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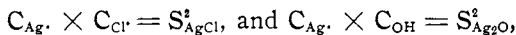
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THE SOLUBILITY EQUILIBRIUM BETWEEN SILVER CHLO-
RIDE, SILVER OXIDE, AND SOLUTIONS OF POTAS-
SIUM CHLORIDE AND HYDROXIDE.

By A. A. Noyes and D. A. Kohr.

The theoretical application of the Mass-Action Law and the Ionic Theory to the type of equilibria to which the case named in the title belongs has already been made by Nernst,[1] who also interpreted the well-known results of Guldberg and Waage with barium carbonate and sulphate in accordance with the theory. The principle of the equilibrium is very simple; namely, since

$$C_{Ag\cdot} \times C_{Cl\cdot} = S^2_{AgCl}, \text{ and } C_{Ag\cdot} \times C_{OH} = S^2_{Ag_2O},$$

it follows that

$$C_{Cl'}/C_{OH'} = S^2_{AgCl}/S^2_{Ag_2O} \; ;$$

that is, that the ratio of the concentrations of the chlorine and hydroxyl ions in any solution which is simultaneously saturated with silver chloride and oxide is constant and equal to the ratio of the squares of the solubilities of these two salts in pure water, it being assumed that the two salts are completely dissociated. This principle is of importance not only because it underlies a frequently occurring type of chemical reaction, but also because it

[1] " Theoretische Chemie," Second edition, p. 498.

furnishes an indirect means of determining the solubility in water of salts which are so difficultly soluble that the concentration of their saturated solutions can not be directly determined by analytical methods. We have therefore thought it worthy of further investigation.

An experimental investigation of the analogous principle that applies in the case where one of the difficultly soluble salts is tri-ionic has been made by Findlay,[1] who studied the equilibrium between lead sulphate, lead iodide, and solutions of sodium sulphate and iodide. The theory was found to be confirmed.

Our own investigation consisted in determinations of the solubility in water of silver oxide (and incidentally of silver iodate), and of the concentrations of solutions containing both potassium chloride and hydroxide that are in equilibrium simultaneously with silver chloride and oxide.

The substances used were prepared as follows: Silver oxide was made by precipitating silver nitrate solution with a clear solution of barium hydroxide, and the precipitate was washed by decantation with four liters of freshly boiled water and collected on a filter. The precipitation, washing, and filtration were carried out in an apparatus so arranged that the precipitate did not come at any time in contact with ordinary air containing carbon dioxide. Its purity was established by "rotating" successively the same portion of the oxide with fresh quantities of water, and determining the amount dissolved, which proved to be constant. Silver chloride was prepared by precipitating silver nitrate solution with hydrochloric acid and washing the precipitate thoroughly in a beaker protected from the light. A potassium hydroxide solution was made by dissolving commercial potassium hydroxide "from alcohol" in water, determining analytically the amount of carbonate present, adding the amount of barium hydroxide solution necessary to precipitate it, and decanting the solution after the precipitate had settled. This solution was found to give a faint test for carbonate upon adding more barium hydroxide; but, as it also gave a slight precipitate with sulphuric acid, it was evident that a quantity of barium substantially equivalent to the carbonate had been added. A potassium chloride solution was made from

1 *Ztschr. phys. Chem.*, **34**, 409 (1900).

salt which had been precipitated by hydrochloric acid and ignited.

The solutions of the pure silver salts in water were saturated by rotating them in a thermostat at 25° for four or five hours in the apparatus described by Noyes.[1] The state of saturation was approached both from the undersaturated and from the supersaturated side. After allowing the solid particles to settle for a short time, the solutions were sucked out of the bottles, which were left standing in the thermostat, through a filter placed in a closed funnel into a 250 cc. graduated flask. The solutions were then precipitated with potassium iodide, about 0.5 cc. of a saturated barium nitrate solution being also added to promote the coagulation. The precipitates were collected in platinum Gooch crucibles upon a layer of finely divided platinum, dried at 160°, and weighed.

