7. In ester decomposition the olefin derivative comes solely from the alkoxy portion of the ester.

8. Ester pyrolysis does not represent a reversed Tischtschenko reaction.

9. The decomposition into acid and olefin by pyrolysis of an organic ester containing hydrogen attached to the β-carbon atom of the alkoxy radical is a general type of reaction.

MONTREAL, CANADA RECEIVED JANUARY 22, 1936

[CONTRIBUTION FROM THE GEOCHEMICAL LABORATORY, ILLINOIS STATE GEOLOGICAL SURVEY]

Formation of Hydrogen Peroxide in the Silver Reductor: A Micro-analytical Method for Iron[1]

BY CHARLES F. FRYLING AND FAY V. TOOLEY

An investigation of the decolorization of silica containing less than 0.1% of ferric oxide indicated the desirability of an accurate and rapid analytical method applicable to small samples. After considering various procedures, that of Walden, Hammett and Edmonds[2] appeared most promising. This method involves reduction of ferric ion in dilute hydrochloric acid by passage over metallic silver followed by titration with standardized ceric sulfate solution using orthophenanthroline–ferrous complex as indicator.

The possibility of applying this method depends primarily on the completeness of reduction of ferric ion to ferrous ion by metallic silver. An idea of the extent of reduction can be obtained from theoretical considerations. The ratio of ferrous–ion concentration to ferric-ion concentration at equilibrium can be calculated by substituting the concentration of silver ions given by the solubility product of silver chloride (S_{Ag}) in the expression for the equilibrium constant (K) of the reaction $Fe^{+++} + Ag = Ag^+ + Fe^{++}$. The numerical values of S_{Ag} and K are commonly recorded as 1.1×10^{-10} and 0.1.

In our analyses, 10 cc. of solution containing approximately 0.0015 g. of ferric ion was diluted to 50 cc. with N hydrochloric acid and passed through the reductor. The concentration of chloride ion $[Cl^-]$ was therefore 0.8 M and the initial concentration of ferric ion $[Fe^{+++}]_i$ was 5.38×10^{-4} M. Using the solubility product gives a value of 1.38×10^{-10} for the concentration of silver ion. To simplify the calculation it is accurate to assume that the equilibrium ferrous-ion concentration $[Fe^{++}]$ is equal to the initial concentration of ferric ion. The equilibrium concentration of ferric ion $[Fe^{+++}]$ is therefore calculated as 7.4×10^{-13} and the equilibrium ratio, $[Fe^{++}]/[Fe^{+++}]$, is 7×10^8. Since it seems unlikely that significant errors are introduced by neglecting the activities of Ag^+ and Cl^- in the solubility product, the reduction can be considered as proceeding to completion.

First attempts to apply this method employing 0.01 N ceric sulfate solution and a micro buret to samples containing 1.5 mg. of iron (about one-tenth the quantity studied by Walden, *et al.*) yielded exceedingly discordant results. It was found that these discrepancies could be eliminated by applying two corrections: one for the indicator, and, due to the formation of hydrogen peroxide, a reductor correction, which must be reduced to as low a value as possible.

The Indicator Correction

When titrating 1.5 mg. of iron, approximately 5% of the 0.01 N ceric sulfate solution is required to oxidize the indicator from the red to the blue modification. It is therefore necessary to determine the titer[3] of the indicator accurately and to subtract this correction from the titer of the iron solution.

In order to determine this correction, the 0.025 M indicator was diluted to 0.0005 M. Titrations were conducted on measured volumes of the diluted indicator in 100 cc. of 1 N hydrochloric acid. The curve obtained by plotting volume of indicator against its titer (cc. of standardized 0.01 N ceric sulfate) is linear, intersects the origin and the experimental points lie on the theoretical curve drawn for a 0.0005 M solution (Fig. 1). This latter correspondence was unexpected, for

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[1] Published with the permission of the Chief, Illinois State Geological Survey, Urbana, Ill.

