4. The total quantum yield of ethyl methyl ketone decomposition with wave lengths below 2000 Å. is nearly one at low pressures when allowance is made for diketone formation.

5. At higher temperatures some methane is formed, but at room temperature the principal hydrocarbons are ethane, propane and butane in approximately equal amounts.

6. Possible secondary reactions have been discussed.

UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK   RECEIVED JUNE 20, 1938

Studies on Aging and Properties of Precipitates. XXIII. The Postprecipitation of Ferrous Sulfide with Cupric Sulfide

BY I. M. KOLTHOFF AND FRANK S. GRIFFITH[1]

Böttger and Druschke[2] found that iron is found in a precipitate of copper sulfide when the latter is formed under such conditions that no precipitation of iron sulfide alone occurs. Even when the copper sulfide was precipitated from solutions which were 2 N in nitric, hydrochloric or sulfuric acid, iron was found in the precipitate. In the present paper it is shown that iron sulfide is not *co*-precipitated but *post*-precipitated with cupric sulfide.

Experimental

The materials used were C. P. products. The stock ferrous sulfate solution was kept in 0.1 N sulfuric acid, the latter inhibiting the air oxidation. A fresh solution was prepared frequently. Concerning the method of treatment of the solutions with hydrogen sulfide reference is made to previous papers.[3]

After shaking in an atmosphere of hydrogen sulfide for a given period of time the solutions were filtered and the precipitate washed with 0.1 N hydrochloric acid which had been saturated with hydrogen sulfide. The filtrate and washings were evaporated to a volume of 25–50 ml., thus removing the hydrogen sulfide, 5 ml. of 5 N hydrochloric acid was added and any ferric iron formed reduced with a slight excess of stannous chloride. After the further classical treatment the ferrous iron was titrated with 0.05 N potassium dichromate using sodium diphenylamine sulfonate as indicator. In those cases in which the amount of iron removed from solution was very small the iron was determined in the washed precipitate. The latter was dissolved, the iron oxidized and precipitated with ammonia. The precipitate was dissolved, the iron reduced to the ferrous state and titrated with 0.005 N potassium dichromate.

(1) From a thesis submitted by Frank S. Griffith to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1937.

(2) W. Böttger and K. Druschke. *Ann.*, **453**, 315 (1927).

(3) I. M. Kolthoff and D. R. Moltzau, *J. Phys. Chem.*, **40**, 779 (1936); Kolthoff and Griffith, *ibid.*, **42**, 531 (1938); see also thesis of junior author.[1]

Experimental Results

In order to get an impression of the order of magnitude of the precipitation of iron, various preliminary experiments were carried out. One hundred ml. of solution containing 5 mmol. of cupric sulfate and 1.25 mmol. of ferrous sulfate and being 1.55 N in sulfuric acid (after precipitation of copper 1.65 N) was treated with hydrogen sulfide for fifteen minutes, filtered, and the iron determined in the precipitate. Only 0.05 mg. of iron or 0.07% of the original amount was found in the precipitate. The experiment was repeated with the solution heated to 95° before saturating with hydrogen sulfide; 0.19 mg. of iron (0.27%) was found in the precipitate. A similar set of experiments was run with the solution being 0.53 N in sulfuric acid (after precipitation of copper sulfide 0.63 N): precipitation at room temperature, 0.42 mg. of iron in precipitate (0.60%); precipitation started at 95°, 0.75 mg. of iron in precipitate (1.07%). The amounts of iron found in the precipitates (room temperature) are about one-fifth of those expected from the results of Böttger and Druschke. However, these authors do not state the time of precipitation; it is shown later that the amount of iron entering the precipitate increases with the length of time of contact with the copper sulfide.

Evidence of Postprecipitation: Effect of Time before Filtration, Concentration of Acid and of Temperature.— In the following experiments a mixture was used containing 5 mmol. of copper sulfate and 1.25 mmol. of ferrous sulfate in 100 ml. In some of the experiments the iron was present during the precipitation of the copper sulfide, in others it was added one or two minutes after precipitation of the copper. Hydrogen sulfide was bubbled through continuously during the course of the experiments; in the one-month experiments the gas outlet, after a few hours, had a fine capillary. The flasks were shaken continuously except in the one-month experiments. After the period of shaking given in Table I the filtrates were analyzed for iron.