The results obtained with silver oxide and with silver iodate[2] are given below. The figures represent the grams of silver iodide obtained from 250 cc. of saturated solution.

TABLE I.

Silver oxide.		Silver iodate.	
From under-saturation.	From super-saturation.	From under-saturation.	From super-saturation.
0.0125	0.0127	0.0109	0.0112
0.0130	0.0120	0.0107	0.0113
0.0125	0.0133	0.0112	0.0117
0.0102[3]	0.0112[3]	0.0108	0.0106
.....	.....	0.0111	0.0114
0.0127	0.0127	0.01094	0.01124

It will be seen that the means of the "undersaturated" and "supersaturated" values agree completely in the case of the silver oxide, and fairly well in the case of the iodate.

The solubilities expressed in mols per liter corresponding to the final means are 2.16×10^{-4} for silver oxide, and 1.89×10^{-4} for silver iodate.

The solubility of the silver iodate was determined with the idea that it might prove a satisfactory salt to use in connection with silver oxide in testing the theory under consideration. But, since

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[1] *Ztschr. phys. Chem.*, **9**, 606 (1892).

[2] The silver iodate was prepared by precipitating a solution of silver sulphate with one of potassium iodate made from the recrystallized salt. The precipitate was washed thoroughly with hot water.

[3] Omitted in the calculation of the mean.

the solubilities proved to be so nearly identical, and since therefore the ratio of them would not differ greatly from the ratio of their squares, it was decided to combine silver chloride with the silver oxide; and no further work was done with the iodate.

In the first series of experiments with mixed salts, an excess of moist silver oxide and chloride was added to an approximately 1/3 normal solution of potassium hydroxide, and the mixtures were rotated in the thermostat at 25° for a number of hours. In half of the experiments, the mixtures were heated above 25° and shaken, before placing them in the thermostat; but no systematic difference was shown by the results. After the rotation, the solutions were allowed to settle, filtered in the manner above described, and portions of 50 cc. and 200 cc. measured out. The 50 cc. portion was titrated with 0.5217 normal nitric acid[1] to determine the hydroxide present, and was then united with the 200 cc. portion. The whole was then acidified with nitric acid and precipitated with silver nitrate; the precipitated silver chloride was collected in Gooch crucibles, dried, and weighed.

The experimental results and the calculated ratio are given in the following table: The first column contains the number of the experiment; the second, the grams AgCl obtained from 250 cc. of saturated solution; the third, the cubic centimeters of 0.5217 normal HNO_3 neutralized by 50 cc. of saturated solution; the fourth and fifth, the corresponding number of millimols of KCl and KOH respectively per liter; and the sixth, the ratio $C_{Cl}:C_{OH}$, calculated in the manner described below.

TABLE II.

Expt. No.	AgCl. Gram.	HNO_3. Cc.	C_{KCl}	C_{KOH}	$C_{Cl}:C_{OH}$
1	0.1181	31.60	3.295	329.7	0.01070
2	0.1184	32.10	3.303	334.9	0.01056
3	0.1231	34.30	3.434	357.8	0.01028
4	0.1269	34.35	3.540	358.3	0.01058
5	0.1256	34.20	3.503	356.8	0.01052
6	0.1222	33.50	3.410	349.5	0.01045
Mean					0.01052

A second series of two experiments (Nos. 7 and 8) was made

[1] This had been standardized through a sodium hydroxide solution against a hydrochloric acid solution in which the acid had been determined by precipitation with silver nitrate.

in which a weaker potassium hydroxide solution (about 0.065 molar) was substituted for the stronger (one-third molar) solution. And in a third series, consisting of four experiments (Nos. 9-12), five times as much solid potassium chloride was added at the start to the potassium hydroxide solution as was present after equilibrium was reached. The results are given in the following table:

TABLE III.

