

assumed to not exist. It was found that the apparent concentration of the *un-ionized part* is affected normally by the addition of non-common ion salts; is affected abnormally by the presence of salts having a common univalent ion in that it gives an extraordinary depression; is affected even more abnormally by the addition of salts having a common trivalent ion, giving a rapid rise in the apparent solubility. These abnormalities disappear if intermediate ions are assumed to be present.

5. The theoretical discussion has not been summarized, since it has been given in a condensed form in the body of the paper.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE EFFECT OF SALTS UPON THE SOLUBILITY OF OTHER SALTS. VIII_a. THE SOLUBILITY RELATIONS OF A VERY SOLUBLE BI-UNIVALENT SALT.

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Introduction.

Since, as has been shown in previous papers of this series,¹ the moderately soluble uni-bivalent salts show such a wide variation from the solubility product principle, an investigation of the effect of the addition of salts to a bi-univalent salt of extremely high solubility was considered advisable. Strontium chloride with a solubility at 25° of 7.034 equivalents per 1000 grams of water, seemed to be the salt best suited for this purpose. Its solubility at 25° was determined in water and in various concentrations of strontium nitrate, sodium nitrate, nitric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, potassium iodide, potassium chloride, cupric chloride, and potassium nitrate. The densities of all solutions and mixtures were measured. In calculations the atomic weights for 1911 were used and all weighings reduced to vacuum.

Preparation of Salts.

Strontium Chloride.—A special grade of strontium chloride was recrystallized from conductivity water and the salt preserved in a moist condition in closely stoppered bottles.

Sodium Nitrate.—Sodium nitrate was recrystallized twice from conductivity water.

Hydrochloric and Nitric Acids.—"C. P." acids were used after careful testing.

Hydriodic Acid.—This acid was prepared by careful hydrolysis of phosphorus triiodide, with exclusion of air. The product obtained was carefully redistilled and showed no test for free iodine.

Hydrobromic Acid.—The acid was prepared in a manner analogous to that used for hydriodic acid.

¹ THIS JOURNAL, 33, 1808 (1911).

Potassium Chloride.—Potassium chloride "Zur analyse" was recrystallized twice from conductivity water.

Potassium Iodide.—The best potassium iodide obtainable was recrystallized from conductivity water.

Cupric Chloride.—This salt was recrystallized twice from conductivity water.

Potassium Nitrate.—Potassium nitrate was recrystallized three times from conductivity water.

Methods of Analysis.

Chloride, Bromide or Iodide.—The halogens were determined by adding to the solutions, containing these radicals, a little less than an equivalent amount of dilute silver nitrate solution, allowing to stand overnight, and adding a slight excess of silver nitrate the next day.¹ The precipitates were transferred to platinum Gooch crucibles and washed with very dilute silver nitrate solution and then with water containing a little nitric acid. The weight of the precipitate weighed was about 2 g.

Acids.—These were determined by titration with 0.1 *N* sodium hydroxide which had been previously standardized against hydrochloric acid, the strength of which was determined gravimetrically.

Nitrates.—Several methods were thoroughly tried out and in every case where the nitrogen was finally obtained as ammonia, from strongly alkaline solution, it was found that the gelatinous strontium hydroxide precipitate adsorbed the nitrate sufficiently to destroy the accuracy of the result. The Pelouze-Fresenius method which depends on the oxidation of ferrous iron in a solution strongly acidified with hydrochloric acid was used. This was done in an atmosphere of carbon dioxide, carefully freed from oxygen, obtained from a Kipp generator charged with marble previously boiled in conductivity water, and hydrochloric acid boiled for fifteen minutes just previous to use. Cuprous chloride was added to absorb any remaining oxygen and a layer of oil poured over the acid on the surface exposed to air.

The carbon dioxide produced was further purified by passing through a tower of chromous acetate and then through conductivity water. A weighed amount of pure iron was dissolved in hydrochloric acid and the nitrate solution run in through a dropping funnel, care being taken to prevent the entrance of air. After standing for fifteen minutes at 100° the compound resulting from the addition of nitric oxide to the ferrous chloride was broken up by boiling, the solutions cooled, and in duplicate experiments titrations were made with both potassium permanganate and potassium dichromate. Carefully carried out this method gave, with solutions of known concentration, results always within 0.1% of the amount taken.

Strontium.—When required the strontium was determined by precipitation as carbonate and weighing both as carbonate and sulfate.

