

that the salts of the alkalis are less soluble in solutions of bases, than in the corresponding salt solutions. Cupric chloride depresses the solubility much more than potassium chloride. The curve for the non-common ion effect of potassium nitrate is not plotted in the figure, but it lies close to the sodium nitrate curve, and only slightly above it. It was shown in an earlier paper that solubility effects, in general, can be divided into four classes. The specifically great depressing action of the acids upon very soluble salts gives a fifth class which is important.

Other specific effects have been noticed in work upon very soluble salts. For example, other salts seem in general to show a specially high solubility when the added salt is a nitrate. Thus a chloride depresses the solubility of a nitrate much more than the nitrate depresses the solubility of the chloride.

The fact that solutions of the halogen acids are much poorer solvents for salts of the alkalis and alkaline earths is important in connection with the determination of the relative degrees of ionization of these acids and salts. From conductivity measurements alone it was at one time supposed that hydrogen chloride is more highly ionized in aqueous solution than is potassium chloride. However, a study of the change of the migration values of the ions with the concentration has led to the idea that it is quite probable that the acid is not more highly ionized. The evidence obtained from solubility measurements has been opposed to the idea that both have the same ionization, since in dilute saturated solutions the solubility of a chloride is more depressed by hydrochloric acid than by an equivalent amount of potassium chloride. Now that it has been shown that hydrochloric acid is a poorer solvent for salts than a solution of potassium chloride, it destroys the supposed value of the evidence obtained by solubility measurements; or, since in dilute solutions the difference between the salting out effects of the acid and the salt is very small, it may be considered that if anything the solubility results tend to help prove that potassium chloride and hydrochloric acid are dissociated to practically the same extent.

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THE EFFECT OF SALTS UPON THE SOLUBILITY OF OTHER SALTS. VIII^b. THE SOLUBILITY RELATIONS OF SOME EXTREMELY SOLUBLE SALTS.

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Introduction.

In the preceding paper the solubility relations of the very soluble uni-bivalent salt, strontium chloride, have been discussed, and the present

paper will extend the work to three other salts, strontium bromide, which is extremely soluble (8.6 equivalents to 1000 g. of water), and to two pentaionic salts, potassium and sodium ferrocyanides. Extremely variable results have heretofore been obtained upon the solubility of potassium ferrocyanide in water. Thus the results vary from 28 to 48 g. per 100 g. of water at 25°. The data obtained by us give this value as 24.796 g. per 100 g. of water.

The principal object of this paper was to see if with these extremely soluble salts the effect of the presence of intermediate ions upon the solubility relations could be found, after allowances are made for the specific effects which are extremely large in solutions of such high concentration. The effect to be expected, if intermediate ions are present, is that the solubility should not be depressed by the addition of a salt with a common ion of a valence of more than one, and that the increase of solubility should increase with the valence of the common ion. That this is just what is found experimentally may be seen, but it is difficult to determine how much of the effect is due to the presence of intermediate ions, since there is no exact method for determining the magnitude of what have been called the specific solubility effects. However, the results of the work presented in these two papers, when compared with the data collected in the literature on lower type salts, seem to indicate that a part of this effect must be due to intermediate ions.

Experimental.

Preparation of Solutions.—Salts of the highest purity obtainable commercially were crystallized from conductivity water in all cases and the method of procedure was the same as the one referred to in the preceding paper.

The Solubility of Strontium Bromide in Strontium Nitrate.—The bromine was determined by weighing as silver bromide. The precipitant, 0.01 *N* silver nitrate, was added in very slight excess. The precipitate was washed with 0.01 *N* nitric acid and finally with water very slightly acid. It was weighed in a Gooch crucible.

The nitrogen was determined by the Kjeldahl-Gunning-Jodwohl method with the usual precautions, *viz.*, letting the digestion mixture stand overnight and when distilling to continue the process until the flask is nearly dry. The results in grams per 1000 g. of water are given in Table I and shown graphically in Fig. 1.