Expt. No.	AgCl. Gram.	HNO$_3$. cc.	C_{KCl}	C_{KOH}	$C_{Cl'}/C_{OH'}$
7 · · · · · ·	0.0239	6.78	0.666	70.7	0.00995
8 · · · · · ·	0.0190	5.72	0.530	59.7	0.00938
9 · · · · · ·	0.0177	5.20	0.494	54.2	0.00961
10 · · · · · ·	0.0222	6.23	0.620	65.0	0.01006
		Mean ·			0.00975
11 · · · · · ·	0.0375	10.50	1.046	109.5	0.01020
12 · · · · · ·	0.0329	9.05	0.918	94.4	0.01038
		Mean ·			0.01029

It will be seen that the values of the ratio $C_{Cl'}/C_{OH'}$ check fairly well in each set of experiments where the potassium hydroxide concentration was approximately the same. This is true especially of the values of Table II where that concentration and the weight of silver chloride obtained were the greatest. There is a slight decrease in the ratio (from 0.0105 to 0.0098) with decrease of concentration (from 0.35 to 0.06 molar KOH). This is, however, of a secondary magnitude, and the general agreement of the results obtained at different concentrations and by different methods of approaching the equilibrium-condition proves that there can be no considerable error in the results.

A few words must be added in regard to the manner of calculating this ratio. It consisted in first multiplying the concentrations of the two salts given in the fourth and fifth columns of the tables by their respective degrees of dissociation. These last were determined by the following method, which seems to us to be the most exact one for the calculation of the dissociation of salts, in the presence of each other, which do not follow the Mass-Action Law. It is based on the principle demonstrated by solubility experiments,[1] that the concentration of the undissociated part of

[1] See Noyes and Abbott : *Ztschr. phys. Chem.*, **16**, 138 (1895).

a salt has the same value, when the product of the concentrations of its ions has the same value, whatever may be the two separate factors of that product. This principle may be applied to the present case in the following manner. In the experiments in Table II the potassium chloride solution is about 0.0033 molar and the hydroxide solution about 0.35 molar. As a first rough approximation we may assume each salt to be 85 per cent. dissociated; and we then get for the product $C_K \cdot \times C_{Cl}$, the approximate value, $(0.35 + 0.0033) \times 0.85 \times 0.0033 \times 0.85$. The square root of this quantity (or 0.030) is 85 per cent. of the concentration (0.0355) of pure potassium chloride at which the degree of dissociation is the same as it is in the solution of the mixed potassium salts. This degree of dissociation can then be ascertained by reference to a table, or better a plot, of molar-conductivity values. In this case with the help of the data of Kohlrausch and Maltby,[1] it is found to be 90 per cent. In a similar way the dissociation of the potassium hydroxide is found to be 84 per cent.[2] These values are used in calculating the ratios for all six experiments given in Table II. For experiments 7-10 in Table III, the dissociation of the chloride is found to be 95 per cent., and that of the hydroxide 90 per cent. For experiments 11 and 12, the corresponding values are found to be 94 and 88 per cent., respectively.

Adopting for the ratio the round value 0.0100, which is as accurate a conclusion as the experiments admit of, it follows from the equation given at the beginning of this article that the solubility of the chloride should be almost exactly one-tenth $(= \sqrt{0.01})$ of that of the oxide, or 2.16×10^{-5} mols per liter, adopting our analytically determined value for the oxide. The value found by Kohlrausch and Rose[3] by conductivity measurements at 25° was 1.50×10^{-5}. These two quantities are of the same order of magnitude, and to that extent they furnish a confirmation of the theory. Thus, if the fact of the electrolytic dissociation of the two silver salts was not taken into account, it might be expected that the ratio of the solubilities themselves, instead of that of their squares, would be equal to the ratio C_{Cl}/C_{OH}, and consequently

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[1] *Sitzungsber. königl. preuss. Akad. der Wissenschaften*, (1899), p. 665 ; (1900), p. 1006.

