

Thesis.

Some Experiments on the influence  
of salts on the solubility of  
other salts.

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Course 0'96.

1.

Some Experiments on the influence of salts on the solubility of other salts.

Contents. 1. Aim and principle of the investigation.  
2. Preparation and analysis of the salts. 3. Methods of procedure 4. Analytical results and Experimental data.  
5. Conclusion.

## Aim and principle of the investigation

The application of the laws of chemical mass action to the case of solutions of partially dissociated salts, leads to the following principle, which was first expressed by van't Hoff:

The product of the masses of the ions of a salt with which a solution is saturated remains constant, even in the presence of another salt.

The exactness of this principle is, however, not as yet established. The first experiments relative to this principle were conducted by van't Hoff, [Zeit.chrift für physikalische Chemie 4. 372] and by Noyes,

[Ibid 6.241]. The solubility of a difficultly soluble salt was determined in pure water and in the presence of another salt one of whose ions was common with the first salt. In these experiments, the agreement between the observed and the calculated solubility values was only approximate. There was considerable doubt, however, whether the cause of this deviation was due to the failure of the Nernst principle or to the inaccuracy of the assumption that the electrical conductivity of a salt is directly proportional to its dissociation.

Later experiments by Goodwin. [Zeitschrift für physikalische Chemie 13.603] indirectly gave proof

of the principle: for he shows that other methods, i.e. the electromotive force and conductivity method, lead to the same values for the dissociation as the application of the Nernst principle itself.

Still later, experiments by Noyes and Abbot, [Technology Quarterly Vol VIII No 1 pp 47-62] working with no other data than the experimentally derived solubility values and the principles of solubility effect, obtained values for the dissociation, which agreed almost exactly with those obtained by the electrical conductivity methods.

In all these experiments, however, the salts whose dissociation was calculated

were of slight solubility.

Considerable doubt exists as to whether the dissociation values obtained by the two methods, will agree as closely when more readily soluble salts are used, since the deviation from all other laws of solutions increases with the concentration.

With the idea of finding this deviation, if it exists, the following experiments were conducted along the lines followed by Hoyer and Abbot, the difference being that salts of a solubility of about 0.5 normal were used instead of those whose solubility was only about 0.02 normal.

The principles of solubility upon which the determinations

are based may be stated as follows. (a) In a saturated solution of a salt, the absolute amount of the undissociated parts remains a constant even in the presence of another salt: (b) The product of the masses of the ions of the salts also remains constant.

From these laws we may derive the following formulae.

Let  $m_0$  and  $m'_0$  be the solubilities of the two salts in pure water,  $m$  and  $m'$  be their corresponding solubilities when both are present in excess, and  $a_0, a'_0, a$  and  $a'$  the corresponding values of their dissociations. Since the undissociated parts remains constant,

7.

$$m_0(1-a_0) = m(1-a) \quad (1)$$

$$m'_0(1-a'_0) = m'(1-a') \quad (2)$$

and since the product of the masses of the ions is constant,

$$m_0^2 a_0^2 = ma(ma + m'a') \quad (3)$$

$$m_0'^2 a_0'^2 = m'a'(ma + m'a') \quad (4)$$

These four equations contain only four unknown quantities i.e. the values of  $a_0$ ,  $a'_0$  etc. and can be readily solved.

In preparing for an investigation of this kind, it was first necessary to find three suitable salts. Such salts must fulfil two conditions, (1) their solubilities at the temperature used must be nearly the same, (2) there must be a satisfactory method of analysis of each salt, alone and in the presence of each of the



other salts. The Chlorate, Bromate and Iodate of Potash was chosen as three salts having one ion in common, which most nearly fulfilled these conditions.

The solubility of each salt was determined in pure water and in a saturated solution of each of the other salts.

## 2.

Preparation and analysis of the salts.

The salts used in all these experiments were prepared by recrystallization from the ordinary commercial salts. The salt was dissolved in the smallest possible quan-

lity of boiling water and crystallized out by cooling with ice. The salt crystallized out was filtered off on a porcelain plate, washed with a small quantity of ice water and sucked dry with the pump. This process was repeated three times for each salt, until, owing to its far greater solubility, any haloid salt of Potash was completely removed. The salts were then dried at  $110^{\circ}\text{C}$ ., finely pulverized and ready for use. The purity of the salts was established by test analyses, which showed them to be free from any harmful impurity. The analysis, made as is described under

procedure later, gave the following results.

Salt	Ag. haloid.	Salt taken	per cent.
$KClO_3$	0.4112	0.3503	100.00
"	0.3853	0.3289	100.00
$KBrO_3$	0.4091	0.3626	100.00
"	0.5097	0.4537	100.00
$KIO_3$	0.4499	0.4100	100.10
"	0.4434	0.4049	100.30

3.