From the fact that the extent of precipitation of the iron is about the same, regardless of whether the copper sulfide is precipitated in the presence of iron or the iron is added after precipitation of copper, it follows conclusively that we are dealing with a phenomenon of postprecipitation. The amount of postprecipitation decreases rapidly with

TABLE I

POSTPRECIPITATION OF IRON SULFIDE. EFFECT OF TIME, ACID AND TEMPERATURE

Temp. after addition of iron, °C.	Concn. of H_2SO_4 after pptn. of Cu. N	Iron added before or after pptn. of Cu	Iron in precipitate in % after			
			15 min.	4 hours	4 days	1 month
25	0.25	Before	0.4	0.8	1.0	
25	.25	After	.4	.8	...	..
25	.125	Before	.8	3.3	5.0–5.8	5.5
25	.125	After	1.0	4.0	...	..
75[a]	.252	Before	2.1	3.6	4.5–5.0	
75[a]	.252	After	2.0	4.0	...	..
75[a]	.125	Before	6.4	7.3	9.5–10.0	
75[a]	.125	After	5.0	7.0	...	
98[a]	.125	Before	10.2		12.5	14.5
95[b]	.25	Before	...	9.5–9.8	...	..
95[b]	.125	Before	...	16–18		

[a] Temperature is given at beginning of experiment after precipitation of copper sulfide. No further heat was applied.
[b] The suspension was reheated to 95° four times during the course of an experiment.

increasing sulfuric acid concentration. The rate of postprecipitation and probably also the amount of postprecipitation increases with the temperature. It is doubtful whether distribution equilibrium of iron between solution and solid has been attained in any of the experiments. The copper sulfide ages with time and, as will be shown later, its effect upon the postprecipitation of iron decreases with increasing age.

Precipitation at Higher Temperatures.—When higher temperatures were *maintained* the rate of postprecipitation was found to be much greater. Experiments were carried out with solutions of the same composition as those in Table I, the acid concentration being 0.125 N. The following are a few typical figures: temperature 50°; precipitated after one hour 7.0%, after four hours 8.0%, after thirty hours 9.6% of iron. Temperature 90°, precipitated after forty-five minutes 13 to 14% of iron, after twelve hours 15 to 16%. Apparently, most of the postprecipitation occurs during the first fifteen to thirty minutes.

Effect of Varying the Iron and Acid Concentrations.— In the following experiments 100 ml. of solution was taken containing 5 mmol. of copper sulfate and varying amounts of ferrous sulfate and sulfuric acid. The solutions were heated to the boiling point, put on the shaker in the airbath at 95° and hydrogen sulfide was passed through for one hour. At the time these experiments were performed it was believed that the iron sulfide was present in the solid phase in the form of a solid solution. The experiments were made with the intention of determining the distribution coefficient of the iron sulfide between the liquid and solid phases. From the results given in Table II it is seen that the amount of iron postprecipitated increases with increasing iron concentration of the solution and decreases markedly with increasing acid concentrations, but the value of the distribution coefficient of the iron sulfide calculated from the results was not found to be constant. From the analytical view-point it is of interest to mention that no postprecipitation of iron is found at room temperature from solutions being at least 0.5 N in hydrochloric or 1 N in sulfuric acid, when filtration is made soon after the precipitation of copper.

