THE USE OF A SULFATE–HYDROSULFATE BUFFERED SOLUTION FOR THE PRECIPITATION OF ZINC SULFIDE

BY C. E. P. JEFFREYS AND ERNEST H. SWIFT

It has been realized for over half a century that there are advantages in precipitating zinc sulfide from an acid solution rather than one which is neutral or alkaline; specifically, certain separations can be made by proper adjustment of the hydrogen-ion concentration and the precipitate usually separates in a form which is more readily handled. Because of these effects many early workers[1] recommended the use of various organic acids for acidifying the solution and thereby obtained, somewhat uncertainly, the effect of a buffered solution considerably prior to the development of the modern theory and use of such solutions.

Somewhat more recently the use of sulfuric acid solutions was studied by Weiss,[2] who recommended that the precipitation be made from a solution 0.01 N in sulfuric acid by means of a very rapid stream of hydrogen sulfide, but he apparently provided no means for controlling the increase in hydrogen ion concentration taking place during the precipitation; by Waring,[3] who once more recommended the use of formic acid; by Funk[4] who studied the effect of various organic acids on the precipitation and on the separation of zinc from various other elements; while Glixelli[5] made a comprehensive study of the effect of the nature of the solution on the forms and apparent solubility of the precipitate, also on the time factor which enters in establishing the precipitation equilibrium.

In the excellent work of Fales and Ware[6] the limits of the hydrogen-ion concentration between which quantitative precipitation could be effectively made were first precisely determined and means provided for controlling the acidity within these limits. They found that 0.01 N sulfuric acid solutions were near the limiting hydrogen-ion concentration above which precipitation is incomplete. Therefore they rejected sulfuric acid solutions in favor of formic acid–formate buffered solutions, and found that for such solutions the hydrogen-ion concentration most favorable for quantitative precipitation of zinc sulfide was 10^{-2} to 10^{-3}. They seem not to have

[1] (a) Deeffs, Chem. News, 41, 279 (1880); (b) Bragard, Dissertation, Berlin, 1887; Z. anal. Chem., 27, 209 (1888); (c) Beilstein, Ber., 11, 1715 (1885); (d) Mühlhäuser, Z. angew. Chem., 15, 731 (1902); (e) Berg, Z. anal. Chem., 25, 512 (1886); (f) Dohler, Chem.-Ztg., 23, 399 (1899); (g) Neumann, Z. anal. Chem., 28, 57 (1889).

[2] G. Weiss, Dissertation, München, 1906.

[3] Waring, THIS JOURNAL, 26, 26 (1904).

[4] Funk, Z. anal. Chem., 46, 93 (1907).

[5] Glixelli, Z. anorg. Chem., 55, 306 (1907).

[6] Fales and Ware, THIS JOURNAL, 41, 487 (1919).

investigated the possibility of using sulfate and hydrosulfate as a buffer for controlling the acidity during the precipitation.

Lundell, Hoffman and Bright[7] have recently recommended the precipitation of zinc sulfide from a 0.01 N sulfuric acid solution and state that the best precipitation is obtained from a sulfuric acid–sulfate solution. They do not present any discussion or experimental data in support of this recommendation.

This paper presents the results of a study of the use of sulfate–hydrosulfate mixtures as buffer solutions, of the precipitation of zinc as zinc sulfide from such solutions, and of the separation of zinc under such conditions from nickel, cobalt, iron, manganese, chromium and aluminum.

There are certain advantages in using sulfate–hydrosulfate buffered solutions for this particular precipitation. The second ionization constant of sulfuric acid having been determined[8] as 1.15×10^{-2}, and the optimum hydrogen-ion concentration for the precipitation of zinc sulfide from sulfate solutions having been found to be about 10^{-2}, it would seem that the required ratio of sulfate to hydrosulfate should be about one, the most favorable ratio for effective buffer action. As compared with this, Fales and Ware had to use an acid-to-salt ratio of 84:1, with the formic acid concentration 4.7 formal, in order to obtain an initial P_H of 1.86, a value at which, in our experiments, quantitative precipitation was obtained. This P_H was experimentally obtained in the sulfate–hydrosulfate solution by using an acid-to-salt ratio of 20.7:66, with the total concentration of sulfate and hydrosulfate 0.347 formal. In addition, Fales and Ware recommended the use of considerable ammonium citrate and 6.25 g. of ammonium sulfate in 200 ml. of solution. It is stated that: "ammonium citrate is used for the purpose of forming complexes with interfering metals," thus assisting in holding in solution such elements as iron and manganese. We find that from a sulfate–hydrosulfate solution of the proper P_H, such an agent is not needed. The ammonium sulfate was added as a "salting-out agent." In our experiments the need of adding an additional salting-out agent was not apparent, as quantitative precipitation was obtained, and as the form of the precipitate left nothing to be desired as to ease of filtration and washing. It is believed that under the conditions of our experiments, the hydrogen-ion concentration is the predominant factor governing the form as well as the solubility of the precipitate. It should also be mentioned that when using this precipitation of zinc as a means of effecting a qualitative separation it is a decided advantage not to have to add organic matter to the solution, for, especially in a group analysis, such material as citrates may cause difficulties in subsequent operations.