The Solubility of Potassium Ferrocyanide and Sodium Ferrocyanide in Each Other.—The determination of hydroferrocyanic acid was made by a modification of de Haen's method. It was found necessary to use a very dilute solution and titrate in a definite time. To about 1 g. of ferrocyanide 100 cc. solution and 10 cc. of 0.5 *N* sulfuric acid were added and three minutes' time was taken for the titration.

The determination of potassium and sodium¹ were made by modification of the method given in Lunge's "Technical Analysis."² In order to get a satisfactory decomposition when the concentration of the added salt was high the following procedure was necessary: About 1 g. was taken for analysis. This was transferred to a beaker and diluted with 50 cc. of water; then 5 drops of sulfuric acid (1 : 10) were added, and

¹ Cf. Treadwell-Hall, Vol. II, p. 497.

² *Ibid.*, p. 729, Part 1; and *Ber.*, 36, 1930 (1903).

30 cc. of a filtered 0.1 *N* solution of ammonium persulfate. The solution was then warmed on water bath until colorless. If it was as still blue after forty minutes, another 30 cc. of ammonium persulfate were added. From this point on the method referred to gave satisfactory results.

To prevent oxidation, pure hydrogen was used to saturate all solutions before rotation and the air in the bottles was replaced by it. In spite of this precaution, decomposition certainly took place in some cases, as was made evident by the formation of a blue precipitate. In no case, except when the two solid phases were present, was a solution that gave a blue color to the asbestos mat through which it was filtered, used for analysis. In the exception mentioned, the solution analyzed showed only a faint coloration. All titrations were made and the samples for the potassium and sodium determinations taken, as quickly as was possible. However, it was noted that in all the solutions a blue precipitate was formed on standing, the amount of which increased with the time and with the concentration of the hydroferrocyanic acid. Although the change was very slight, and the agreement of duplicate analyses was good, so that the results when plotted give a fairly smooth curve, the degree of accuracy is not so great as was obtained in the work on the other salts.

Solubility Measurements.

The results of the solubility measurements are given in Tables II and III and are shown graphically in Fig. 1.

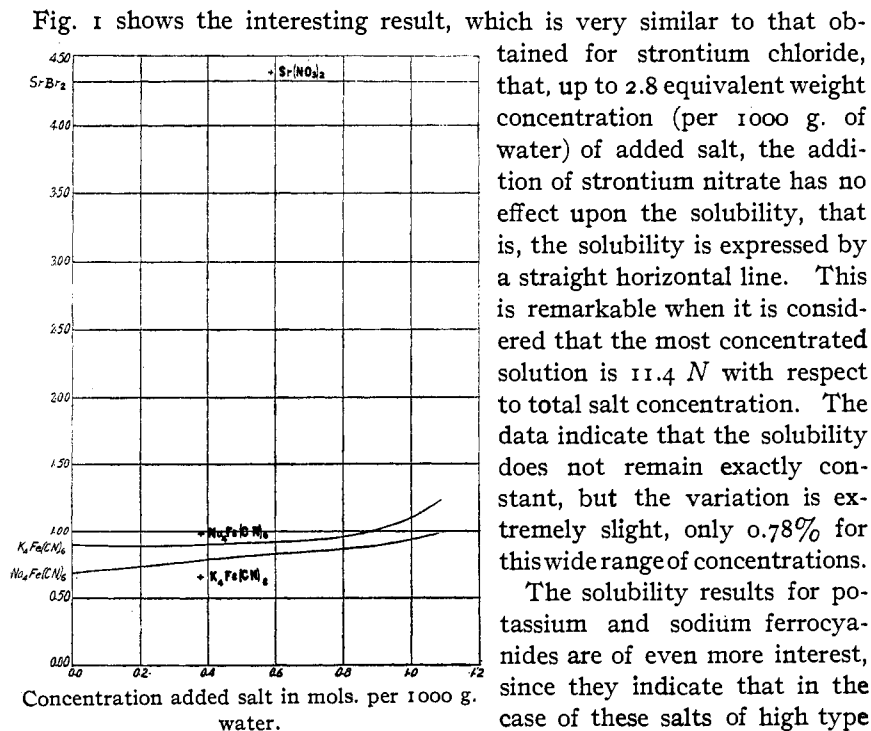


Fig. 1.—Solubility of some very soluble salts in solutions of other salts.