Methods of procedure.

Oil vials of about 50cc capacity were filled nearly full of water and an excess, about 5 grams, of the finely pulverized salts added. In order to approach the point of saturation from

either side, duplicate bottles were filled, one of which was heated to  $30^{\circ}\text{C}$  and well shaken to ensure supersaturation before immersion in the bath. The bath and rotating apparatus was the same as generally employed for solubility rotations and will be found described in *Zeitschrift für physikalische Chemie* 9. 606. The solubilities of the salts were such that  $25^{\circ}\text{C}$  was chosen as a suitable temperature and the bath kept constant within  $0.02^{\circ}\text{C}$  of that temperature. The temperature coefficient of these salts was so large, about 10% for  $1^{\circ}\text{C}$ , that even this slight variation can be held responsible for the variations in some of

The analytical results. The solutions were rotated in the bath from three to four hours and then placed upright and allowed to settle until perfectly clear, requiring from one to three hours more. When clear, 10<sup>cc</sup> were removed in a pipette, specially calibrated to deliver exactly for solutions of this viscosity and specific gravity, and analyzed by methods here described!—

The analysis of the simple salts was easy. A slight excess of sulphurous acid was added to the measured salt solution which had been diluted to 150<sup>cc</sup> volume. The solution was now allowed to stand in a moderately warm place

for about twenty minutes.  
10<sup>cc</sup> of nitric acid (1.42 sp. g.)  
were then added to those  
solutions not containing  
Iodine. Addition of strong nitric  
acid was found to oxidize  
hydriodic acid to free iodine,  
in which state it is not com-  
pletely precipitated by silver  
nitrate. Nitric acid was acce-  
dingly added to these portions  
until they just began to turn  
brown, and then a drop of  
sulphurous acid added turned  
all free iodine into hydro-  
iodic acid. An excess of silver  
nitrate was then added and  
in case of the iodine solu-  
tions, 10<sup>cc</sup> of nitric acid,  
after the silver nitrate, and  
the precipitates were allowed

to stand over night. The precipitates were then filtered off on previously weighed Gooch filters, washed, dried for one hour at  $175^{\circ}\text{C}$  in an oil-bath, cooled and weighed.

No attempt was made to obtain constant weights, as test samples when heated for a second period in the bath, showed no perceptible diminution in weight.

The analyses of the mixed haloids was a more difficult matter. At first it was attempted to treat the mixed silver salts obtained by the precipitation with silver nitrate, with chlorine or bromine as the case might be, and to calculate the composition

of the precipitate from the loss in weight. The crucibles containing the mixed silver salts, chlorine and bromine or chlorine and iodine, were heated with a ring burner, for periods of one hour in a stream of chlorine gas, until a constant weight was obtained. The bromide and iodide were placed in a small vessel and the salt covered with liquid bromine and allowed to stand over night, after each treatment being heated to expel excess bromine, this treatment being also continued to constant weight. This method was found to be unsatisfactory for two reasons.

- (1) although the asbestos for



the filter had been treated with nitric and hydrochloric acids, chlorine and bromine and then ignited, it was found that the values of the silver salt calculated from the loss in weight were abnormally high, indicating that the asbestos was losing weight under the treatment.

(2) The time required to obtain a constant weight was so long that any large number of analyses was rendered impossible. In some cases it was found necessary to repeat the chlorine treatment as many as eight or nine times before a constant weight was reached.

Some weeks were spent in trying to perfect this method

but in the time allowed, it was found necessary to use some other method if any results were to be obtained.

A combination gravimetric and volumetric process was then tried. In this process the treatment with sulphurous and nitric acid was the same as before described. The silver nitrate, however, was added in the form of a standardized solution, and run in accurately from a burette. After standing over night, the precipitates were filtered off on Gooch filters and weighed as before. The filtrates were saved and the excess of silver nitrate was titrated for with potassium sulphocyanate solution.

In this process, ferric iron was used as an indicator, giving a red color in the presence of the sulphocyanate, but only when the silver nitrate had been precipitated. Theoretically, the titration is very accurate, one drop of a 0.1 normal solution being sufficient to produce a marked end point. In order to obtain the amount of the individual silver salts in the precipitate, we have to resort to computations like the following.

Mixture,  $a$ g Cl,  $b$ g Br.

Let  $x = a$ g Cl &  $y = b$ g Br

Then  $x + y =$  amount salts weighed

$\frac{108}{143.5}x + \frac{108}{188}y =$  silver as obtained from titration.

Here we have two unknown

quantities in two equations and can readily solve for  $x$  and  $y$ . The results obtained by this method were not as satisfactory as might be desired since a very small error in the titration was multiplied some twenty five times in the computation. While the values for the mixed silver salts as weighed agreed very closely, the values from the titrations varied in a very unaccountable manner and the results of computation differed widely. I think that with long practice this error could be reduced to a small fraction of that now existing and the results obtained might be comparable.

