of a larger proportion of sulphate sulphur in these concentrated solutions than was found in the dilute solutions boiled in open air also favors the supposition that the reaction by which pentasulphide is produced at the expense of thiosulphate is accompanied by the formation of calcium sulphate. The smaller proportion of sulphate sulphur in some of the more concentrated solutions seems to oppose this view, however. On the other hand, the analytical methods for distinguishing quantitatively between these several forms of sulphur compounds are not yet thoroughly perfected and it may be that this apparent objection to the reaction would be removed if more exact methods of analysis were available. In the absence of better analytical methods, these results are presented as the best obtainable, and the conclusions suggested as a possible step toward a better knowledge of the reactions between lime and sulphur under varying conditions.

LABORATORY OF THE
WASHINGTON AGRICULTURAL EXPERIMENT STATION,
PULLMAN, WASH.

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

THE RELATIVE SOLUBILITY OF THE SILVER HALIDES AND SILVER SULPHOCYANATE.

BY ARTHUR E. HILL.

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The theory of electrolytic dissociation teaches that if saturated solutions of two very insoluble salts which have an ion in common could be mixed without increase of volume, precipitation of both salts would occur. For example, saturated solutions of AgCNS and AgCl would, upon mixing, precipitate both compounds in part, since by the addition of silver ion the solubility product of each salt would be exceeded. The quantities of chloride and sulphocyanate precipitated would be such as to leave the solution saturated in respect to both salts, and the equilibrium finally reached would be expressed for the respective compounds by the equations $C_{\overset{+}{Ag}} \times C_{\overline{CNS}} = K_1$ and $C_{\overset{+}{Ag}} \times C_{\overline{Cl}} = K_2$, where C stands for concentration in equivalents per unit volume, K_1 and K_2 are the products of the free ions (solubility products), and the subscripts denote the respective ions. By division,

$$\frac{C_{\overset{+}{Ag}} \times C_{\overline{CNS}}}{C_{\overset{+}{Ag}} \times C_{\overline{Cl}}} = \frac{K_1}{K_2} \qquad \text{(Equation 1).}$$

The common term $C_{\overset{+}{Ag}}$ may be cancelled out, the relation becoming

$$\frac{C_{\overline{CNS}}}{C_{\overline{Cl}}} = \frac{K_1}{K_2} \qquad \text{(Equation 2).}$$

The same equilibrium will be attained if to a solution of AgCl, in presence of excess of the salt, a *soluble* sulphocyanate, such as KCNS, be added in sufficient quantity to exceed the solubility product of AgCNS. Precipitation of AgCNS will result, reducing the concentration of silver ions; the solution will therefore become temporarily undersaturated with respect to AgCl, and the latter salt will dissolve, thereby increasing the concentration of chloride ions and also of silver ions, so that the cycle of reactions will again be set in operation. Simultaneous precipitation of AgCNS and solution of AgCl will continue until the mixture contains the ions $\overline{Cl}$ and $\overline{CNS}$ in such quantities as are in equilibrium with the two silver salts, as expressed in equations 1 and 2. The solution thus obtained differs from the hypothetical solution discussed in the preceding paragraph in having present an additional cathion (potassium ion) and in having the chloride and sulphocyanate ions present in amounts measurable by ordinary analytical methods. The theory of solution equilibria of this character was first stated by Nernst.[1]

By the application of equation 2 to reactions such as the foregoing it becomes possible to determine the relative solubility of two difficultly soluble salts whenever (1) the concentration of the free ions ($C_{\overline{CNS}}$ and $C_{\overline{Cl}}$ in the example given) can be calculated from the total concentration of the substances in the solution as analytically determined, and (2) the degree of dissociation of the two insoluble salts in saturated solution is known, so that the total solubility can be calculated from the solubility products (K_1 and K_2). Following this method a number of such equilibria have been investigated, and the solubility of the salts determined. Guldberg and Waage's classic results on the reaction $BaCO_3 + K_2SO_4 = BaSO_4 + K_2CO_3$ have been shown by Nernst[2] and by Meyerhoffer[3] to refer to an equilibrium of this class, although originally interpreted otherwise. Other investigators have studied the following reactions of this type:

$TlCl + KCNS \rightleftarrows TlCNS + KCl$ (Knüppfer[4]).
$PbI_2 + Na_2SO_4 \rightleftarrows PbSO_4 + 2NaI$ (Findlay[5]).
$CaCO_3 + K_2C_2O_4 \rightleftarrows CaC_2O_4 + K_2CO_3$ (Foote[6]).
$2AgCl + 2KOH \rightleftarrows Ag_2O + 2KCl + H_2O$ (Noyes and Kohr[7]).
$BaC_2O_4 + CaCl_2 \rightleftarrows CaC_2O_4 + BaCl_2$ (Foote and Menge[8]).