TABLE I.—SOLUBILITY OF STRONTIUM BROMIDE IN STRONTIUM NITRATE AT 25°. Concentration in mols. per 1000 g. H₂O.

No.	Conc. Sr(NO ₃) ₂ .	Solubility SrBr ₂ .	Mean solubility.	Solubility grams per 1000 H ₂ O.	Density 25°/4°.	Fractional conc. of added salt.	Fractional solubility.
1.....	0.0000	4.3081s
2.....	4.3080
3.....	4.3079
4.....	4.3081s	4.30805	1066.10	1.7002	0.0000	1.0000
5.....	0.0360	4.3105
6.....	4.3105s	4.3105	1066.95	0.008356	1.0006
7.....	0.07216	4.3125s
8.....	4.31249	4.3125	1067.42	1.70325	0.016750	1.0010
9.....	0.14568	4.31702s
10.....	4.31697	4.3170	1068.54	1.72844	0.033815	1.0021
	0.30663
	4.3180	1068.80	1.73766	0.071173	1.0023
	0.61124	4.3190	1069.17	1.74866	0.14188	1.0025
	1.8610	4.3390	1073.97	1.77368	0.43199	1.0072

TABLE II.—SOLUBILITY OF POTASSIUM FERROCYANIDE IN SODIUM FERROCYANIDE AT 25°.

Concentrations in mols. per 1000 g. H₂O.

Conc. Na ₄ Fe(CN) ₆ .	Solubility K ₄ Fe(CN) ₆ av. of sev'l anal.	Solubility in grams per 1000 g. H ₂ O.	Density 25°/4°.
0.00000	0.894585	247.96	1.09081
0.05072	0.882720	1.09900
0.06633	0.88544	1.10039
0.12306	0.88088	1.09350
0.25972	0.89116	1.12796
0.4900	0.91600	1.17241
0.87034	0.99000	1.19700
0.91060	1.01200	1.21190
0.95879	1.05177	1.22673
1.04380	1.11590	1.25789

TABLE III.—SOLUBILITY OF SODIUM FERROCYANIDE IN POTASSIUM FERROCYANIDE AT 25°.

Concentrations in mols. per 1000 g. H₂O.

Conc. K ₄ Fe(CN) ₆ .	Solubility Na ₄ Fe(CN) ₆ av. of sev'l anal.	Solubility g. per 1000 g. H ₂ O.	Density 25°/4°.
0.0000	0.6818	207.25	1.0595
0.1327	0.7056	214.47	1.0199
0.1624	0.7117	216.30	1.0768
0.1789	0.7213	219.23	1.0792
0.2115	0.7253	220.44	1.1006
0.2722	0.7610	231.29	1.1113
0.3532	0.7814	237.49	1.1243
0.5850	0.8652	262.97	1.1567
0.6111	0.8712	264.79	1.1581
0.6994	0.8984	273.05	1.1830
1.0578	0.9588	291.40	1.2267

Summary of Papers on Extremely Soluble Salts.

I. This paper and the one which precedes it give data for the solubility of the higher type salts, strontium chloride, strontium bromide, potassium ferrocyanide and sodium ferrocyanide, in solutions of different salts and acids. In these extremely concentrated solutions what may be called specific effects have become very prominent, so that the behavior of these salts does not give very definite evidence for or against the hypothesis of intermediate ion formation, but, nevertheless, the general solubility relations seem to be what would be expected if intermediate ions are present.