provided one assumes the age of the earth to be of the order of 2×10^9 years.

The writer wishes to express his appreciation to Professor G. P. Baxter of the Department of Chemistry, Harvard University, who very kindly prepared and furnished eleven of the twelve samples used. It was only through his interest and coöperation that this work was possible.

Summary

1. A mass spectrographic study of the isotopes of twelve samples of common lead shows that the relative abundances vary considerably in spite of a nearly constant atomic weight.

2. A tentative explanation for the variations is found if one arbitrarily considers some of the samples to be "uncontaminated" lead and the others "uncontaminated" lead to which has been added approximately equal quantities of uranium and thorium leads. As the minerals from which the lead was obtained are essentially free of thorium and uranium, such contamination probably took place before the mineral was formed.

3. A search for the isotopes Pb^{210}, Pb^{209}, Pb^{205}, and Pb^{203} indicated that if such isotopes exist at all they must exist with much lower abundances than was at one time supposed.

Cambridge, Mass. Received May 7, 1938

[Contribution from the School of Chemistry of the Institute of Technology of the University of Minnesota]

Studies on Aging and Properties of Precipitates. XXII. The Induced Precipitation of Mercuric Sulfide from Sodium Mercuric Sulfide Solutions by Zinc Sulfide. A New Case of Postprecipitation

By I. M. Kolthoff, Frank S. Griffith and D. Romund Moltzau

It was found by Feigl[1] that when a solution of a zinc salt is added to a solution of sodium mercuric sulfide under such conditions that the resulting liquid phase is not supersaturated with regard to mercuric sulfide, the precipitate which separates contains mercury and its color varies from white to yellow orange or brown, depending upon the amount of mercury in the precipitate. The mercury is not removed readily from the precipitate by extracting with sodium sulfide solutions. Moreover, Feigl found that the sulfides of cadmium, lead and manganese acted in a manner similar to zinc sulfide whereas the sulfides of silver, cupric and cuprous copper, ferrous and ferric iron, thallium, bismuth and cobalt did not induce the precipitation of mercuric sulfide from a sodium mercuric sulfide solution. In the present paper it is shown that the induced precipitation of mercuric sulfide by zinc sulfide is a phenomenon of postprecipitation. This case of postprecipitation is different from others[2] previously investigated in this Laboratory, in that the mercuric sulfide is taken up by the zinc sulfide from a solution which is *not supersaturated* with regard to the former. Such a postprecipitation will occur only when the following two conditions are fulfilled: (1) the postprecipitated substance is soluble in the primary precipitate or forms a compound with it; (2) the speed of separation of the primary precipitate is greater than that of the postprecipitated substance. If the former condition is not fulfilled no postprecipitation can occur from solutions which are not supersaturated with regard to the second precipitate. If the first condition is fulfilled but not the second a coprecipitation and not a postprecipitation will take place.

Materials Used

Zinc sulfate solutions were made from recrystallized c. p. chemicals. They were standardized against potassium ferrocyanide.[3]

Mercuric perchlorate solutions were made from reagent quality mercuric oxide and perchloric acid. A 0.05 *M* perchloric acid solution in equilibrium with mercuric oxide was found to be 0.004 *N* in free acid.

Sodium Sulfide.—The commercial products available were not suitable for the present work because of large amounts of impurities (thiosulfate). Therefore, the sodium sulfide solutions were made by passing washed hydrogen sulfide through a measured quantity of 5.30 *N* sodium hydroxide. A slight excess of hydrogen sulfide as measured by the increase in weight of the solution, was absorbed and the concentrated solution diluted with oxygen-free water. The solution was then analyzed for sulfide and total basicity and the appropriate amounts of

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(1) F. Feigl, *Z. anorg. allgem. Chem.*, **157**, 269 (1926).

(2) For a review see I. M. Kolthoff and D. R. Moltzau, *Chem. Rev.*, **17**, 293 (1935).

(3) I. M. Kolthoff and E. A. Pearson, *Ind. Eng. Chem., Anal. Ed.*, **4**, 147 (1932).

sodium hydroxide solution and water needed to give the desired composition were calculated and added. In order to guard against air oxidation the air above the liquid was swept out with nitrogen.