[2] Walden, Hammett and Edmonds, THIS JOURNAL, **56**, 350 (1934).

[3] Throughout this paper the term "titer" is used to indicate the volume of standardized solution required for titration.

the results of Walden, Hammett and Chapman[4] indicated that the color change should occur at points corresponding to 90% oxidation of the indicator.

The experimental results were very constant, the average deviation being ±0.002 cc. for the indicator concentrations tested. As the result of these tests a standard procedure for using the indicator was adopted. Two cc. of 0.0005 *M* indicator was added from a pipet to the solution being titrated. The titer of this amount of indicator was 0.096 cc. of 0.01014 *N* ceric sulfate.

It can be demonstrated mathematically that, if Beer's law holds for both color modifications of orthophenanthroline, if both exhibit approximately the same molecular weight (*i. e.*, one form is not a polymer of the other), and if the colors of the two modifications are approximately complementary, the ratio of the concentrations of the two forms at the end-point is a constant which is independent of dilution. The results shown in Fig. 1 are in accord with this theory.

It is interesting that values from 2 to 6 times the theoretical were obtained by titrating the indicator in distilled water. In the presence of ions contributed by cerous sulfate, ferric sulfate and hydrochloric acid end-points in agreement with theory were obtained.

After titration, a tendency for the return of the red indicator color frequently was noted. Experimentally it was found that the addition of cerous sulfate to the solution being titrated retarded the disappearance of the end-point; but in most cases the numerical results obtained were identical with those obtained in its absence, and the use of excess cerous sulfate was usually unnecessary.[5]

The Reductor Correction

The titers of 1 *N* hydrochloric acid blanks after passage through the reductor were variable and higher than the indicator titer, thus revealing the formation of a substance (or substances) oxidizable by ceric sulfate. It was found that repeated passages through the reductor increased the concentration of the interfering substance sufficiently to yield qualitative tests for hydrogen peroxide. A yellow color was developed by titanic acid, dilute potassium permanganate solutions were decolorized, and iodine was liberated slowly from potassium iodide. The dichromate–ether test was found to be insufficiently sensitive to yield positive results. The potassium iodide test was conducted simultaneously with identical amounts of reagents on two solutions, the unknown, and a solution of hydrogen peroxide adjusted to the same titer as the unknown. The blue starch–iodine color developed slowly and apparently with the same intensity in both solutions throughout the duration of the test. This indication of the equality of the reaction velocity constants for the liberation of iodine by the two substances, hydrogen peroxide and unknown, was considered valid proof of their identity.

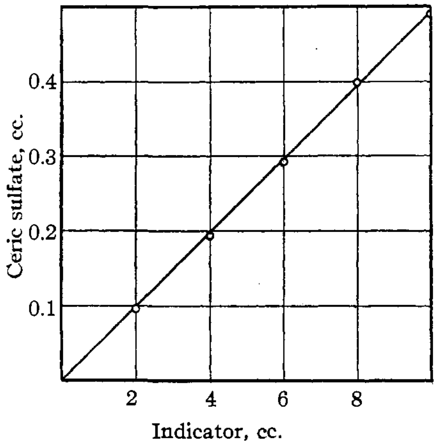

Fig. 1.—Titration of 0.0005 *N* *o*-phenanthroline-ferrous complex with 0.01014 *N* ceric sulfate in *N* hydrochloric acid solution.

The formation of hydrogen peroxide is ascribable to the reduction of atmospheric oxygen by silver in a manner analogous to the reduction of ferric ion to ferrous ion. According to Traube,[6] hydrogen peroxide is always an intermediate product in the reduction of molecular oxygen. That the formation of hydrogen peroxide is thermodynamically possible under the conditions existing within the reductor can be shown by calculation based on the Standard Free Energy Table of Lewis and Randall[7] to yield the following

$$2Ag + O_2 + 2H^+ + 2Cl^- = 2AgCl + H_2O_2\,(aq) \quad \Delta F^0_{298} = -21{,}100$$

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[4] Walden, Hammett and Chapman, THIS JOURNAL, **55**, 2649 (1933).

