taken as the standard for the solubility of silver chloride an old result of Kohlrausch and Rose and further does not make use of the more recent values,[1] known at the time, for comparison with the other solubilities calculated by him. If this is done, conditions are not changed markedly. The evidence of solubility determinations, according to a method based upon assumptions insufficiently complied with, is not to be valued too highly in the cases under discussion. Yet one may draw the conclusion from the results obtained in the system AgBr + AgCNS, that the partial solubilities of the two components, as compared with the solubilities of the pure substances, are diminished in practically the same ratio. This follows from the fact that the solubilities of the two solid components in one another, in mol percentages, are of the same magnitude.

MARBURG A/L GERMANY.

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

THE RELATIVE SOLUBILITY OF CERTAIN SILVER SALTS.

BY ARTHUR E. HILL.

Received December 24, 1914.

The foregoing paper[2] by Professor Thiel contains five specific criticisms of my publication on "The Relative Solubility of the Silver Halides and Silver Sulfocyanate."[3] They may be stated briefly as follows: (1) the publication criticised shows unfamiliarity with the work of Küster and Thiel,[4] who have shown that solid solutions exist in the cases of AgBr and AgCNS and of AgBr and AgI; (2) if equilibrium experiments had been made with the salts AgCl and AgBr, the method would have been found unsuited for solubility calculations; (3) the correct value obtained for the solubility ratio of AgBr and AgCNS is accidental; (4) the correct value obtained for the solubility ratio of AgBr and AgI is due probably to a false equilibrium, and finally, (5) all agreement shown may be due to the use in the calculations of the old value obtained by Kohlrausch and Rose for the solubility of silver chloride, instead of more recent values to which Thiel refers. Brief comment may be made on each of these criticisms.

The first criticism must be accepted as justified. I did not know of Küster and Thiel's work on these solid solutions until after the publication of my paper. In this instance it seems to me fortunate that I was unacquainted with their work at that time, for if I had read the publications I might possibly have been discouraged from using these salts in my research. In that event the equilibrium method might not have been ap-

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[1] F. Kohlrausch, *Z. physik. Chem.*, **44**, 197 (1903); **50**, 355 (1908); W. Böttger, *Ibid.*, **46**, 521 (1903).

[2] THIS JOURNAL.

[3] *Ibid.*, **30**, 68 (1908).

[4] *Z. anorg. Chem.*. **19**, 81 (1899); **24**, 1 (1900); **33**, 129 (1902).

plied in a case where it has actually led to very accurate results, having to do with widely dissimilar solubilities. It should be stated, however, that during the progress of the experiments, the behavior of the precipitated silver bromide and sulfocyanate did suggest the formation of a solid solution. as was specifically noted in the publication;[1] for this reason the limitation of the experiments to certain concentrations was found necessary. It appears, therefore, that the experimental method of attacking this problem led to a correct estimate of the influence which solid solution has upon it, whereas an approach to the question from the theoretical side has led Thiel to an over-estimate of this influence.

The second criticism is founded on an assumption as to errors which might have been committed but were not. It seems to require no answer.

The third criticism is that the correct value for the silver bromide-sulfocyanate ratio is accidental. It is odd to find that the same accident, if Thiel maintains it to be such, has affected the experiments which Thiel has made on the same salts, for it is possible to calculate from Küster and Thiel's experiments[2] a relative solubility of these two salts in substantial agreement with my own values. One may take from Experiments 4, 5^1, 5^2, and 5^3 of their table on page 133 the mean value 33.1 as the molecular percentage of bromide in solution in equilibrium with silver bromide and sulfocyanate, or with solid solutions of the two, if solid solution is the condition of the solid phases. The graphic representation which they give shows that this value (33.1% bromide in solution to 66.9% sulfocyanate) is very constant, even when the composition of the solid phase varies all the way from about 3% silver bromide to 97% bromide. Throughout this wide range, therefore, the equilibrium solution remains constant in composition. Applying to Küster and Thiel's experiments the same method of calculation used in my publication[3] we have

$$\frac{\text{Solubility of AgBr}}{\text{Solubility of AgCNS}} = \frac{\sqrt{\text{Bromide in solution}}}{\sqrt{\text{Sulphocyanate in solution}}} = \frac{\sqrt{33.1}}{\sqrt{66.9}} = 0.703.$$

This value is in very reasonable agreement with the average value found by myself, *viz.*, 0.735. The experiment differs from my own in that the total concentration of soluble salt was about 0.1 *N*, whereas in my experiments the concentrations were 0.2 *N* and 0.05 *N*. A tabular presentation of these values will make clear the substantial agreement.

	Concentration in solution.	Solubility ratio. $\frac{\text{AgBr}}{\text{AgCNS}}$.
(Hill)	0.2 *N*	0.737
(Küster and Thiel)	0.1 *N*	0.703
(Hill)	0.05 *N*	0.732

[1] THIS JOURNAL, **30,** 73 (1908).