4.

## Analytical results.

The experimental data and computed results are set forth in the following tables. The temperature was  $25^{\circ}\text{C}$  in all cases, the variation never being more than  $0.02^{\circ}\text{C}$  -  $0.03^{\circ}\text{C}$  and in the last few series not over  $0.02^{\circ}\text{C}$ .

KClO<sub>3</sub> in Pure Water.

	AgCl from 10 <sup>cc</sup>	KClO <sub>3</sub>		AgCl from 10 <sup>cc</sup>	KClO <sub>3</sub>
1	1.1557	0.9867*	11	0.9645	0.8233
2	0.9138	0.7802*	12	0.9642	0.8231
3	0.9525	0.8132*	13	0.9665	0.8247
4	0.7517	0.6419*	14	0.9660	0.8242
5	0.7556	0.6449*	15	0.9662	0.8249
6	0.7462	0.6373*	16	0.9625	0.8217
7	0.8764	0.7478*	17	0.9649	0.8238
8	0.7056	0.6024*	18	0.9684	0.8266
9	0.9726	0.8290	mean. 0.8249 ± 0.034		
10	0.9692	0.8273	mol. per liter 0.6734 ± 0.032		

\* omitted in calculation of mean.

The quantities following the  $\pm$  signs are the average deviations of the mean, calculated from the formula  $\frac{\sum d}{n}$  where  $\sum d$  is the arithmetical sum of the deviations and  $n$  is the number of measurements.

KBrO<sub>3</sub> in Pure Water.

	AgBr from 10 <sup>cc</sup>	KBrO <sub>3</sub>		AgBr from 10 <sup>cc</sup>	KBrO <sub>3</sub>
1	0.9718	0.8630*	11	0.9033	0.8023
2	0.8934	0.7936*	12	0.9016	0.8007
3	0.9001	0.7995*	13	0.9022	0.8013
4	0.9884	0.8766*	14	0.9042	0.8034
5	0.8942	0.7945*	15	0.9000	0.7994
6	0.8963	0.7961*	16	0.9029	0.8020
7	0.9008	0.7989*	17	0.9033	0.8023
8	0.8970	0.7977*	18	0.9042	0.8030
9	0.9047	0.8035	mean. 0.8018 ± 0.034		
10	0.9008	0.8008	mol. per liter. 0.4265 ± 0.0418		

\* omitted in calculation of mean.

KIO<sub>3</sub> in Pure Water.

	AgI from 10 <sup>cc</sup>	KIO <sub>3</sub>		AgI from 10 <sup>cc</sup>	KIO <sub>3</sub>
1	1.0142	0.9233*	11	1.0836	0.9871
2	0.9315	0.8484*	12	1.0847	0.9878
3	0.0128	0.9223*	13	1.0868	0.9896
4	1.0451	0.9506*	14	1.0806	0.9843
5	1.1085	1.0090*	15	1.0858	0.9888
6	1.0891	0.9917*	16	1.0802	0.9834
7	1.0942	0.9943*	17	1.0857	0.9888
8	1.0891	0.9917*	18	1.0830	0.9861
9	1.0753	0.9800	mean 0.9860 ± 0.0363		
10	1.0790	0.9826	mol. per liter. 0.4196 ± 0.0426		

\* omitted in calculation of mean.

The following tables show the solubility values as derived by the method of Cl or Br treatment. They are here appended to show the deviations, probably due to analysis.



KClO<sub>3</sub> and KBrO<sub>3</sub> in each other.

	KClO <sub>3</sub> from 10 <sup>cc</sup>	KBrO <sub>3</sub> from 10 <sup>cc</sup>
1	0.2357	0.5560
2	0.5295	0.4546
3	0.1506	0.5826
4	0.4258	0.6932
5	0.5400	0.3471
mean	0.3672 ± 0.0648	0.5266 ± 0.0539

KClO<sub>3</sub> and KIO<sub>3</sub> in each other.

	KClO <sub>3</sub> from 10 <sup>cc</sup>	KIO <sub>3</sub> from 10 <sup>cc</sup>
1	0.4208	0.6788
2	0.3737	0.7243
3	0.4239	0.6932
4	0.4140	0.7144
5	0.6713	0.7450
6	0.6594	0.5525
mean	0.4942 ± 0.0467	0.7180 ± 0.0090

KBrO<sub>3</sub> and KIO<sub>3</sub> in each other.

	KBrO <sub>3</sub> from 10 <sup>cc</sup>	KIO <sub>3</sub> from 10 <sup>cc</sup>
1	0.6316	0.5891
2	0.6068	0.7316
3	0.4960	0.8582
4	0.3539	0.9234
5	0.4220	1.0330
6	0.5319	0.8334
mean	0.5070 ± 0.0344	0.8288 ± 0.0458

In the above three tables the average deviation of the mean is so large that they are practically worthless.