Copper.—This was determined by the iodide method using the modification suggested by Lowe.² In this as in all other volumetric methods employed, weight burets were used, and weighed amounts of solutions were taken.

Iodides.—In the determination of strontium chloride in potassium iodide a total halogen analysis was made and the iodine determined in a fresh portion of solution by the method of Bray and MacKay.³

Solubility Measurements.

The results of the solubility determinations are given in Table I. In the majority of cases each point was checked by four duplicates.

¹ Richards, "Researches Concerning Atomic Weights," *Carnegie Publication*, p. 17 (1907).

² "Technical Methods of Ore Analysis," p. 77.

³ THIS JOURNAL, 32, 1193-1204 (1910).

TABLE I.—SOLUBILITY OF STRONTIUM CHLORIDE IN SALT SOLUTIONS AT 25°.

Salt added.	Equiv. of added salt in 1000 g. H ₂ O.	Sol. per 1000 g. soln.	Sol. per 1000 g. H ₂ O.	Sol. equiv. per 1000 g. H ₂ O.	Density 25°/4°.
None	None	358.0	557.6	7.034	1.4015
Sr(NO ₃) ₂	0.1372	354.2	558.5	7.044	1.4113
	0.5766	344.7	558.0	7.038	1.4336
	1.0988	333.0	557.2	7.030	1.4636
	3.318	289.7	551.4	6.956	1.6664
Solid Sr(NO ₃) ₂					
NaNO ₃	0.3621	356.3	570.6	7.198	1.4216
	0.5010	356.0	576.4	7.270	1.4588
	3.553	308.8	584.8	7.276	1.5214
	6.856	255.3	542.6	6.844	1.5581
Solid Sr(NO ₃) ₂					
HNO ₃	0.1771	355.2	557.0	7.028	1.4038
	0.3521	354.0	557.6	7.034	1.4059
	1.277	340.4	557.6	7.034	1.4175
HCl.....	0.1551	351.7	545.6	6.882	1.3953
	0.5162	336.0	515.5	6.502	1.3788
	1.017	314.2	475.2	5.996	1.3563
	2.165	263.3	385.6	4.864	1.3065
	9.205	30.55	42.09	0.530	1.1498
HBr.....	0.06817	354.7	552.8	6.974	1.4020
	0.4191	339.2	530.7	6.696	1.4010
	0.9716	315.2	496.5	6.262	1.3992
	1.154	207.8	486.2	6.132	1.3995
HI.....	0.1641	348.5	546.2	6.890	1.4058
	0.4462	332.8	527.3	6.650	1.4121
	0.4126	334.8	529.1	6.672	1.4119
	0.7539	315.2	504.6	6.366	1.4196
KI.....	0.09199	354.5	557.6	7.034	1.4093
	0.5401	337.9	556.2	7.016	1.4466
	0.6015	336.0	558.0	7.038	1.4513
	1.445	309.0	554.4	6.992	1.5154
KCl.....	0.0719	356.2	556.2	7.016	1.4032
	0.433	348.0	550.9	6.950	1.4085
	0.8576	338.9	545.5	6.882	1.4152
	1.594	324.0	536.2	6.764	1.4266
CuCl ₂	0.7134	340.05	540.0	6.812	1.4200
	2.276	304.0	503.6	6.352	1.4595
KNO ₃	0.09796	358.6	564.6	7.122	1.4107
	0.4755	359.0	587.0	7.406	1.4349

The principal object of this investigation was to show that the predictions based upon the earlier investigations on the less soluble salts of the uni-bivalent type is true, namely, that the form of the solubility curve for the addition of a salt with a common bivalent ion is, on the whole, the same as that for the addition of a salt with no common ion when the

saturating salt is a very soluble one.¹ The first step in the ionization of strontium chloride is



and in a very concentrated solution this should be almost the only form of ionization. However, the second step in the ionization



must take place to a slight extent, and for this reason in solutions of strontium chloride and nitrate there should be a small percentage of the common Sr^{++} ion. Since the ions present to the greatest extent are the non-common Cl^- , NO_3^- , SrCl^+ , and SrNO_3^+ ions, the curve should have the same form as for the addition of a salt with no common ion, but might fall slightly below the non-common ion curve on account of the presence of the small percentage of the common Sr^{++} ion.