Air Oxidation of Sodium Sulfide Solutions.—Most of the work was first carried out without taking precautions against air oxidation of the sulfide. The results were not well reproducible and were sometimes confusing due to air oxidation of sulfide. This oxidation can be considerable after a relatively short time of exposure to air as is evident from the following experiments. Two hundred milliliters of a freshly prepared sodium sulfide solution which was 0.1 N in excess of sodium hydroxide was distributed between four 250-ml. flasks, the latter were partially stoppered with one-hole rubber stoppers and shaken gently with a rotary motion for twenty-four hours. The contents of the flasks were mixed and analyzed for sulfide, polysulfide, thiosulfate and total basicity (see below). The freshly prepared solution was 0.189 M in sulfide, the total alkalinity being 0.472 N. After exposure for twenty-four hours the sulfide concentration was 0.110 M, that of polysulfide less than 0.001 M, the thiosulfate concentration 0.035 M and the total alkalinity 0.402 N. Hence about 37% of the sulfide was oxidized after twenty-four hours of exposure to air. This air oxidation is prevented by taking precautions to exclude air. A large number of experiments were run in which the flasks containing the sulfide solutions were swept out with nitrogen both before the solutions (kept under nitrogen) were added and before the flasks were stoppered. Under such conditions only 0.53% of the sulfide was found to be oxidized after twenty-four hours.

Methods of Analysis.—The sum of sulfide, polysulfide and thiosulfate was determined by oxidation with bromine (bromate–bromide and acid) to sulfate.[4] The thiosulfate was determined by the method recommended by the Committee on Analytical Reagents of the American Chemical Society[5] for testing the purity of sodium sulfide. The sulfide and polysulfide are precipitated by adding an excess (enough to remove excess of alkali) of oxygen-free zinc sulfate solution. After standing for half an hour the solution is filtered and an aliquot portion of the filtrate titrated with standard iodine. The polysulfide was usually determined by Schulek's[6] method in which it is transformed into thiocyanate. The latter is oxidized to bromocyanide and determined iodometrically.

The total alkalinity was determined by titrating with standard acid. Just before the end-point most of the hydrogen sulfide was removed by aspiration of air and the titration finished with methyl orange as indicator.

Mercury.—In the study of the postprecipitation of mercuric sulfide with zinc sulfide from sodium mercuric sulfide solutions the remaining mercury in solution was determined volumetrically.

After investigating various procedures the following method was found to be suitable for routine analyses. An excess of hydrochloric acid was added to the sodium mercuric sulfide solutions to precipitate the mercuric sulfide, the solution boiled for a few minutes to remove hydrogen sulfide and then 2 ml. of concentrated nitric acid added. Oxidation was complete within a few seconds but boiling was continued for a few minutes to remove oxides of nitrogen and to gather the finely divided sulfur into larger particles. After removing the flask from the hot-plate 5 ml. of 6 N sodium hydroxide was added, the solution cooled, indicator added and the solution exactly neutralized. If the indicator is added to the strongly acid solution it is sometimes oxidized. A mixture of equal volumes of brom cresol green (0.1%) and methyl red (0.1%) was found to be a very suitable indicator, the color change being from red (acid) to blue (alkaline). After neutralization, the mercury is determined by the cyanide method[3] (p. 198) by adding an excess of standard potassium cyanide solution and titrating back with standard hydrochloric acid.

$$HgCl_2 + 2KCN \longrightarrow Hg(CN)_2 + 2KCl$$
$$KCN + HCl \longrightarrow HCN + KCl$$

Degree of Saturation of Sodium Mercuric Sulfide with Mercuric Sulfide.—Although the air oxidation of sulfide was prevented by carrying out the experiments in an atmosphere of nitrogen, it was desirable, especially in long period experiments, to have a quick method available to test for an accidental change of the sulfide concentration solution. This can be done roughly by titrating with a standard mercuric chloride solution until the turbidity does not disappear on further shaking.

$$2S^{=} + HgCl_2 \longrightarrow HgS_2^{=} + 2Cl^-$$
$$HgS_2^{=} + HgCl_2 \longrightarrow 2HgS + 2Cl^-$$

As the solubility of mercuric sulfide in sodium sulfide is dependent upon the concentration of sodium hydroxide,[7] the method cannot be used to determine accurately the sulfide content of solutions. It is suitable, however—with an accuracy to 1 to 2%—to determine the amount of mercuric salt needed to saturate a sodium sulfide (or sodium mercuric sulfide) solution with mercuric sulfide.