[5] In the determination of high iron concentrations we have observed that, when fairly large quantities of potassium acid sulfate (4 g.) are used to dissolve the residue obtained after removal of silica with hydrofluoric acid, the disappearance of the end-point becomes troublesome and may introduce error. This can be corrected to some extent either by treatment of the solution with bromine before passing through the silver reductor, or by having an excess of cerous sulfate in the titration. This behavior, however should be investigated more thoroughly.

[6] J. W. Mellor, "Treatise on Inorganic Chemistry," Vol. I, Longmans, Green and Co., London, 1922, p. 923.

[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923.

This equation is tentatively suggested as describing the formation of hydrogen peroxide in the silver reductor.

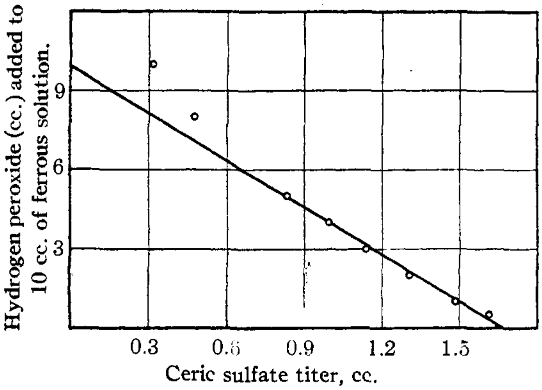

Fig. 2.—Titration of solutions containing ferrous ion and hydrogen peroxide: 0.01014 N ceric sulfate; 10 cc. of ferrous solution ≈ to 1.666 cc. of ceric; 10 cc. of hydrogen peroxide ≈ to 1.679 cc. of ceric.

References to similar examples of formation of hydrogen peroxide are to be found in the literature,[8] but the information is by no means commensurate with the apparent importance of the reaction. The formation of hydrogen peroxide may afford a theoretical explanation for numerous examples[9] of otherwise anomalous reactions of hydrochloric acid, chloride solutions and other reagents on silver. Dunstan, Jowett and Goulding[8c] proposed a general theory of metallic corrosion based on the intermediate formation of hydrogen peroxide. The simultaneous action of oxygen and acids on cadmium amalgam has been developed recently by Müller and Barchmann[10] for the commercial production of 3% hydrogen peroxide. Finally, N. H. Furman and W. M. Murray, Jr.,[11] have independently noted the formation of hydrogen peroxide due to the reduction of oxygen by mercury in contact with hydrochloric acid solutions.

The identification of hydrogen peroxide revealed the source of the largest error in the determination and indicated that the reductor correction should be added to the titer of the reduced solution of the sample being analyzed. This conclusion was substantiated by the results shown in Fig. 2, which presents experimental data on the titration of ferrous ammonium sulfate solution to which varying amounts of hydrogen peroxide were added. The straight line is theoretical (assuming complete reduction of hydrogen peroxide by ferrous ion) being constructed from the titers of the hydrogen peroxide and ferrous solutions which were used. Good agreement of the experimental points with the theoretical curve was obtained for that portion of the curve which is of significance.

However, the addition of a reductor correction obtained on a blank cannot be considered an accurate method of correcting for the formation of hydrogen peroxide. Some of the peroxide formed is undoubtedly reduced within the reductor by ferrous ion and the ferric ion so produced may be reduced subsequently by the silver before leaving the reductor. No method for completely circumventing this difficulty was devised. It was found possible, however, to decrease the reductor correction to an almost negligibly small amount by using an apparatus (Fig. 3) in which atmospheric oxygen was displaced from the solution to be reduced and in which the reduction was conducted in an atmosphere of hydrogen. By this