In the following tables the values are shown as derived by the second analytical method, that is, the compound volumetric and gravimetric method.

KClO<sub>3</sub> and KBrO<sub>3</sub> in each other.

	Ag salts	Ag by titration	AgCl in 10cc	AgBr in 10cc
1	1.2200	0.8941	1.0848	0.1352
2	1.2233	0.9236	1.0685	0.1524
3	1.2227	0.9592	0.8748	0.3479
4	1.2198	0.8449	0.8091	0.4107
5	1.2224	0.8585	0.8770	0.3454
6	1.2267	0.8765	0.9646	0.2621
7	1.2314	0.8598	0.8557	0.3757
8	1.2593	0.9064	0.6270	0.2321
9	1.2439	0.8973	1.0258	0.2181
10	1.3220	0.9302	0.9590	0.3630
mean.			0.9546 ± 0.0254	0.2845 ± 0.0261

KClO<sub>3</sub> and KIO<sub>3</sub> in each other.

	Ag salts	Ag by titration.	AgCl from 10 <sup>cc</sup>	AgI from 10 <sup>cc</sup>
1	1.1331	0.5211	+0.1024	1.0307
2	0.9947	0.4500	-0.0144	1.0191
3	1.0654	0.4896	-0.0629	1.1683
4	1.1076	0.4920	-0.0583	1.1659
5	1.0436	0.4637	-0.0444	1.0980
6	1.1353	0.5180	-0.0128	1.1481
7	0.9941	0.4542	-0.0093	1.0034
8	1.0474	0.4840	+0.0088	1.0386
9	1.0858	0.4954	-0.0035	1.0893
10	1.0983	0.4791	-0.0740	1.0823
11	1.0657	0.4304	-0.2026	1.2683
12	1.0893	0.4898	-0.0370	1.1263
mean			-0.0340 ± 0.113	1.1115 ± 0.193

In this series it would seem that the Chlorate of potash had been entirely thrown out of solution by the Iodate. The results however vary so widely that they are unreliable.

KBrO<sub>3</sub> and KIO<sub>3</sub> in each other.

	Ag Salts	Ag by titration	Ag Br from 10 <sup>cc</sup>	Ag I from 10 <sup>cc</sup>
1	1.5793	0.8612	1.1784	0.4009
2	1.5818	0.8453	1.0852	0.4961
3	1.5682	0.8399	1.0883	0.5299
4	1.5784	0.8473	1.0687	0.5097
5	1.5791	0.8472	1.0566	0.5225
6	1.5858	0.8739	1.2628	0.3230
7	1.5781	0.8647	1.2132	0.3649
8	1.5730	0.8426	1.0409	0.5321
9	1.5818	0.8462	1.0374	0.5444
10	1.5808	0.8434	1.0174	0.5634
11	1.5658	0.8144	0.8251	0.7407
12	1.5791	0.8583	1.1583	0.4206
mean.			1.1652 ± 0.0305	0.4957 ± 0.0227

In the above three tables the deviation of the mean is so large that the mean could not be used with any degree of confidence in its accuracy.

The fact that the weights of the mixed silver salts agree so well would indicate that the saturation was complete and that the variation of results was due to analytical work. The non agreement of the figures for silver by titration confirm this supposition. The silver nitrate solution used, was of strength such that 1cc was equivalent to 0.02407<sup>gm</sup> of silver. It will thus be seen that a small error in the titration will be largely multiplied in obtaining the value for total silver. This would, perhaps, account for some of the deviation. The case of the Chlorate and Iodate, in which it appears that all the chlorate has been thrown out

of solution, is especially interesting and would bear still further investigation, did time permit. In this series the figures for both the weights of mixed silver salt and for the silver by titration, agree much more closely with each other than in either of the other two mixtures. This would lead to the supposition that the case is as before stated and can be accounted for only by the theory that a double salt of the chlorate and iodate had been formed, having such composition that all chlorate is removed while enough iodate is left in solution to saturate it. The solubility value is however considerably higher than in

pure water.

5.

### Conclusion.

In conclusion, I can only say that the original purpose of the investigation, the comparison of dissociation values as determined by this method and by electrical dissociation, was not fulfilled, owing to the fact that satisfactory solubility values had not been obtained, up to the time the investigation was closed. On the other hand, the solubility of the simple salts was determined for the temperature  $25^{\circ}\text{C}$ , more accurately than has probably ever been done before. The interesting fact



about the mixture of chlorate and iodate, as enumerated above, may also prove of value to future investigators. If such be the case, the work spent in the investigation will not be entirely lost.

Stephen DeW. Gage.

Course V.

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