[7] Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, 1931, p. 388.

[8] Sherrill and Noyes, THIS JOURNAL, **48**, 1873 (1926).

This study was originally undertaken in order to devise a suitable method for the qualitative separation of zinc from nickel and cobalt which would be more quantitative than those commonly employed in qualitative systems, such as, for example, the treatment of the mixed sulfides with dilute hydrochloric acid or the use of sodium hydroxide and peroxide. We wish to express our obligation to Mr. W. H. Pickering and to Mr. D. F. Bender for a large number of preliminary experiments in which the limiting conditions were determined and in which the effect of such modifications as carrying out the precipitation at elevated temperatures under considerable pressure of hydrogen sulfide was studied.

Materials

Preparation and Standardization of a Zinc Sulfate Solution.—A c. p. grade of zinc sulfate was recrystallized once from distilled water and once from conductivity water. The solution, saturated at 70°, was cooled in an ice-bath and the crystals collected by suction filtration. A stock solution containing approximately 40 mg. per ml. was made, and a working solution containing 10 mg. per ml. was prepared from it by dilution. This latter solution was standardized by precipitating the zinc as sulfide from sulfate–hydrosulfate solutions at such a P_H that the precipitation was quantitative, *i.e.*, initial P_H's of 2.18 and 1.86. The zinc sulfide was then converted to sulfate and weighed as such. The values thus obtained were 257.0 mg. per 25 ml. and 257.3 mg. per 25 ml. Some difficulty was experienced in igniting the zinc sulfate samples to constant weight. Fales and Ware, after igniting the paper and precipitate, added concentrated sulfuric acid and heated to constant weight in an air-bath. With their particular arrangement they mention no difficulty. Scott[9] directs that the zinc sulfate be ignited to dull red heat. It was found difficult to drive off all the sulfuric acid on an air-bath, and very difficult to ignite with a Bunsen burner without decomposing some of the sulfate. However, constant weight was easily obtained by fuming off the excess acid on an air-bath and heating the precipitate to 500 ± 20° for one hour (an electric furnace with a tem‧ perature indicator and control was used). Lundell, Hoffman and Bright[7] recommend igniting to zinc oxide at 900°, and indicate that in this case also the temperature of ignition must be fairly closely controlled. Our experiments confirmed this and indicate that either method is capable of consistent results with careful control of the temperature of ignition.

The Gases Used.—Hydrogen gas for the hydrogen electrode was taken from a cylinder. Using standard buffer solutions it was found that with this hydrogen constant and reproducible e. m. f. values were obtained which agreed with the accepted values for these solutions. Hydrogen sulfide, also from a cylinder, was used after passing it through a bottle of distilled water. Carbon dioxide was obtained from a cylinder.

Buffer Solutions.—The buffer solutions were made by weighing out the proper quantity of c. p. sodium sulfate decahydrate, and adding the required amount of either standard sulfuric acid or a weighed quantity of c. p. sodium hydrosulfate.

Sulfates of Other Metals.—The best available c. p. grade sulfates of cobalt, iron, nickel and manganese were used without further purification. Qualitative tests showed that the cobalt contained no nickel, and the nickel no cobalt. The source of the chromium and aluminum were c. p. grades of potassium aluminum sulfate and potassium chromium sulfate.

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[9] Wilfred W. Scott, "Standard Methods of Chemical Analysis," 4th ed., D. Van Nostrand Co., 1927, p. 599.