Experimental Results

Rate of Postprecipitation of Mercuric Sulfide from Sodium Mercuric Sulfide Solutions in the Presence of Freshly Precipitated Zinc Sulfide.—In the following experiments zinc sulfate solution was added to the sodium mercuric sulfide solution which contained an excess of sulfide. Ten ml. of 0.05 M zinc sulfate was added to a mixture of 25 ml. of 0.189 M sodium sulfide which was 0.094 N in sodium hydroxide and 10 ml. of 0.044 M mercuric perchlorate which was 0.004 N in free acid. If no co- or postprecipitation occurred the supernatant liquid after precipitation of 0.5 mmol. of zinc sulfide would be 0.051 N in sodium hydroxide, 0.075 M in sodium sulfide and 0.0098 M in sodium mercuric sulfide. About 8 ml. of the 0.044 M mercuric perchlorate solution could be added before the solution became saturated with mercuric sulfide. Before mixing the solutions in screw-cap bottles the air was swept out with nitrogen, and this gas was passed over again before screwing the caps on. The bottles were shaken for a given length of time, centrifuged and 25 ml. was taken for analysis for mercury. The color of the freshly formed zinc sulfide was white, indicating that *no coprecipitation of mercuric* sulfide had occurred, after two

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[4] I. M. Kolthoff and H. Menzel, "Die Maszanalyse," 2d edition, Verlag von Julius Springer, Berlin, 1931, p. 514.

[5] *J. Ind. Eng. Chem.*, **19**, 1372 (1927).

[6] E. Schulek, *Z. anal. Chem.*, **65**, 352 (1925).

[7] J. Knox, *Trans. Faraday Soc.*, **4**, 29 (1908).

minutes of shaking a yellow tinge of the precipitate was noticeable and after one hour the precipitate was of a cadmium sulfide yellow. The results on the rate of postprecipitation of mercury are given in Table I. A similar set of experiments was run in the presence of a larger excess of sodium sulfide. After precipitation of 0.5 mmol. of zinc sulfide the supernatant liquid was 0.062 N in sodium hydroxide, 0.19 M in sodium sulfide and 0.011 M in sodium mercuric sulfide. The results are given in Table II.

TABLE I

RATE OF POSTPRECIPITATION OF MERCURIC SULFIDE WITH ZINC SULFIDE

Time of shaking	6 min.	52 min.	7.5 hrs.	24 hrs.	7 days
Mercury pptd., %	14.0	27.9	32.1	34.0	34.2, 35.5

TABLE II

RATE OF POSTPRECIPITATION OF MERCURIC SULFIDE IN THE PRESENCE OF LARGER EXCESS OF SULFIDE

Time of shaking	5 min.	35 min.	2.5 hrs.	45 hrs.	7 days
Mercury pptd., %	8.4	12.8	14.0	16.4	15.5

A comparison of Tables I and II (see also Fig. 1) reveals that the amount of postprecipitation mercury decreases to about one-half when the excess of sulfide in solution is doubled. Moreover, it is evident that after about one to two days of shaking with freshly precipitated zinc sulfide a state of equilibrium in the distribution of mercury between solution and the solid state is attained.

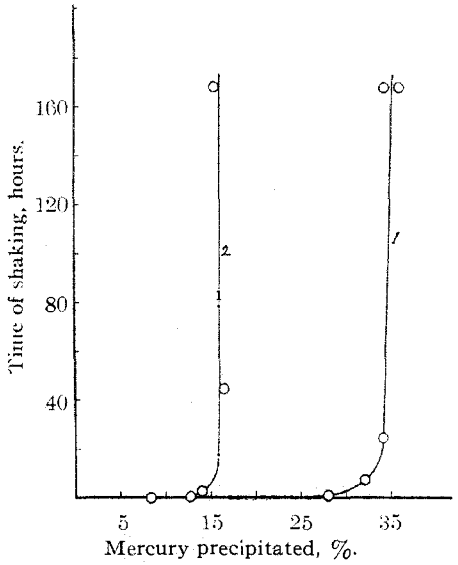

Fig. 1.—1. Small excess of sulfide; 2, larger excess of sulfide.

Rate of Postprecipitation of Mercuric Sulfide with Zinc Sulfide of Varying Degree of Perfection and Age.—The results of the following experiments in which sodium mercuric sulfide solution was added to a zinc sulfide suspension show conclusively that the induced precipitation of mercuric sulfide by zinc sulfide is a phenomenon of postprecipitation. The rate of this postprecipitation decreases with increasing degree of perfection and decreasing surface development of the zinc sulfide. Zinc sulfide samples of various degree of perfection and age were prepared.

1. **Precipitation from and Aging in Alkaline Solution.**—Ten ml. of 0.05 M zinc sulfate was added to 2.8 ml. of a solution which was 0.19 M in sodium sulfide and 0.116 N in sodium hydroxide. The bottles were swept out with nitrogen and the zinc sulfide aged for the indicated periods of time.

2. **Precipitation from and Aging in Slightly Acid Medium** (pH about 5).—Ten ml. of 0.05 M zinc sulfate containing 0.25 g. of sodium acetate trihydrate was saturated with hydrogen sulfide. After aging for the given period of time most of the excess of hydrogen sulfide was removed by evacuating the bottle while swirling well (blanks showed that only about 0.004 mmol. of hydrogen sulfide stayed in solution after this treatment). After evacuation 0.17 ml. of 0.19 M sodium sulfide, 0.25 ml. of 5.3 N sodium hydroxide and 2.4 ml. of water were added, thus making the volume, amount of sulfide and hydroxide the same as in the suspensions of product 1.