[2] Assuming the limiting value ($\Lambda K + \Lambda OH$) to be equal to 239 at 18° (Kohlrausch : *Sitzungsber.* just cited, (1901), p. 1031) and using also his data for the higher concentrations.

[3] *Ztschr. phys. Chem.*, **12**, 242 (1893).

that the solubility of silver chloride would be 0.216×10^{-5} —an enormous divergence from the result by the conductivity method. It is, nevertheless, true that the deviation of the solubility-ratio directly determined from that predicted from the equilibrium experiments is greater than can, with any degree of probability, be accounted for by the experimental errors, even though these may be considerable in the case of the solubilities of two such difficultly soluble salts.   There is, moreover, one explanation of a theoretical nature that would account for the results; namely, the assumption, by no means *a priori* improbable, that silver hydroxide in saturated solution is not even approximately completely dissociated.   If Kohlrausch and Rose's value for silver chloride be considered correct and by means of the ratio $C_{Cl'} : C_{OH'}$, the "solubility" of silver oxide be calculated from it, this is found to be 1.50×10^{-4}, while the analytically determined value is 2.16×10^{-4}.   The former value which has been considered to be the solubility represents in reality, according to the theory, only the concentration of the dissociated portion in the saturated solution; and, admitting the accuracy of the data, the conclusion might be drawn from them that silver hydroxide in its saturated solution is 70 per cent. dissociated.   No independent evidence can be cited, as far as we know, either for or against this conclusion. We have considered the possibility of verifying it by conductivity measurements; but, in view of the difficulties known to exist in the case of such very dilute solutions of bases, it has seemed to be hopeless to obtain sufficiently accurate results, at any rate unless extraordinary precautions were taken, and the matter were made the subject of an extended investigation.

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The results of this investigation may be fully summarized as follows:

Solubility determinations at $25°$, in which the ordinary methods of analysis were employed, gave for silver oxide 2.16×10^{-4} mols AgOH per liter, and for silver iodate 1.89×10^{-4} mols $AgIO_3$ per liter.

The ratio of the concentrations of the chlorine and hydroxyl ions in solutions of potassium chloride and hydroxide which are simultaneously saturated with silver chloride and oxide increases

only 8 per cent. with a sixfold multiplication of the concentrations of the former salts, and has very nearly the value, 0.0100.

Assuming that the two silver compounds are completely dissociated in their saturated solutions, the requirement of the Mass-Action Law and the Ionic Theory that the ratio of the squares of their solubilities be equal to the concentration-ratio just referred to, leads to the conclusion that the solubility of silver oxide in water is ten times that of silver chloride. The value for silver oxide determined directly by us is, however, 14.4 times that obtained for silver chloride by Kohlrausch and Rose by the conductivity method. It is pointed out that this divergence would be accounted for by the assumption that silver hydroxide in saturated solution is only 70 per cent. dissociated.

An exact method is described of deriving the dissociation of two dissolved salts in the presence of each other, which consists essentially in considering the dissociation of each salt to be that which conductivity measurements show it to have when it is alone present at a concentration of its ions equal to the square-root of the product of the concentrations of its ions in the solution of the mixed salts.

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SOME NOTES CONCERNING HALPHEN'S ¡TEST FOR COTTONSEED OIL.

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SINCE Halphen's reaction for cottonseed oil was first published in 1897,[1] it has been submitted to more or less rigid test by a considerable number of investigators. Although some differences of opinion have arisen as to its merits and general applicability, it seems to have been quite generally accepted as the most reliable method at hand for detecting the presence of cottonseed oil in admixture with other oils or fats.

K. Mazher,[2] after using nitric acid, Hirschsohn's reagent, Becchi's test, and Halphen's reaction, concludes that only the latter is to be depended upon.

[1] J. Pharm. Chim., 9, 392 (1897).
[2] Ibid., 17, 159.