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[1] "Theoretische Chemie," 5th edition, p. 535.
[2] "Theoretische Chemie," 5th edition, p. 535.
[3] Z. physik. Chem., **53,** 513 (1905).
[4] Ibid., **26,** 255 (1898).
[5] Ibid., **34,** 407 (1900).
[6] Ibid., **33,** 740 (1900).
[7] Ibid., **42,** 336 (1902). This Journal, **24,** 1141 (1902).
[8] Am. Chem. J., **35,** 432 (1906).

$$BaCO_3 + CaCl_2 \rightleftarrows CaCO_3 + BaCl_2 \text{ (Foote and Menge).}$$
$$BaF_2 + CaCl_2 \rightleftarrows CaF_2 + BaCl_2 \text{ (Foote and Menge).}$$

The investigation here described has as its object the study of the relative solubility of the silver halides and silver sulphocyanate by means of the solution equilibrium discussed above. The reactions studied were the following:

$$AgCl + KCNS \rightleftarrows AgCNS + KCl.$$
$$AgCNS + KBr \rightleftarrows AgBr + KCNS.$$
$$AgBr + KI \rightleftarrows AgI + KBr.$$

The series seemed worthy of investigation both because of the value of additional data on the solubility of these important silver salts and further because the reactions appeared to be particularly well adapted to the method. The degree of dissociation of the four potassium salts was calculated from electrical conductivity data;[1] the values were found to agree within 1.8 per cent. in fifth-normal, 0.6 per cent. in twentieth-normal, and 0.1 per cent. in hundredth-normal solutions, and the salts may therefore be regarded as equal in dissociation. (As will be seen from what follows, the small error introduced by this assumption of equality is reduced by the extraction of the square roots in equation 4.) Since salts of equal dissociation constant having a common ion become equally dissociated when mixed in any proportions,[2] it follows that the ratio of the free ions (Equation 2) will be the same as that of the total chloride and sulphocyanate present, as analytically determined. Equation 2 then becomes

$$\frac{C_{\text{SULPHOCYANATE}}}{C_{\text{CHLORIDE}}} = \frac{K_1}{K_2} \quad \text{(Equation 3),}$$

in which the subscripts denote total concentration. Furthermore, the four silver salts have been shown by Böttger[3] to be completely dissociated in saturated solutions, so that the ratio of the products of the ionic concentrations, $\frac{K_1}{K_2}$, becomes the ratio of the squares of the actual solubilities of the salts, $\frac{S^2_{AgCNS}}{S^2_{AgCl}}$. By substitution of this value for $\frac{K_1}{K_2}$ in equation 3, and extraction of the square roots, the relation becomes

$$\frac{S_{AgCNS}}{S_{AgCl}} = \frac{\sqrt{C_{\text{SULPHOCYANATE}}}}{\sqrt{C_{\text{CHLORIDE}}}} \quad \text{(Equation 4),}$$

that is, the ratio of the solubilities of the two salts is equal to the ratio

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[1] Landolt-Börnstein-Meyerhoffer, Tabellen, 3rd edition, p. 744.

[2] Nernst's "Theoretische Chemie," 5th edition, p. 509.

[3] Z. physik. Chem., **46**, 602 (1903).

of the square roots of the total concentrations of anions, free and combined. This simple relation renders unnecessary the corrections for inequalities in dissociation which have been applied in all the previously noted studies on solution equilibria except that of Knüppfer, thereby freeing the results from that source of possible error. In one particular only does the series fail of the ideal for an investigation of this character—the solubilities are in two cases widely divergent, so that small errors in analysis would cause noticeable variations in the ratios found. It has been possible, however, to reduce these errors to such an extent that they do not greatly affect the constancy of the ratios obtained.

The silver salts used in the experiments were prepared by precipitating pure silver nitrate in hot dilute solution with excess of the haloid salt, and washing the precipitates by decantation until the wash waters were free from halogen. The silver chloride was dissolved in ammonia, reprecipitated by nitric acid and again washed by decantation. All the silver salts were kept in a moist condition and protected from the light. The potassium chloride and sulphocyanate were Kahlbaum's C. P. preparations, and the latter was found by analysis free from chloride; the potassium iodide and bromide were Baker & Adamson's analyzed preparations, the iodide containing 0.005 per cent. and the bromide a mere trace of chloride.