3. **Precipitation from and Aging in More Acid Solution** (final pH about 1.15).—Ten ml. of 0.05 M zinc sulfate was saturated with hydrogen sulfide. After aging the samples were subjected to the same treatment as products 2. If the samples were aged for less than one hour a small amount of the zinc might have remained unprecipitated. For complete precipitation of zinc sulfide Jeffries and Swift[8] recommend a pH of 1.6.

Procedure of Postprecipitation Experiments

The 100-ml. bottles containing the zinc sulfide suspensions which had been aged for the indicated periods of time were swept out again with nitrogen whereupon 35 ml. of sodium mercuric sulfide solution of about the same composition as that used in Table I was added. Immediately after mixing, the liquid phase was 0.058 N in sodium hydroxide, 0.0845 M in sodium sulfide and 0.0105 M in sodium mercuric sulfide. The bottles were stoppered and shaken vigorously, some for two hours and some for two days, centrifuged and 25 ml. of the supernatant liquid was analyzed for mercury by the procedure outlined previously. The mercuric sulfide separating from mixtures containing acetate (products 2) was filtered off, washed, and treated with aqua regia. The fibers of filter paper were filtered off before titrating the mercury. The filtration of mercuric sulfide was necessary as the acetate interferes with the mercury titration. The results are given in Table III and reproduced graphically in Fig. 2.

When a range of time is given in the table the shorter time refers to zinc sulfide products 1, and the longer time to products 2 and 3. The experiments referring to an age of zinc sulfide of zero (in parentheses in Table III) were carried out in a way similar to those in Tables I and II; the zinc sulfate solution was added to a solution containing sodium mercury sulfide, sodium sulfide and sodium hydroxide of appropriate concentrations so that after precipitation of the zinc sulfide the solution had the same composition as prevailed in the other experiments. It is seen that zinc sulfide precipitated in the absence of mercury and which was only seven minutes old (product 1) is

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(8) C. E. P. Jeffries and E. H. Swift, THIS JOURNAL, **54**, 3219 (1932).

TABLE III

RATE OF POSTPRECIPITATION OF MERCURIC SULFIDE WITH ZINC SULFIDE OF VARYING DEGREE OF PERFECTION AND AGE

Age of ZnS	% Hg in ppt. after 2 hours of shaking with Na_2HgS_2 soln. Products 1	2	3	% Hg in ppt. after 2 days of shaking with Na_2HgS_2 soln. Products 1	2	3
(0)	(25.5)	..	...	(28.4)	..	..
3–7 min.	24.0	15.4	7.5	28.4	18.0	13.1
1 hour	14.2	11.5	...	19.0	11.6	10.0
12–16 hours	12.0	6.8	3.4	14.1	8.5	2.5
7 days	10.9	3.9	0.6	11.8	5.5	0.6
7 days hot[a]	0.9	0	−1	8.0	0.7	−1

[a] Aged on gravel at a temperature of about 80–90°.

about as effective as fresh zinc sulfide precipitated in the presence of mercury.

Products 3 are much coarser and more perfect than samples 2 and the latter more so than products 1. The rate of postprecipitation of mercuric sulfide (see 3–7 minutes old zinc sulfide) decreases in the order of products 1, 2, 3. It is also evident that product 3 ages much more rapidly at a *p*H of 1.15 than product 2 at a *p*H of 5 and the latter more than product 3 in alkaline medium. After aging for seven days at room temperature product 3 hardly takes up any mercury even after shaking for two days with the sodium mercuric sulfide solution. Product 1 ages very slowly at room temperature but the perfection becomes pronounced when aged at 80–90°. Apparently the speed of postprecipitation of mercuric sulfide with zinc sulfide is a good indicator of the degree of perfection of the latter.

Effect of Varying Amounts of Zinc Sulfide and of Mercury and Sulfide Concentrations.—During the postprecipitation of mercuric sulfide the sodium sulfide concentration in the solution increases: $Na_2HgS_2 \longrightarrow [HgS] + Na_2S$. When the initial sulfide composition of the solutions is identical, but the amount of postprecipitation after attainment or approximate attainment of equilibrium different, a quantitative comparison of the results is not simple. A series of experiments was run adding different amounts of zinc sulfate and mercuric perchlorate to sodium sulfide solutions of such concentrations that the sulfide concentrations after the formation of the zinc sulfide and mercuric sulfide complex were identical. The amount of postprecipitation was determined after four days of shaking at room temperature. For the sake of brevity the experimental details are omitted and the results given in a condensed form in Table IV.