The Experiments

*P*H **Measurements on the Buffer Solutions.**—The buffer solution was made up in a 500-ml. Erlenmeyer flask, and 25 ml. of zinc sulfate solution containing 257 mg. of zinc was added with a pipet. The total volume in all experiments was 250 ml. The *P*H of the solution was measured by means of a Hildebrand type bubbling electrode, and a saturated calomel half-cell. The electrodes and assembly for the hydrogen-ion concentration measurements were checked against a standard acetate solution, and also against a $M/20$ potassium acid phthalate solution. A sample of Bureau of Standards potassium acid phthalate was used for checking an electrode, then with the same electrode a solution prepared from a c. p. brand of potassium acid phthalate was measured. The e. m. f.'s agreed to within one millivolt. This latter solution was then used for checking the electrode from time to time during the course of the work.

Precipitation of the Zinc Sulfide.—The method of precipitation closely followed that given by Fales and Ware.[10] The solution from which the zinc was to be precipitated was heated to 60°, hydrogen sulfide bubbled through rapidly and the heating continued until the temperature reached 90–95°. As the solution cooled, hydrogen sulfide was also bubbled through it until the precipitate began to settle rapidly, and finally the solution was saturated when cold. Twenty-five to forty minutes were usually required before rapid settling was obtained. The precipitation was found to be quantitative in forty minutes when carried out in this way in solutions of the proper acidity.

The mixtures were allowed to stand until the supernatant liquid was entirely clear. Some solutions were filtered after standing for three hours, and others were allowed to stand overnight; no difference was detected as to ease of filtering or completeness of precipitation. The precipitate was of a dense, granular form, which filtered rapidly and did not cling tightly to the glass of the flask as is the case with zinc sulfide precipitated from less acid or alkaline solutions.

*P*H **Measurements on the Filtrate.**—The filtration was made through a dry paper, the filtrate freed of hydrogen sulfide by bubbling carbon dioxide through it, and the *P*H measured after removing the carbon dioxide by passing hydrogen through. A blank was run on a solution made up as was the solution in Expt. 3 of Table I. Instead of precipitating the zinc in this case, an amount of sulfuric acid was added corresponding to the acid liberated on precipitating 257 mg. of zinc. The *P*H change was from 1.86 to 1.68, which corresponds closely with the change observed in the experiments shown in the tables.

The Solubility of Zinc Sulfide in Sulfate–Hydrosulfate Solutions.— In Table I are given the results of a group of experiments in which the

[10] Ref. 6, p. 493.

solubility of zinc sulfide with various ratios of hydrosulfate to sulfate and various P_H values was studied. Column 2 gives the ratios of $NaHSO_4/Na_2SO_4$ initially in the solution, columns 3 and 4 the initial and final P_H values, respectively, and column 5 the milligrams of zinc remaining in solution after the precipitation with hydrogen sulfide. The values in the last column were obtained in the following way. After making the final P_H measurement, ammonia was slowly added to the filtrate until it remained just acid to litmus, and again hydrogen sulfide was passed in to precipitate any zinc which had remained in the filtrate. The size of the precipitate thus obtained was compared with that obtained on precipitating known quantities of zinc under the same conditions. Fales and Ware[6] estimated the unprecipitated zinc by weighing the precipitate obtained and calculating the difference from the amount taken. The method here used is a more direct way of estimating the small amounts of zinc remaining in solution, and is sufficiently accurate for estimating the quantities involved. Confirmatory experiments showed that under these conditions 0.1 mg. of zinc would give a detectable opalescence on treatment with hydrogen sulfide. A blank was run to prove that no free sulfur would be obtained under the same conditions. This possibility was minimized by the fact that the solution had been freed from oxygen by being saturated with carbon dioxide, and contact with air thereafter prevented so far as possible.

TABLE I

THE SOLUBILITY OF ZINC SULFIDE IN SULFATE–HYDROSULFATE SOLUTIONS OF VARIOUS
HYDROGEN-ION CONCENTRATIONS

Volume, 250 ml. Zinc taken, 257 mg.

Expt.	Initial ratio NaHSO₄/Na₂SO₄ in millimoles	P_H initial	P_H final	Zinc found in the filtrate, mg.
1	8.3/66	2.18	1.83	0.0
2	12.4/66	2.08	1.78	Trace
3	20.7/66	1.86	1.66	0.20
4	22.8/66	1.78	1.62	Trace[a]
5	24.9/66	1.77	1.62	0.1–0.2
6	27.0/66	1.72	1.57	0.3–0.5
7	27.0/66	1.72	1.56	0.3–0.5
8	27.0/66	1.72	1.58	0.3–0.5[a]
9	27.0/66	1.72	1.58	0.3–0.5[b]
10	31.0/66	1.67	1.47	0.3–0.5[b]
11	37.3/66	1.57	1.46	0.5
12	45.0/66	1.49	1.39	0.8–1.0
13	58.0/66	1.38	1.29	1.5
14	70.5/66	1.31	1.22	4.0
15	87.2/66	1.19	1.14	6.0

[a] Filtered after standing for three hours. [b] Filtered after standing overnight.