[2] *Z. anorg. Chem.*, **33,** 133 (1902).

[3] THIS JOURNAL. **30,** 68 (1908) (Equation 4).

It appears, therefore, that there is agreement within a few per cent. between Küster and Thiel's experiments, and those criticized. Since these tabulated figures represent four experiments by Küster and Thiel, equilibrium being attained from one direction, and four experiments by myself, equilibrium being attained from both directions, it seems fair, on the basis of the theory of chances, to exclude accident from the list of causes contributing to the agreement of these figures with those obtained by other methods.

It seems equally unnecessary to adopt Thiel's hypothesis of a false equilibrium as responsible for the correct results in the silver bromide-iodide solubility ratio. One can calculate again from Thiel's independent[1] experiments, substantially the same ratio found by myself. Experiments 4, 5 and 6 of Thiel's table suggest the same condition as in the case previously discussed, *i. e.*, while there is a wide variation in the composition of the precipitate, there is substantial constancy in the composition of the solution. This is evidently the solution in equilibrium with the two solids, and its composition is the mean of 0.38, 0.32 and 0.32 parts of iodide to the mean of 997, 998, and 997 of bromide, *i. e.*, 0.34 to 998. From these figures the solubility ratio is calculated as 0.01845, which is again in reasonable agreement with the mean value 0.014 found by myself. This is as close as can be expected, considering that the three figures of Thiel's taken vary by 18%, and that the analytical method used by myself was conceded to have necessarily a large possible error. The ratio of these two solubilities, as given in Thiel's compilation, has been found as follows at the temperature of these experiments (25°):

Thiel, 0.0130 by potential measurements;
Holleman, 0.0115 by conductivity measurements;
Goodwin, 0.0147 by potential measurements.

The value of Holleman, which varies most from the value 0.014 found by me, has been obtained by calculation from measurements made at other temperatures. Since the value 0.014 is between the extremes found by others, and since that value is at least partially sustained by Thiel's own experiments quoted, with a different total concentration of soluble halide present, it seems to be entirely unnecessary to explain it away by an assumption of a false equilibrium.

The final statement, that the apparent agreement may be due to the use of antiquated solubility figures, is less careful than one expects from a critic; the figures in Abegg and Cox's[2] compilation were used and quoted, thus taking cognizance of all reliable data existent at that time. The additional references which Professor Thiel gives are for other temperatures, and therefore entirely unsuited to the calculations under discussion.

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[1] *Z. anorg. Chem.*, **24**, 29 (1900).

[2] *Z. phys. Chem.*, **46**, 11 (1903).

If any other of the accepted values for 25° is taken as standard in place of the classical value of Kohlrausch's selected by me, the agreement between my method and the others which have been used will be found to be better than was stated in my earlier publication. This is so obvious on inspection of my table[1] that it seems unnecessary to quote figures.

To Professor Thiel's conclusion with reference to the partial solubilities of silver bromide and sulfocyanate, may be added the conclusion that in these cases solid solution is not a factor of sufficient influence to affect the solubility equilibria noticeably, as proved by the experiments under discussion. The question is also suggested, though its discussion would be out of place in this reply, as to what is really meant by "solid solution" when applied to amorphous bodies such as the salts used by Thiel and myself.

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ABSORPTION AND THE SURFACE TENSIONS OF AQUEOUS SOLUTION OF HOMOLOGOUS FATTY ACIDS AND ALCOHOLS.

BY MARKS NEIDLE.

Received December 23, 1914.

Duclaux[2] was the first to present the following relationship between the concentrations of aqueous solutions of homologous fatty alcohols and acids and their surface tensions; the ratio of the concentrations of any two homologous acids or alcohols which have the same surface tension is a constant, independent of the value of the surface tension. In symbols this may be expressed by the following equation, which will be referred to as the Duclaux equation:

$$c = bf(\gamma), \qquad (1)$$

where c is the concentration, $f(\gamma)$ a fixed function of the surface tension for all members of a series, and b a constant depending upon the particular member of the series. The experimental basis for this rule comprised the surface tensions of methyl, ethyl, isopropyl, isoamyl and caprylic alcohols, and formic, acetic and butyric acids, determined by a very crude drop method. The values of the concentration ratios reproduced in Table I show as good agreement as could be expected from such rough data. The concentrations c are expressed in percentages by volume, and the temperature of observations is 15°.

Using the Morgan drop-weight method, Morgan and Neidle[3] found the surface tensions of aqueous solutions of methyl, ethyl and amyl alcohols,

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[1] *Loc. cit.*, 74.

[2] *Ann. chim. phys.*, [5] 13, 76 (1878).

[3] THIS JOURNAL, 35, 1856 (1913).