That this is true is shown by the data in Table I. Thus the solubility of strontium chloride in solutions of strontium nitrate is practically the same as in water itself, and this is true also for nitric acid. Here the curves representing the effect of the common bivalent ion, and of no common ion, are the same. If, however, sodium nitrate is added the solubility of the strontium chloride increases slightly up to a concentration of 3.5 equivalents of sodium nitrate, but this increase amounts to only 5%. When the non-common ion salt potassium iodide is added, the solubility of the strontium chloride remains constant, just as when nitric acid or strontium nitrate is added. It is therefore found that in saturated solutions the solubility relationships seem, in so far as they bear upon the question at all, to accord with the hypothesis of intermediate ion formation, though the specific solubility effects are so great in these extremely concentrated solutions that this fact cannot be considered as bearing very strongly upon this question.

The principal work upon the effects of salts on the solubility of extremely soluble salts was done by Engel,² who developed the empirical rule that the addition of an acid to the saturated solution of an extremely soluble salt precipitates an equivalent quantity of the salt, and Armstrong³ and others suppose that the reduction of solubility caused by an acid, or by a salt, is caused by the appropriation of solvent molecules by the substance which is introduced. According to the idea of Armstrong, strontium nitrate, potassium iodide and nitric acid do not appropriate any of the solvent.

The data given in Table I show that the solubility of strontium chloride

¹ However it was realized that in the case of so soluble a salt as strontium chloride, what may be called specific solubility, might largely, but probably not entirely, mask this result.

² *Compt. rend.*, 102, 619 (1886); 104, 433 (1887); *Ann. chim. phys.*, [6] 13, 376 (1888).

³ *Proc. Roy. Soc.*, (A) 79, 564; 84, 123.

is greatly decreased by the addition of any halogen acid, whether or not the acid contains a common ion, but the solubility is not very greatly depressed by the addition of any of the alkali salts of the halogens which were used. While the salting out effect of the common chlorine ion is marked, it is plain that what may be called specific effects have become very prominent in these extremely concentrated solutions. This may be considered as probably due to a real solubility effect, and it seems that solutions of the halogen acids are poor solvents for salts, at least for the salts of the alkalis and alkaline earths.

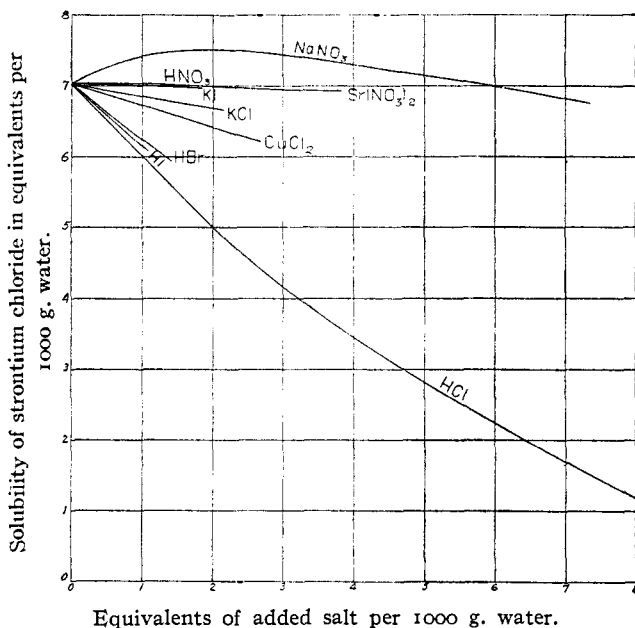


Fig. 1.—Solubility of strontium chloride in equivalents per 1000 g. water at 25° C.

Fig. 1 shows that of the non-common ion acids, hydrobromic and hydriodic very greatly depress the solubility of strontium chloride, while in nitric acid the solubility per 1000 g. of water is the same as in the water alone. Since the curve for hydrobromic lies above that for hydriodic acid, it may be assumed that the hydrochloric acid curve would lie higher still were it not for its common ion effect. Just as hydrochloric acid depresses the solubility more than hydrobromic acid, so potassium chloride gives this effect more strongly than potassium iodide. The curves for sodium nitrate and nitric acid have, on the whole, the same relative positions as those for potassium iodide and hydriodic acid, and for potassium chloride and hydrochloric acid. In all of these cases the strontium chloride is much less soluble in the acid than in the corresponding salt solution. From the literature of the subject we would judge

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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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

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 univalent salt, strontium chloride, have been discussed, and the present