The reactions were carried out in half-liter flasks suspended in an Ostwald thermostat regulated to 25°, and the reaction mixtures stirred by glass paddles operated by a gas engine. In each experiment a solution of the potassium salt of approximately the desired concentration was taken, and about twice its equivalent of the moist silver salt added to it. The mixture was stirred for about two hours, after which a further quantity of the silver salt was added and the stirring continued two to four hours longer. The time thus allowed was considerably greater than was necessary, as the reactions are apparently very rapid in all cases; equivalents of AgCl and KCNS have previously been shown[1] to react to the extent of about 43 per cent. in two minutes in solution of hundredth-normal concentration. Further experiment on this reaction showed that the equilibrium was reached in less than one hour; the velocity of the other reactions was not investigated. After equilibrium had been reached, the solutions were allowed to stand in the thermostat until the precipitates had settled and samples were then pipetted out and analyzed. Each equilibrium was approached from two directions. The concentration of the potassium salt was varied through a considerable range, so that any irregularity in the ratios, due to hydrolysis or the formation of complex salts, might be noticed. The constancy of the ratios shows that no

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[1] Rosanoff and Hill, This Journal, **29**, 272 (1907).

measurable irregularities occur within the range of concentrations selected, and that the assumptions leading to equations 3 and 4 are justified.

Table I shows the results obtained for the equilibrium $AgCl + KCNS \rightleftarrows AgCNS + KCl$. The solutions were analyzed for total chloride and sulphocyanate by the method of Volhard,[1] and for sulphocyanate by the colorimetric method, the chloride being determined by difference. For the Volhard determination 25 cc. samples were taken in experiments 1*a* and 1*b*, 50 cc. samples in 2*a* and 2*b*, and 100 cc. samples in 3*a* and 3*b*. For the colorimetric tests the standards were made in every way identical with the analyzed solutions by mixing solutions of potassium chloride and potassium sulphocyanate in such quantities that the total salt in the standard was equal to that in the sample tested, and by adding equal quantities of iron-ammonium alum to the two solutions. In the following table, column 1 gives the number of the experiment, column 2 the approximate concentration of the soluble salt used, column 3 the salts taken for the reaction, and columns 4 and 5 the final concentration of chloride and sulphocyanate as analytically determined. Column 6 gives the ratio of the square roots of these concentrations, which, according to equation 4, is equal to the ratio of the solubility of the two salts.

TABLE I.

Equilibrium $AgCl + KCNS \rightleftarrows AgCNS + KCl$ at 25°.

No.	Approx. concen.	Reacting salts.	Conc. Cl.	Conc. CNS.	$\sqrt{\frac{C_{CNS}}{C_{Cl}}}$
1*a*	N/5	AgCNS + KCl	0.197	0.00104	0.0726
1*b*	N/5	AgCl + KCNS	0.193	0.00100	0.0719
2*a*	N/20	AgCNS + KCl	0.0501	0.000293	0.0764
2*b*	N/20	AgCl + KCNS	0.0489	0.000280	0.0759
3*a*	N/100	AgCNS + KCl	0.010	0.000060	0.0774
3*b*	N/100	AgCl + KCNS	0.010	0.000057	0.0750

Mean ratio, $\frac{S_{AgCl}}{S_{AgCNS}} = 0.0748$

TABLE II.

Equilibrium $AgCNS + KBr \rightleftarrows AgBr + KCNS$ at 25°.

No.	Approx. Concen.	Reacting salts.	Conc. Br.	Conc. CNS.	$\sqrt{\frac{C_{Br}}{C_{CNS}}}$
1*a*	N/5	AgCNS + KBr	0.0647	0.1205	0.732
1*b*	N/5	AgBr + KCNS	0.0665	0.1207	0.742
2*a*	N/20	AgCNS + KBr	0.0165	0.0312	0.727
2*b*	N/20	AgBr + KCNS	0.0176	0.0324	0.737

Mean ratio $\frac{S_{AgBr}}{S_{AgCNS}} = 0.735$

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[1] J. pr. Chem., 9 (N. F.), 217 (1874). See also this Journal, **29**, 269 (1907).

Table II shows the results obtained by comparing AgBr and AgCNS. The solutions were analyzed for bromides by the method of Rosanoff and Hill,[1] the total bromide and sulphocyanate being determined by the method of Volhard. The columns have the same significance as in the previous table.