Postprecipitation of Iron Sulfide with Aged Copper Sulfide.—At room temperature it was found to make little

TABLE II

EFFECT OF CONCENTRATION OF IRON AND OF ACID

Concn. of H_2SO_4 after pptn. of CuS. N	Concentration of $FeSO_4$		Fe in ppt., %	Fe in ppt., mmol.
	Original M	Final		
0.125	0.0013	0.00079–.00083	39 to 36	0.051–0.046
.125	.013	.0113	12.5 to 13	.16 – .17
.250	.0013	.00115	11	.014
.250	.013	.0121–.0123	6.5 to 5.2	.085– .067
.250[a]	.0130		8.6	.11
.250	.1295	.1275	1.4 to 1.5	.19 – .18

[a] Ten millimoles of copper sulfide instead of five.

difference whether the iron was present during the precipitation of copper sulfide or added a few minutes afterward. At higher temperatures, however, the amount of iron found postprecipitated was always less (3 to 4%) when the iron was added after precipitation of the copper sulfide, indicating a rapid aging of copper sulfide at elevated temperatures. In order to study the effect of aging more systematically experiments were carried out in the following way. The acidified copper solution was introduced in an Erlenmeyer flask closed by a rubber stopper with two holes. Through one hole passed the inlet tube of the hydrogen sulfide; through the other a tube sealed to an ampoule containing 10 ml. of acid iron solution. The bottom of the ampoule had been blown thin in order to facilitate breaking. It was provided with a small hole in the neck which served as an exit for the gas. The copper solution was heated to the boiling point, and kept there for at least five minutes to bring the iron solution in the ampoule to the same temperature. After this time the flask was placed in a box maintained at 90°, and hydrogen sulfide passed through the copper solution. The mixture was shaken for the time specified in Table III as the "age of CuS" after which time the iron solution was added by punching a hole in the bottom of the ampoule with a glass rod. After shaking for fifteen minutes more the mixture was filtered and the filtrate analyzed for iron. The mixture contained 5 mmol. of copper sulfide, and 1.25 mmol. of ferrous sulfate in 100 ml.; the sulfuric acid concentration after adding the iron solution was 0.125 N.

TABLE III

EFFECT OF AGING OF COPPER SULFIDE AT 95°

Age of CuS	0	2 min.	7 min.	20 min.	4 hours	17 hours	36 hours
Fe in ppt., %	12.5	9	6.0	5.5	2.0	0-1	0

The copper sulfide ages rapidly at 95° and becomes much less effective in its promotion of the precipitation of iron sulfide. Kolthoff and Pearson[4] showed that aged copper sulfide is more effective than the fresh product in causing the postprecipitation of zinc sulfide. The mechanism of the zinc postprecipitation is quite different from that of iron sulfide. The zinc sulfide separates from supersaturated solution as a separate phase; the iron, on the other hand, is removed from a solution undersaturated with respect to ferrous sulfide.

The rapid aging of cupric sulfide at 95° explains why it is not possible to attain distribution equilibrium of the iron in the long period experiments. Thus, working at 95° it was not possible to obtain more than 16 to 18% of the iron in the precipitate under conditions specified in Table I (final acidity 0.125 N). When, on the other hand, the copper solution was added slowly to the acid ferrous sulfate solution which was kept at 95° and saturated with hydrogen sulfide it was possible to obtain a precipitate containing 23 to 25% of the iron (final conditions as above).

All results reported so far indicate that the iron sulfide in the solid phase is present either as a solid solution or in the form of a chemical compound. X-ray investigations, kindly carried out by Mr. M. L. Fuller[5] of the New Jersey Zinc Co., Palmerton, Penna., by the power method with a mixed precipitate revealed the lines of copper sulfide and of chalcopyrite, $CuFeS_2$. Apparently, then, the speed of formation of copper sulfide is greater than that of chalcopyrite. The former, however, is not stable in the presence of ferrous iron and hydrogen sulfide in the solution, and at not too high acidities, it is slowly transformed into chalcopyrite.

Solubility of Ferrous Sulfide.—It has been stated before in this paper that the iron sulfide is postprecipitated with copper sulfide from solutions in which the solubility product of iron sulfide is not exceeded. Since the solubility of most slightly soluble sulfides depends much upon the degree of perfection and crystal modification it was decided to determine the solubility of iron sulfide aged under various conditions. Bruner and Zawadski[6] determined the solubility of ferrous sulfide by passing hydrogen sulfide through solutions of ferrous sulfate until equilibrium was reached and by dissolving ferrous sulfide in dilute acid. As an average they obtained in solutions saturated with hydrogen and ferrous sulfides a value of $[Fe^{++}]/[H^+]^2$ of 3.4×10^4. Moser and Behr[7] dissolved in 0.01 N sulfuric acid a product which had been precipitated at room temperature and aged for eighteen hours. Using the value of Noyes and Sherrill[8] for the second dissociation

(4) I. M. Kolthoff and E. A. Pearson, *J. Phys. Chem.*, **36**, 549 (1932).