From the above experiments it may be concluded that from these solutions precipitation will be complete to less than 0.25 mg. at a P_H of 1.6 or

at a hydrogen-ion concentration as high as 2.5×10^{-2}. Less than 1 mg. remains in solution at a P_H of 1.54 or hydrogen-ion concentration of 2.9×10^{-2}. It would seem that the conditions of Expt. 4, where the ratio of $NaHSO_4/Na_2SO_4$ is about one-third and the initial P_H 1.78, are best adapted for securing the desired completeness of precipitation of zinc and for holding other elements in solution. At the same initial P_H the solubility of the zinc sulfide in these solutions is about the same or even a little less than in the formic acid–formate solutions of Fales and Ware, in spite of the fact that in our experiments 257 mg. of zinc is precipitated as compared to about 162 in theirs, with consequently more acid liberated due to the precipitation. If desired the buffer action could be made considerably more effective and the change in hydrogen-ion concentration during precipitation made much smaller by increasing the concentrations of sulfate and hydrosulfate in the solution. This effect is shown in the last three experiments of Table I, where with a higher concentration of hydrosulfate the change during precipitation is less than 0.1 of a P_H unit. We have considered it desirable, in order to minimize difficulty in washing the precipitate and to avoid the use of excessive quantities of buffer material, to keep the buffer concentrations at the lowest values which would adequately control the acidity. It should be pointed out that due to the high concentration of electrolyte in these solutions, the evaluation of the activities of the various ions is subject to considerable uncertainty, while a simple calculation of the hydrogen-ion concentration from the formal salt/acid ratios may lead to results considerably divergent from the experimental values. Because of this a series of experiments was made to show the effect of dilution on the P_H of such a solution. The results are given in Table II.

TABLE II

THE EFFECT OF DILUTION ON THE P_H OF SULFATE-HYDROSULFATE SOLUTIONS

Experiment	1	2	3	4	5
$NaHSO_4$ [moles/liter]	0.1	0.05	0.025	0.01	0.0025
Na_2SO_4 [moles/liter]	0.5	0.25	0.125	0.05	0.0125
P_H	1.78	1.48	2.17	2.43	2.82

The decrease in acidity in the more dilute solutions is due to the fact that the fraction of the hydrosulfate ionized into hydrogen and sulfate ions becomes large at these concentrations; the increase in the more concentrated solutions would be predicted because of the effect of the high salt concentrations on the activities of the various ions. It is thus seen that if, in order to control more closely the acidity, a higher concentration of the buffer is used, the initial ratio of hydrosulfate to sulfate should be adjusted accordingly, thus with the sodium sulfate concentration 0.25 formal, a $NaHSO_4/Na_2SO_4$ ratio of one-third is required to produce an initial P_H of 1.78; with the sodium sulfate concentration 0.5 formal this ratio has to

be reduced to one-fifth. The effect of the use of ammonium sulfate was tested in two additional experiments which were duplicates of Expt. 4 except that ammonium sulfate and sulfuric acid were used to adjust the initial hydrosulfate-to-sulfate ratio to the value 22.8/66. No difference could be detected in either the rate or completeness of the precipitation or the nature of the precipitate. This indicates that neither the hydrogen-ion activity nor the salt effect had been greatly changed, and that where desirable ammonium sulfate can be substituted for the sodium salt.

Effect of Chloride Ion on the Precipitation of Zinc Sulfide.—In the following table is gathered a group of experiments in which the solution contained in addition to the buffer mixture 132 milli-equivalents of potassium chloride.

TABLE III

THE EFFECT OF CHLORIDE ION ON THE SOLUBILITY OF ZINC SULFIDE

Potassium chloride added, 132 milli-equivalents. Zinc taken, 257 mg. Volume, 250 ml.

Expt.	Initial ratio $NaHSO_4/Na_2SO_4$ in millimoles	Initial P_H	Final P_H	Zinc found in the filtrate, mg.
16	20.7/66	1.73	1.51	1.5
17	27.0/66	1.62	1.46	2.0
18	37.3/66	1.43	1.37	2.0

The presence of a high concentration of chloride ion lengthens the induction period in the beginning of precipitation, apparently slows down the precipitation and, with the same P_H, increases the solubility of zinc sulfide by three or four times. This is shown by comparing the results in Table III with those obtained at corresponding P_H values in Table II. It should be noted also that the presence of the potassium chloride increases the acidity in solutions where the initial hydrosulfate and sulfate ratios and concentrations are the same; for example, compare Expt. 16, Table III, with Expt. 3, Table I.

