has been explained in the first paper of this series and illustrated in the fourth paper.² It may be recalled that when no common ion is present the total ion concentration (Σi) is taken as the factor determining the ionization relations of the salts. A fundamental assumption made in this method of calculation is that intermediate ions of the type AgSO_4^- or BaBrO_3^+ are not present. Indeed, it is

¹ See article IV of this series, *THIS JOURNAL*, 33, 1683-5 (1911).

² See also Sherrill, *THIS JOURNAL*, 32, 74 (1910).