(5) The authors take this occasion to thank Mr. Fuller for his valuable coöperation.

(6) L. Bruner and J. Zawadski, *Z. anorg. allgem. Chem.*, **65**, 143 (1909).

(7) L. Moser and M. Behr, *ibid.*, **134**, 49 (1924).

(8) M. S. Sherrill and A. A. Noyes, THIS JOURNAL, **48**, 1861 (1926).

constant of sulfuric acid a value of $[Fe^{++}]/[H^+]^2$ of 5.5×10^4 is calculated from their data.[9]

The determination of the solubility of both fresh and well-aged iron sulfide was attempted. The following products were used:

Product 1: Fresh.—A solution of 30 g. of ferrous sulfate and 100 g. of ammonium acetate in 100 ml. of water was kept saturated with hydrogen sulfide at room temperature for one hour. A portion of the precipitate was washed four times with 0.012 N hydrochloric acid using the centrifuge for separating liquid and solid.

Product 2.—A solution of 28 g. of ferrous sulfate and 15 g. of sodium acetate in 100 ml. of water was kept saturated with hydrogen sulfide for eighteen hours at room temperature and the precipitate collected.

Product 3.—A molar solution of ferrous sulfate was saturated with hydrogen sulfide at 0°, the bottle containing the suspension was closed by a rubber stopper held by a wire and placed on the sand-bath at 80° for ten days (final pH was 2.30). The product was composed of black crystals sufficiently large to be seen by the naked eye.

An excess of the iron sulfide was shaken with acid, which previously had been saturated with hydrogen sulfide, for eight hours or longer. The sulfide was then allowed to settle or was centrifuged and the clear solution siphoned out of the flask by means of hydrogen sulfide under pressure from the Kipp generator. The hydrogen ion activity of the solution was determined colorimetrically or by means of the glass electrode and the iron content after filtration was determined by the dichromate method. The results are given in Table IV.

TABLE IV

SOLUBILITY OF IRON SULFIDE OF VARIOUS AGE IN ACID AT 25° (DIRECT METHOD)

Product used	Age	HCl, N	pH	Ml. 0.05 N $K_2Cr_2O_7$ for titrn. 50 ml. of soln.	$[Fe^{++}]/[H^+]^2$
1	Fresh	0.012	3.50 3.60[a]	5.75-5.46	8.3×10^4
1	Fresh	.012	3.60[b]	6.05	9.7×10^4
2	18 hrs., r. t.	.012	3.45[a]	6.33	5.0×10^4
3	10 days 80°	.025	3.19[b]	13.46	3.2×10^4
3	10 days 80°	.025	3.23[b]	12.20	3.5×10^4
3	10 days 80°	.025	3.18[b]	12.85	2.9×10^4
3	10 days 80°	.025	3.13[b]	11.95	2.2×10^4
3	10 days 80°	.025	3.20[b]	11.80	2.0×10^4

[a] Measured colorimetrically with tetrabrom phenol blue.
[b] Measured with the glass electrode.

It should be mentioned that an error of 0.05 in pH causes an error of 20% in the value of the quotient $[Fe^{++}]/[H^+]^2$. The value obtained with product 2 (5.0×10^4) which was prepared according to the directions of Moser and Behr[7] is in good agreement with that calculated from these authors' figures (5.5×10^4). From the results in Table IV it is seen that the solubility of iron sulfide depends little upon the age of the product, the value of $[Fe^{++}]/[H^+]^2$ being about 9×10^4 for a fresh product and about 3×10^4 for drastically aged products.