The Separation of Zinc from Cobalt, Nickel, Iron, Manganese, Chromium and Aluminum.—The following table gives a group of experiments showing the efficiency of the separation of zinc from the common metals most likely to be found with it after an ammonium sulfide precipitation.

The cobalt brought down with the zinc precipitate in Expt. 19 was determined by the method of Engle and Gustavson,[11] after dissolving the precipitate with hydrochloric acid. In Expt. 20 the precipitate was dissolved in acid, the solution made just alkaline, and sodium peroxide added. The black cobaltic oxide was easily detectable. The nickel in the zinc sulfide precipitate was estimated by dissolving the precipitate, making the solution barely basic with ammonia, and adding dimethylglyoxime. The quantity of glyoxime precipitate was estimated by comparison with precipitates obtained with known quantities of nickel under the same condi-

[11] Engle and Gustavson, *J. Ind. Eng. Chem.*, **8**, 90 (1916).

TABLE IV

SEPARATION OF ZINC FROM OTHER METALS

Volume, 250 ml. Initial ratio $NaHSO_4/Na_2SO_4$ in millimoles, 20.7/66 (except Expt. 20). 257 mg. zinc and 250 mg. of other metal taken unless otherwise stated under remarks.

Expt.	Other metal	P_H initial	P_H final	Other metal in ZnS ppt., mg.	Remarks
19	Co	1.82	1.64	7	200 mg. Co
20 ·	Co	1.35		Trace	200 mg. Co. Initial ratio Na-$HSO_4/Na_2SO_4 = 58/66$
21	Co	1.82		Large quant.	100 Zn; 400 Co
22	Co	1.82		No ppt.	No Zn, 500 Co; sol. stood 3 days
23	Ni	1.82	1.66	0.3–0.4	
24	Ni			0.3–0.4	
25	Mn	1.81	1.65	0.1	
26	Mn			0.1	
27	Fe	1.82	1.65	0.5–0.6	
28	Fe			0.5–0.6	
29	Al			<0.25	
30	Cr			0	

tions. Manganese was estimated by adding sodium bismuthate to the nitric acid solution obtained by dissolving the precipitate, then making comparisons of the color developed with that obtained on oxidizing known amounts of manganese. Iron was determined by comparison with standards to which potassium thiocyanate had been added. The precipitates from Expts. 29 and 30 were dissolved in hot 6 N hydrochloric acid and the solutions then made just basic to methyl red with ammonia. No chromium hydroxide and a bare trace of aluminum hydroxide formed. This precipitate was compared with standards.

From the results shown in Table IV it is seen that the separations are satisfactory in all cases except with cobalt. Even in a solution whose initial P_H was 1.35, too high in acid for complete precipitation of zinc, cobalt is still co-precipitated. In Expt. 21 where 100 mg. of zinc is precipitated from a solution containing 400 mg. of cobalt, the zinc sulfide precipitate came down quite white for several minutes, then the precipitate darkened rapidly and finally was almost black in color.

This effect appears to be similar to the induced precipitation of zinc sulfide by copper sulfide in more concentrated acid solutions which has been studied recently by Kolthoff and Pearson.[12] This effect they designate "post-precipitation" and attribute it to an induced precipitation of the zinc sulfide from a supersaturated solution, the induction being caused by adsorption of hydrogen sulfide on the copper sulfide. Under the conditions of certain of their experiments this adsorption became effective in promoting the precipitation of the zinc sulfide only after quantitative precipitation of the copper sulfide had taken place. That the effect obtained

[12] Kolthoff and Pearson, *J. Phys. Chem.*, **36**, 549 (1932).

here is a case of either promoted or of co-precipitation is shown by Expt. 22. This solution, which was identical with that in Expt. 21, but contained 500 mg. of cobalt alone, was saturated with hydrogen sulfide in the usual way, except that the gas was bubbled through for more than an hour; then the flask was closed and allowed to stand for three days. No cobalt sulfide precipitated. Fales and Ware report that cobalt cannot be separated from zinc by hydrogen sulfide precipitation from formic acid–formate solutions. It is of interest to mention that when a few milligrams of cobalt are precipitated with zinc sulfide, as in experiment No. 19, the resulting precipitate is colored green. This phenomenon was noted in a large number of experiments.