Attempts were made to carry out experiments in solutions of hundredth-normal concentration, but fine suspensions of the silver salts resulted, which would not settle in reasonable time and could not be filtered out. The solutions were finally analyzed in the presence of the suspended solid, but under those conditions the results obtained by approaching the equilibrium from the two directions differed by 4 to 5 per cent., the amount of bromide in solution being larger when silver bromide had been taken than when its original source was the soluble potassium bromide. The values for the ratio were 0.0709 and 0.0700 when silver sulphocyanate was the original solid phase, and 0.0787 and 0.0763 when silver bromide was taken; the mean is almost identical with that of Table II. Whether this peculiarity is referable simply to analytical errors due to the presence of the finely suspended silver salts or, as seems to be indicated by Table II, to some change in the nature of the solid phase (mixed crystals, solid-solution, or the like) must remain for the present unanswered.

Analytical difficulties prevent the determination of the relative solubility of silver iodide and bromide from being as accurate as might be desired. The iodide in solution when equilibrium has been attained amounts to only 0.01 to 0.02 per cent. of the bromide present, expressed in equivalents, and no method is known by which such minute quantities of iodides can be exactly determined in the presence of such large amounts of bromides. Of the various methods proposed for this separation, that of Fresenius,[2] which depends upon the oxidation of the iodides by nitrous acid in sulphuric acid solution, extraction of the free iodine by means of an organic solvent and titration with $Na_2S_2O_3$, was thought to be best suited to the estimation of small amounts of iodine. Test analyses were made of solutions containing 0.1 to 0.5 mg. of iodide in presence of 2 to 3 grams of bromide dissolved in 150 cc. of water. The iodine freed by five drops of a solution of nitrous acid in concentrated sulphuric acid was collected by extraction of the aqueous solution with 10 cc. portions of chloroform until no further coloration of the solvent could be detected; the iodine was then titrated with $N/400$ $Na_2S_2O_3$. The quantity found was always less than that taken, and by amounts varying between 12 and 40 per cent. If this maximum error be assumed to have occurred in the analysis of the mixtures recorded in Table III, the error in the ratios calculated will be about 27 per cent., and the ratios

[1] This Journal, **29,** 1461 (1907).

[2] Quan. Chem. Anal. (Braunschweig, 1898), p. 482.

given below may therefore differ from the true ratios by that amount. In the experiments tabulated below, somewhat greater concentrations were used than in the previous experiments, in order that the iodide present might become a measurable quantity.

TABLE III.

Equilibrium AgBr + KI $\rightleftarrows$ AgI + KBr at 25°.

No.	Approx. Concen.	Reacting salts.	Conc. Br.	Conc. I.	$\sqrt{\frac{C_I}{C_{Br}}}$
1*a*	N	AgI + KBr	0.955	$24.4 \times (10)^{-5}$	0.016
1*b*	N	AgBr + KI	0.945	$13.9 \times (10)^{-5}$	0.012
2*a*	N/5	AgI + KBr	0.185	$4.83 \times (10)^{-5}$	0.016
2*b*	N/5	AgBr + KI	0.187	$2.2 \times (10)^{-5}$	0.011

Mean ratio $\frac{S_{AgI}}{S_{AgBr}} = 0.014$

From the ratios recorded in Tables I. II and III the relative solubility of the whole series may be calculated. The values thus obtained are given in Table IV. Column 1 designates the salt, column 2 its relative solubility referred to that of silver chloride as unity, and column 3 the absolute solubility in gram-molecules per liter, taking Kohlrausch and Rose's[1] figure for the silver chloride as the standard. Column 4 gives the maximum and minimum values obtained for the solubility of these salts by other methods; the figures are taken from the table complied by Abegg and Cox.[2]

TABLE IV.

Salt.	Relative solubility.	Absolute solubility.	Extreme values.
AgCl	1.00000	$1.6 \times (10)^{-5}$	$1.25—1.64 \times (10)^{-5}$
AgCNS	0.07480	$1.2 \times (10)^{-6}$	$1.08—1.25 \times (10)^{-6}$
AgBr	0.05500	$8.8 \times (10)^{-7}$	$6.6—8.1 \times (10)^{-7}$
AgI	0.00077	$1.23 \times (10)^{-8}$	$0.97—1.05 \times (10)^{-8}$

The foregoing investigation is one of a series planned in collaboration with Professor M. A. Rosanoff. A change of residence has made it advisable to carry out the separate parts of the work independently. Credit is gladly given to Professor Rosanoff for many of the ideas contained in this paper.

NEW YORK UNIVERSITY,
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ON THE ANALYTICAL ESTIMATION OF GLIADIN.

BY WALTER E. MATHEWSON.

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That the common methods for the determination of gliadin are unsatisfactory is generally recognized. The amount of nitrogenous material

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[1] Abegg and Cox, Z. physik. Chem., **46**, 11 (1903).

[2] *Loc. cit.*