TABLE IV

EFFECT OF VARYING AMOUNTS OF ZINC SULFIDE AND OF MERCURY AND SULFIDE CONCENTRATIONS; 4 DAYS OF SHAKING, TEMP. 25°

ZnS, mmol.	Hg originally in soln., mmol.	Na_2S *final* amount, mmol.	Hg *final* amount in soln., mmol.	Hg in ppt., mmol.	Hg pptd., %
0.5	0.5	3.41	0.341	0.159	31.8
1.0	.5	3.44	.222	.278	55.6
0.5	1.0	3.41	.696	.304	30.4
1.0	1.0	3.52	.502	.498	49.8
0.5	0.5	7.08	.416	.084	16.8
1.0	.5	7.02	.329	.171	34.2
0.5	1.0	7.00	.854	.146	14.6
1.0	1.0	7.01	.727	.273	27.3

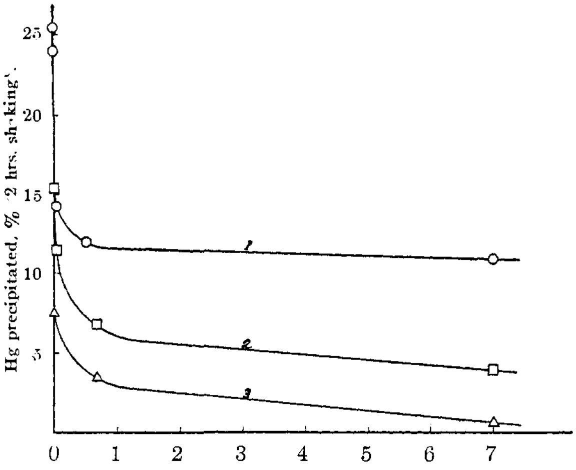

Fig. 2.—1, Zinc sulfide, aged in basic solution; 2, aged at *p*H of 5; 3, aged at *p*H of 2.

Postprecipitation at 80°.—In the following experiments the state of equilibrium of the distribution of mercuric sulfide between solution and the solid was approached at 80°. After running some preliminary series the sulfide concentration in each set was adjusted in such a way as to give identical sulfide concentrations in the solutions after attainment of distribution equilibrium. The bottles containing the sodium mercuric sulfide solution were placed in a beaker of hot water until the temperature of the contents was 90° and then zinc sulfate solution (25°) was added from a pipet. After thorough mixing the bottles were capped and kept for two days at a temperature of 80° in the beaker of hot water, the contents of the bottle being shaken by hand several times during the course of an experiment. After the heating period the bottles were allowed to cool to room temperature, centrifuged and an aliquot part of the supernatant liquid analyzed for mercury. In several cases a thin film of black mercuric sulfide separated at the gas–liquid interface during the heating process which after cooling did not dissolve easily in the solution although the latter was far from saturated with mercuric sulfide. The amount of mercuric sulfide formed at the interface was less than 1% of the total amount of mercury present and was not considered in the calculation of the results which are reported in an abbreviated form in Table V.

TABLE V

POSTPRECIPITATION OF MERCURIC SULFIDE AT 80° AFTER SHAKING FOR 2 DAYS

ZnS, mmol.	Hg originally in solution, mmol.	Na_2S final amount, mmol.	Hg finally in soln., mmol.	Hg in ppt., mmol.	Hg pptd., %	Color of ppt. after 2 days
0.5	0.5	3.57	0.286	0.214	42.8	Orange-brown
1.0	.5	3.55	.180	.320	64.0	Orange
0.5	1.0	3.60	.444	.556	55.6	Dark brown
1.0	1.0	3.51	.368	.632	63.2	Brown
0.5	0.5	7.01	.398	.102	20.4	Yellow
1.0	.5	7.10	.315	.185	37.0	Yellow
0.5	1.0	7.03	.817	.183	18.3	Orange-brown
1.0	1.0	7.02	.673	.327	32.7	Orange

Extractability of Mercuric Sulfide from the Mixed Zinc-Mercuric Sulfide.—A mixed precipitate containing 0.125 mmol. of mercuric sulfide and 0.5 mmol. of zinc sulfide which had been aged for two weeks was extracted several times with 0.2 *M* sodium sulfide solutions. In the first extraction the precipitate was shaken for ten hours with the sulfide solution; only 0.043 mmol. of mercury was found in the solution. After removing the supernatant liquid the precipitate was shaken with a fresh 50-ml. portion of sodium sulfide solution for two days after which time only 0.018 mmol. of mercury had been further removed from the precipitate. A further extraction for a day with a new portion removed only 0.007 mmol. of mercury.