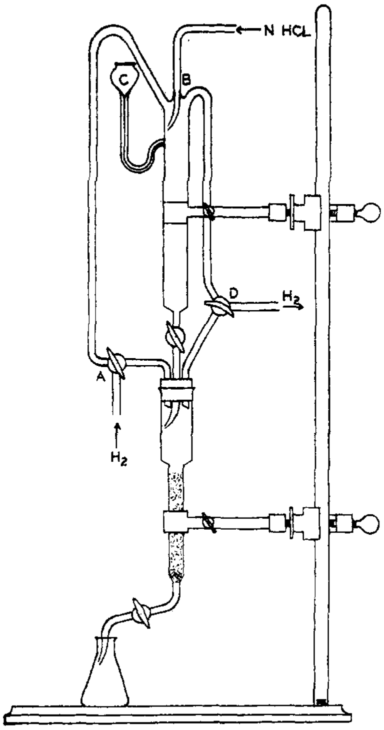

Fig. 3.—Hydrogen saturator and Walden reductor.

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(8) (a) Schoenbein, *J. prakt. Chem.*, **105**, 218 (1868); (b) L. Birckenbach, "Die Untersuchungsmethoden des Wasserstoffperoxydes," Vol. VII. of Die chemische Analyse, Ferdinand Enke, Stuttgart, 1909; (c) Dunstan, Jowett and Goulding, *J. Chem. Soc.*, **87**, 1548–74 (1905).

(9) Ref. 6, Vol. III, 1923, pp. 346–348.

(10) E. Müller and H. Barchmann, *Z. Elektrochem.*, **40**, 188–93 (1934).

(11) N. H. Furman and W. M. Murray, Jr., This Journal, **58**, 429 (1936).

means the reductor correction was decreased from a variable quantity ranging from 0.05–0.5 cc. to approximately 0.015 cc. This latter value was less than 1% of the titer usually obtained in our determinations. The accuracy of this procedure was substantiated by determinations conducted on a standardized ferric ammonium sulfate solution.

It was observed on blanks consisting of normal hydrochloric acid that the magnitude of the reductor correction is also a function of the rate at which the solution is passed over the silver. Slow passage favors the formation of increased amounts of hydrogen peroxide. The correction of 0.015 cc. obtained using hydrogen is attributed to incomplete removal of atmospheric oxygen. If this assumption is correct, an explanation is furnished for the fact that after a number of determinations, the reductor correction tends to increase even when the reduction is conducted in an atmosphere of hydrogen. The correction can be decreased again by washing the silver with a dilute solution of ammonium hydroxide, thus dissolving the silver chloride which accumulates on the silver. This suggests that the formation of hydrogen peroxide is catalyzed by one of its reaction products, possibly at the solid–solid interface of silver and silver chloride.

In conclusion it has been found necessary, in order to secure satisfactory analytical results, to determine the reductor correction after each determination of iron and to add to the titer of the sample. This precaution indicates the sufficiency of removal of oxygen and keeps a constant check on the condition of the silver reductor.

Materials.—Anhydrous ceric sulfate was dissolved in dilute sulfuric acid and diluted to yield approx. 0.01 *N* ceric sulfate. C. P. hydrated ferric ammonium sulfate and 112 cc. of concd. sulfuric acid were dissolved in distilled water to yield 10 liters of 0.1 *N* Fe^{+++} solution. This latter was standardized gravimetrically and diluted to concentrations desired. Solutions of ferrous ammonium sulfate were prepared as needed. Orthophenanthroline-ferrous complex was prepared according to the directions of Walden, Hammett and Chapman[4] and diluted to exactly 0.0005 *M*. Hydrogen, taken from a cylinder, was passed through two wash bottles containing alkaline pyrogallol.

Apparatus.—Calibration of analytical equipment showed it to be well within the limits of accuracy required. A 5-cc. capacity microburet, of commercial design, subdivided to 0.01 cc. and readable by interpolation to 0.001 cc., was used for titrating with the standardized ceric sulfate solution. End-points were judged in the illumination of a blue daylight lamp.