(9) Kolthoff, *J. Phys. Chem.*, **35**, 2711 (1931), in calculating this ratio from Moser and Behr's data made a mistake in that he failed to take into account the decrease of the concentration of the strong acid by the dissolved iron sulfide.

It was also attempted to reach solution equilibrium from the other side. One hundred milliliters of 0.125 M ferrous sulfate was placed in a flask which was shaken continuously while a slow stream of hydrogen sulfide was passed through. If the time of precipitation was longer than seven days, the flask was stoppered after that time and allowed to stand without further shaking.

TABLE V

SOLUBILITY OF IRON SULFIDE AFTER PRECIPITATION

Time of pptn.	Temp., °C.	pH	Ml. of 0.05 N $K_2Cr_2O_7$ for titrn. of 10 ml. of soln.	$[Fe^{++}]/[H^+]^2$
20 hours	25	3.01	23.68	1.2×10^5
70 hours	25	2.94	23.64	9.0×10^4
7 days	25	2.64	23.33	2.2×10^4
1 month	25	2.00	20.90	1.0×10^3
20 hours	90	2.60	23.28	1.9×10^4
70 hours	90	2.31	27.65	$5 \quad \times 10^3$

The solubility of iron sulfide at 90° in solutions saturated with hydrogen sulfide seems to be slightly less than that at room temperature. The figures indicate that the post-precipitation of iron sulfide with copper sulfide even at higher temperature (Tables I, II and III) cannot be a separation of the former in the pure form.

In order to substantiate this conclusion in an unequivocal way the following experiment was carried out. One hundred ml. of 0.0125 M ferrous sulfate in 0.125 N sulfuric acid was saturated with hydrogen sulfide and heated to the boiling point, whereupon some of the well-aged, crystalline product No. 3 of iron sulfide was added. The mixture was shaken for one hour at 90° while hydrogen sulfide was passed through the flask. The filtrate and washings required 41.9 ml. of 0.05 M potassium dichromate, whereas the original iron solution required only 26.00 ml. Thus, some of the iron sulfide had gone into solution. If cupric sulfide instead of the well-aged iron sulfide had been added (Tables I, II) some of the iron would have been removed from solution. This conclusion is in agreement with the results of the X-ray analysis, which showed that the iron is present in the precipitate in the form of chalcopyrite.

That the postprecipitated iron sulfide is incorporated in the copper sulfide precipitate was also shown by experiments in which mixed precipitates were extracted with 0.2 N hydrochloric acid. Hardly any of the postprecipitated iron was extracted. Even upon washing at room temperature with 1 and 3 N hydrochloric acid (saturated with hydrogen sulfide) it was impossible to extract all of the iron. A hot extraction with 3 N acid removed all of the iron.

Finally, experiments were made in which zinc and mercuric sulfides instead of cupric sulfides were used as promoting agents of the precipitation of iron in acid solution. In agreement with Böttger and Druschke[2] it was found that these sulfides did not cause the precipitation of any iron at room temperature and at 80° at an acidity of 0.125 N sulfuric acid, even after seventeen hours of shaking.

Summary

1. Iron sulfide is postprecipitated with cupric sulfide from acid solutions which are undersaturated with regard to pure ferrous sulfide. The postprecipitated iron sulfide is difficultly extracted with 3 N hydrochloric acid. The presence of $CuFeS_2$ in the mixed precipitate was shown by X-ray analysis.

2. The rate of postprecipitation is small at room temperature but large at 70–95°. Due to aging of the cupric sulfide it is difficult to attain the true state of equilibrium.

3. The amount of postprecipitated iron increases with increasing ferrous iron concentration and decreasing hydrogen ion concentration and increasing amounts of cupric sulfide.

4. The promoting effect of cupric sulfide upon the precipitation of iron sulfide decreases rapidly upon aging at 90°.

5. The solubility of fresh iron sulfide expressed by the ratio of $[Fe^{++}]/[H^+]^2$ in solution saturated with hydrogen sulfide was found to be 9×10^4 at room temperature, that of mildly or drastically aged products 5 to 3×10^4.