The resulting precipitate was washed once with water and then extracted once with 0.5 *N* hydrochloric acid saturated with hydrogen sulfide; this treatment removed 95% of the zinc. After adding the acid the orange precipitate darkened slowly, within three minutes it was orange-brown and within ten minutes it was black. The acid was removed after seventy minutes of shaking, the precipitate washed with water and extracted for three hours with 50 ml. of sodium sulfide solution. The remainder of the mercury (0.059 mmol.) was thereby extracted. Feigl[1] also found that mercury was difficultly extractable from the mixed precipitate by sodium sulfide, but our interpretation is quite different from his.

Discussion

All the results reported so far tend to show that the postprecipitation of mercuric sulfide from solutions which are far from saturated with this compound is to be attributed to a solid solution formation with zinc sulfide. If such a solution of mercuric sulfide in zinc sulfide is considered ideal, it is possible to calculate the distribution coefficient of mercury between liquid and solid phases.

If the solution is in thermodynamic equilibrium with the solid, the thermodynamic potential of the mercuric sulfide in both phases is identical. Taking the activity of the mercuric sulfide in the pure solid as the standard state, we find that in case the solid solution behaves as an ideal solution

$$(a\mathrm{HgS})_1 = S_{\mathrm{HgS}} \cdot N_{\mathrm{HgS}} \qquad (1)$$

in which $(a\mathrm{HgS})_1$ denotes the activity of the mercuric sulfide in the liquid phase, S_{HgS} the solubility product of mercuric sulfide and N_{HgS} the mole fraction of mercuric sulfide in the solid.

In the presence of an excess of sulfide practically all of the mercury in the liquid phase is present in the form of $\mathrm{HgS_2^=}$ ions; from practical viewpoint we are interested in the distribution of total mercury between solution and solid.

$$\mathrm{HgS_2^=} \rightleftarrows (\mathrm{HgS})_1 + \mathrm{S^=}$$

or

$$(a\mathrm{HgS})_1 = K_{\mathrm{HgS_2^=}} \frac{a\mathrm{HgS_2^=}}{a\mathrm{S^=}} \qquad (2)$$

Since both $\mathrm{HgS_2}$ and S ions are divalent their activity coefficients at various ionic strengths may be expected to be of the same order of magnitude and equation (2) may be approximated to

$$(a\mathrm{HgS})_1 = K_{\mathrm{HgS_2^=}} \frac{[\mathrm{HgS_2^=}]}{[\mathrm{S^=}]} \qquad (3)$$

in which the symbols between brackets denote the molar concentrations in solution. Combining (1) and (3) gives

$$\frac{[\mathrm{HgS_2^=}]}{[\mathrm{S^=}]} = \frac{S_{\mathrm{HgS}}}{K_{\mathrm{HgS_2^=}}} N_{\mathrm{HgS}} = K N_{\mathrm{HgS}} \qquad (4)$$

According to Knox[7] S_{HgS} at 25° is equal to 2.8×10^{-54}, and $K_{\mathrm{HgS^=}}$ to 1.96×10^{-55}. Hence, when equilibrium distribution is established and if the solution is ideal

$$[\mathrm{HgS_2^=}] = K N_{\mathrm{HgS}}[\mathrm{S^=}] = 14.3\ N_{\mathrm{HgS}}[\mathrm{S^=}]\ (25°) \qquad (5)$$

From the results given in Table IV it is possible to calculate the value of *K* at 25°. In these experiments the volume of the solutions was 45 ml., the excess of sulfide in the first four experiments being 3.45 mmols. (average), and in the last four 7.04, corresponding to sodium sulfide concentrations of 0.0766 *M* and of 0.156 *M*, respectively. The concentrations of excess of sodium hydroxide corresponded to 0.064 *N* in the first four experiments and to 0.062 *N* in the last four experiments. Taking the second ionization constant of hydrogen sulfide equal to 10^{-15} and the ionic product of water equal to 10^{-14}, we find from the hydrolysis equation of the sulfide ion

$$\frac{[\mathrm{OH^-}][\mathrm{SH^-}]}{[\mathrm{S^=}]} = \frac{K_w}{K_{2(\mathrm{H_2S})}} = 10 \quad (25°) \qquad (6)$$

If the $\mathrm{HS^-}$ ion concentration is designated by X, then $[\mathrm{OH^-}] = C_{\mathrm{NaOH}} + X$ and $[\mathrm{S^=}] = C_{\mathrm{Na_2S}} - X$. Introducing these expressions into equation (6) yields a quadratic equation which can be solved for X.