The reductor, constructed according to the directions of Walden, Hammett and Edmonds,[3] was closed by a rubber stopper through which were inserted a hydrogen inlet, a hydrogen outlet and the outlet from the hydrogen saturator (Fig. 3). This latter consisted of a 28-mm. diameter glass tube, 22 cm. long with a capacity somewhat in excess of 60 cc. To the top of the hydrogen saturator were sealed inlet and outlet tubes for hydrogen. A tube for introducing hydrogen-saturated normal hydrochloric acid from a 10-liter stock bottle was led into the top through a ring seal. The sample was introduced through the side arm which consisted of a thistle tube with a capillary stem bent to form a trap. Each of the other tubes through which liquids were introduced into the saturator and reductor was drawn out to a nozzle and directed against the glass walls to minimize splashing.

Hydrofluoric acid volatilizations were conducted in small platinum crucibles heated on a hot-plate which consisted of a sheet of brass, about 30 cm. square and 3 mm. thick. By polishing with emery cloth before using it was possible to detect any splattering which might occur. The temperature of the hot-plate was controlled by the aid of a mercury thermometer, the bulb of which was inserted in a small block of brass which stood on the hot-plate.

Standardizations.—The ferric ammonium sulfate solution was standardized gravimetrically using both ammonia and cupferron as precipitating agents.

TABLE I

STANDARDIZATION OF FERRIC AMMONIUM SULFATE

Ppt. agent	G. Fe_2O_3 equiv./25 cc.	Normality
Ammonia	0.1941	0.0972
Ammonia	.1934	.0969
Cupferron	.1945	.0974
Cupferron	.1941	.0972
Av. =	0.1940 ± 0.0003	0.0972 ± 0.0001

A slight variation of the method of Walden, Hammett and Chapman[4] employing Bureau of Standards sodium oxalate with ferrous ammonium sulfate was used for standardizing the ceric sulfate solution. Sodium oxalate (0.6700 g.) was dissolved and diluted to 1 liter to yield a 0.01 *N* solution. To 50 cc. of ceric sulfate solution were added 25 cc. of the 0.01 *N* sodium oxalate, 6 cc. of concd. sulfuric acid, and 2 cc. of 0.0005 *M* ortho-phenanthroline indicator. This was titrated with approx. 0.01 *N* ferrous ammonium sulfate, the equivalence of which in terms of the ceric sulfate solution had been determined previously.

TABLE II

STANDARDIZATION OF CERIC SULFATE

Normality	G. Fe_2O_3 equiv. per cc.
0.01015	0.0008101
.01013	.0008085
.01013	.0008088
.01013	.0008085
.01015	.0008104
.01015	.0008101
Av. 0.01014 ± 0.00001	0.0008094

Analysis of Standardized Ferric Ammonium Sulfate Solution.—Twenty-five cc. of standardized ferric ammonium sulfate was diluted accurately to a liter to furnish a solution containing 1940×10^{-7} g. of ferric oxide equivalent per cc. The reductor and saturator were thoroughly flushed with hydrogen and a blank determination on 80 cc. of *N* hydrochloric acid was made in order to be assured that the reductor correction was sufficiently low. Ten cc. of the diluted standardized ferric ammonium sulfate was introduced from a pipet into the saturator, followed by about 20 cc. of *N* hydrochloric acid added in successive portions to wash out the side arm. Atmospheric oxygen was displaced by turning the stopcocks so that hydrogen entered the reductor and bubbled through the sample contained in the saturator for eight minutes. The sample was then introduced into the reductor by turning stopcock A (Fig. 3) so that the hydrogen entered the top of the saturator and the pressure in the reductor and saturator was equalized. Passage through the reductor was permitted at the rate of 2–3 drops per second, the sample being received in a 300-cc. Erlenmeyer flask. Eighty cc. of *N* hydrochloric acid previously saturated with hydrogen was then introduced in successive portions through B to wash out the reductor and saturator. Two cc. of 0.0005 *M* indicator was added to the sample prior to titration with the 0.01014 *N* ceric sulfate. While conducting the titration, the blank for the reductor correction was passed through the apparatus.