Method Recommended for the Precipitation of Zinc Sulfide, and the Separation of Zinc from Nickel, Iron, Manganese, Chromium and Aluminum.—As a result of the above experiments the following procedure is recommended. To a chloride-free solution of the zinc as sulfate in a 500-ml. flask add sodium (or ammonium) sulfate and hydrosulfate (or sulfuric acid) until the hydrosulfate to sulfate ratio is approximately 1:3 with the total concentration of sulfate and hydrosulfate about 0.35 formal.[13] Dilute the solution to 250 ml., heat it to 60°, rapidly bubble hydrogen sulfide through it and continue heating until the solution reaches 90–95°. Continue the passage of hydrogen sulfide until the precipitate settles rapidly, cool the mixture, again saturate it with the gas, close the flask and allow it to stand until the supernatant liquid is clear. Filter the mixture through a quantitative paper filter and wash the precipitate with 0.01 N sulfuric acid saturated with hydrogen sulfide.

If a gravimetric determination is desired, the precipitate is dried and ignited at as low a temperature as possible, care being taken to avoid the formation of zinc oxide. The cold residue is moistened with concentrated sulfuric acid and the excess fumed off on an air-bath. If carbonaceous material remains it is burned off by carefully heating with a Bunsen flame. Again the residue is moistened with sulfuric acid, the excess fumed off on the air-bath, and the precipitate either heated to 500° and weighed as zinc sulfate, or heated to 900° and weighed as zinc oxide. It is recommended that the temperature of the ignition be controlled to ± 20°.

[13] Solutions containing zinc sulfate and an unknown excess of sulfuric acid can be neutralized with standard sodium hydroxide, preferably using methyl red as indicator, then the proper amounts of sulfate and hydrosulfate added. With aluminum present methyl orange should be used as the indicator; before neutralizing the solution ferric salts should be reduced with sulfur dioxide and the excess expelled; in neutralizing highly colored solutions containing large amounts of cobalt or nickel the formation of the first permanent precipitate can be used satisfactorily. With large amounts of the elements, especially of aluminum, account should be taken of the approximate amount of sulfate associated with them. Volatile acids can be removed by gentle fuming with sulfuric acid.

Summary

The precipitation of zinc sulfide from sulfate–hydrosulfate solutions has been studied. The precipitation was found to be complete to less than 0.25 mg. out of 257 mg. at a hydrogen-ion concentration as high as 2.5×10^{-2}. Nickel, iron, manganese, chromium and aluminum may be separated quantitatively from zinc by this sulfide precipitation, but cobalt cannot be so separated. High chloride-ion concentration increases the solubility of the zinc sulfide. A procedure is outlined for the quantitative precipitation of zinc and its separation from the other metals. Methods of igniting the precipitate have been studied. The temperature should be closely controlled at 500° when igniting the zinc sulfate, and at 900° when igniting the sulfate to oxide.

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THE DIRECT PREPARATION OF HYDROGEN PEROXIDE IN A HIGH CONCENTRATION

BY JAMES H. WALTON AND GEORGE W. FILSON

The fact that hydrazobenzene is readily autoxidized with the formation of hydrogen peroxide has been pointed out by Manchot and Herzog.[1] In an investigation carried out in this Laboratory it was found that in an alcoholic solution the reaction is practically quantitative according to the equation

$$C_6H_5NHNHC_6H_5 + O_2 = C_6H_5N{=}NC_6H_5 + H_2O_2$$
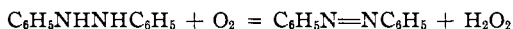
As would be expected a small amount of the alcohol is oxidized by the hydrogen peroxide. The reaction takes place very readily in either ethanol or propanol. By dissolving hydrazobenzene in alcohol and bubbling oxygen through the solution it is possible to follow the speed of reaction by measuring colorimetrically the increasing color of the solution caused by the formation of the azobenzene. The reaction apparently takes place between the dissolved oxygen and the hydrazobenzene, so that in studying the speed of the reaction it is necessary to bubble the oxygen through the solution fast enough to keep the solution saturated. The reaction is bimolecular as evidenced by the following data taken from a series of experiments.

Temp., 30°; 1% solution of hydrazobenzene in 95% C_2H_5OH

t, min.	$a - x$	x	$k \times 10^4$
0	33.1		
16	20.6	12.5	11.4

[1] Manchot and Herzog, *Ann.*, **316**, 331 (1901).