The values of *K* calculated in this way from the results of experiments in Table IV are given in Table VI and plotted in Fig. 3.

An attempt was made to calculate the values of *K* at 80° from the results reported in Table V. According to Jellinek and Czerivinski[9] the degree of hydrolysis of sodium sulfide solutions does not change between 0 and 25°. On the basis of this result we have assumed in our calculations that the hydrolysis constant of the sulfide at 80° is equal to that at 25°. This is probably incorrect as is also evidenced by the fact that the values of *K* calculated from experiments in

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(9) K. Jellinek and J. Czerivinski, *Z. physik. Chem.*, **102**, 476 (1922).

TABLE VI

DISTRIBUTION COEFFICIENT K OF MERCURIC SULFIDE BETWEEN SODIUM MERCURIC SULFIDE AND ZINC SULFIDE AT 25 AND AT 80°

Temp., °C.	N_{HgS}	$[HgS_2^=]$ molar	$[S^=] \times 10^3$	K
25	0.242	0.341	1.06	29.6
25	.218	.222	1.06	21.4
25	.378	.696	1.06	38.6
25	.332	.502	1.06	31.6
25	.214	.727	3.28	23.0
25	.226	.854	3.28	25.6
25	.146	.329	3.28	15.3
25	.144	.416	3.28	19.6
80	.300	.286	1.06	20.0
80	.242	.180	1.06	15.6
80	.527	.444	1.06	17.7
80	.387	.368	1.06	19.9
80	.246	.673	3.28	18.6
80	.268	.817	3.28	20.7
80	.156	.315	3.28	13.7
80	.169	.398	3.28	16.0

which the sodium sulfide concentration was 0.0766 M fall on a different line than those in which the sodium sulfide concentration was 0.156 M (see Fig. 3). On the other hand, the values of K calculated from the results of experiments at room temperature at different sulfide concentrations fall approximately on one straight line. It is seen from the results and particularly from Fig. 3 that the value of K is not constant, but increases as a linear function of the mole fraction of mercury in the solid solution. A similar result was found by Yutzy and Kolthoff[10] for the change of the distribution coefficient of bromide between aqueous solutions and mixed crystals of silver chloride and bromide at different mole fractions of bromide in the solid.

The change of K with the mole fraction of mercury in the solid shows that the solid solutions do not behave as ideal solutions, and that activities cannot be taken equal to mole fractions. It is gratifying that the values of K are of the order of magnitude of the calculated value of 14.3 based on the assumption of ideal solutions and equilibrium constants of Knox.

From the graph it is seen that at 80° the values of K increase less with increasing mole fraction of mercury than at 25°. Hence, at higher temperatures the system approaches that of an ideal system. Qualitatively, a similar result was found again by Yutzy and Kolthoff,[10] who at 100° found in the system silver chloride–bromide a value of the distribution coefficient which was independent of the composition of the solid.

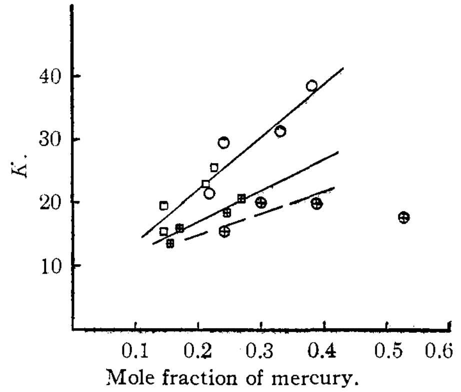

Fig. 3.—○, in 0.0766 M Na_2S at 25°; □, in 0.156 M Na_2S at 25°; ⊕, in 0.0766 M Na_2S at 80°; ⊠, in 0.156 M Na_2S at 80°.

Figure 3 shows that at high mole fractions of mercuric sulfide with solid (at $N_{HgS} > 0.5$) the value of K does not increase further with increasing N_{HgS} at 80°. This might indicate that the solid consists of two phases, the second phase being mercuric sulfide or, more likely, a solution of zinc sulfide in mercuric sulfide.

It is of interest to note that according to equation (5) the distribution coefficient of the mercuric sulfide between solution and precipitate is independent of the chemical nature of the solid as long as the latter can form ideal solid solutions with mercuric sulfide. Hence, it may be expected that under comparable conditions the distribution of mercuric sulfide between sodium mercuric sulfide solution and zinc, lead or manganese sulfides will be of the same order of magnitude.

Direct evidence from X-ray measurements of mixed crystal formation between mercuric and zinc sulfide was given by Moltzau and Kolthoff.[11] They found that zinc sulfide dissolved in mercuric sulfide to a limited extent. The present study shows that mercuric sulfide is soluble—at least to a certain extent—in zinc sulfide.

An X-ray examination of an orange colored precipitate, kindly made for us by Mr. M. L. Fuller of the New Jersey Zinc Co., showed that it had a zinc sulfide cubic lattice expanded about 1%. The broadness of the lines on the film prevented an exact measurement.

Summary

1. Mercuric sulfide is postprecipitated with

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(10) H. C. Yutzy and I. M. Kolthoff, THIS JOURNAL, **59**, 916 (1937).

(11) D. R. Moltzau and I. M. Kolthoff, *J. Phys. Chem.*, **40**, 637 (1936).

zinc sulfide from sodium mercuric sulfide solutions which are undersaturated with mercuric sulfide. Such a postprecipitation occurs only when the mercuric sulfide is soluble in the primary precipitate, and the speed of separation of the latter from solution is greater than the speed of dissociation of the $HgS_2^{=}$ ion into HgS and $S^{=}$.

2. The distribution coefficient of mercuric sulfide between aqueous solution and solid has been determined at 25 and 80°. The solid solution does not behave as an ideal solution, but the values of the distribution coefficient are of the same order of magnitude as the value calculated upon the basis of formation of ideal solutions. This calculated value is independent of the nature of the solid, as long as the latter acts as a solvent for mercuric sulfide.

3. The speed of attainment of distribution equilibrium between sodium mercuric sulfide solution and zinc sulfide is a good indicator of the degree of perfection and the progress of aging of the latter. It is shown that zinc sulfide precipitated at a *p*H of 1.15 is more perfect and ages more rapidly at this *p*H than the sulfide formed and aged at a *p*H of 5 and the latter more so than the sulfide formed and aged in alkaline medium.

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Hydroxyalkyl Ethers of Basic Phenols. The Antipneumococcic Activity of Some 8-Quinolyl Ethers

BY C. L. BUTLER AND ALICE G. RENFREW

It appeared to be of considerable general interest to extend the application of the hydroxyalkylation method used in the cinchona alkaloid field[1] to other types of basic phenolic substances. More specifically, it was hoped that studies carried out on simpler basic phenols would give a partial explanation, at least, of the low yields obtained in attempts to hydroxyethylate phenolic cinchona alkaloids with ethylene chlorohydrin.[2] Further, the preparation of simpler substances, related structurally to these alkaloids, was of interest in the chemotherapeutic study of pneumonia. Experiments undertaken with these considerations in view are described in the present report.

Phenol, aniline, *p*-aminophenol, *p*-acetaminophenol, *m*-diethylaminophenol and 8-hydroxyquinoline were chosen as suitable starting materials for the investigations. The compounds were alkylated in the usual way with benzyloxyalkyl *p*-toluenesulfonates[3] and the resulting aminoaryl benzyloxyalkyl ethers were hydrolyzed in dilute hydrochloric acid to hydroxyalkyl derivatives.[1] Yields were high in nearly all cases. The reaction with *p*-aminophenol was complicated by nitrogen alkylation. *p*-Acetaminophenol, however, gave with benzyloxyethyl *p*-toluenesulfonate, a high yield of the benzyloxyalkyl ether, which was readily converted to β-hydroxyphenetidine. Hydroxyalkylation of *m*-diethylaminophenol and 8-hydroxyquinoline was accomplished without difficulty.

It seemed possible that the failure of ethylene chlorohydrin to hydroxyethylate phenolic cinchona alkaloids[2] might be due to the presence in the cinchona structure of basic groups, with which this substance reacted with greater ease than with the phenolic group; or by which it was destroyed before it could react. Several alkylations with ethylene chlorohydrin were carried out in attempts to get further information on this point. According to Rindfusz[4] a 50% yield of hydroxyethyl phenyl ether is obtained on alkylation of sodium phenolate with this reagent. In the present work the reaction was carried out in the presence of one molecular equivalent of triethylamine. Only 13% of the theoretical quantity of hydroxyethyl phenyl ether was obtained in this experiment. The presence of triethylamine, however, did not decrease the yield of alkylation product when benzyloxyethyl *p*-toluenesulfonate was used as alkylating reagent. 8-Hydroxyquinoline, on alkylation with ethylene chlorohydrin, gave only 19% of the theoretical amount of

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[1] Butler and Renfrew, THIS JOURNAL, **60**, 1473 (1938).

[2] Butler, Renfrew, Cretcher and Souther, *ibid.*, **59**, 227 (1937).

[3] Butler, Renfrew and Clapp, *ibid.*, **60**, 1472 (1938).

[4] Rindfusz, *ibid.*, **41**, 669 (1919); see also Bentley, Haworth and Perkin, *J. Chem. Soc.*, **69**, 164 (1896).