Experimental results are presented in Table III.

TABLE III

ANALYSIS OF STANDARDIZED FERRIC AMMONIUM SULFATE

INDICATOR CORRECTION = 0.096 CC.

Titer	Reductor blank[a]	Corrected titer[b]	Fe_2O_3 equiv. per cc. $\times 10^7$	Dev.
2.474	0.114	2.396	1939	1
2.475	.111	2.394	1938	2
2.465	.110	2.383	1929	11
2.470	.110	2.388	1933	7
2.469	.110	2.387	1932	8
2.487	.124	2.419	1958	18
2.478	.114	2.400	1943	3
2.475	.111	2.394	1938	2
2.474	.111	2.393	1937	3
2.483	.112	2.403	1945	5
2.498	.114	2.420	1959	19
2.460	.119	2.387	1932	8
	Averages	2.397	1940 ±	7

[a] Reductor blank = indicator correction + reductor correction.

[b] The corrected titer is calculated by subtracting the indicator correction from the titer and adding to this result the difference between the reductor blank and the indicator correction.

The concordance of individual values with the average appears to be satisfactory. The exact agreement of the average with the results of the gravimetric standardization is purely accidental; if the two highest results are excluded a value of 1937×10^{-7} is obtained.

Analysis of Bureau of Standards Glass Sand No. 81.—It was considered that analysis of Bureau of Standards glass sand No. 81, the ferric oxide content of which is known with a high degree of accuracy, would constitute as thorough a test as could be applied. At the same time this procedure emphasized certain practical advantages of the method.

A 25-g. portion of sample was ground in an agate mortar to pass completely through 96-mesh bolting cloth. This was dried overnight at 105° and thoroughly mixed by two to three hours of rotation in a 225-cc. bottle on a mixing wheel. Six samples of exactly 2 g. each were then weighed into thoroughly cleaned 30-cc. platinum crucibles. The samples were moistened with 1 cc. of water followed by 5 cc. of hydrofluoric acid. They were held at a low temperature until frothing ceased. When necessary, frothing was controlled by addition of small amounts of water from a wash bottle. Eleven cubic centimeters of hydrofluoric acid and 1 cc. of 1–1 sulfuric acid were then added and evaporated to sulfuric acid fumes with the hot plate at 150–170°. After cooling, 20 cc. of water was added and again evaporated to fumes. The solutions were cooled, taken up in hot water and filtered through Whatman No. 42 paper. After washing, the filter papers were returned to their corresponding crucibles, dried and ignited. The residues were fused with 0.2 g. of sodium carbonate, cooled and dissolved with minimum quantities of hot 1–5 sulfuric acid. These were filtered with washing through Whatman No. 42 papers into the main solutions. The papers were again returned to their corresponding crucibles, dried, ignited, the residues fused with 0.2 g. of potassium bisulfate and the fusions returned to the main solutions as before. To the combined filtrates were added 25-cc. portions of *N* hydrochloric acid and a few drops of bromine water. These were evaporated to approximately 10 cc. and introduced into the hydrogen saturator. They were subsequently treated as described in the previous section. In addition, a correction for the iron in the reagents was obtained by burning two samples of 10 filter papers each to ash and treating in an analogous manner with five

TABLE IV

ANALYSIS OF BUREAU OF STANDARDS GLASS SAND NO. 81

Fe_2O_3 content, 0.0724%. Indicator correction, 0.096 cc.

	Reagent Correction		
Titer	Reductor blank	Corrected titer	Reagent correction
0.286	0.128	0.222	0.044
.338	.109	.255	.051
		Av.	.048

Crucible No.	Titer	Reductor blank	Corrected titer	% Fe_2O_3	Dev.
12	1.927	0.113	1.800	0.0728	0.0001
13	1.961	.111	1.832	.0741	.0012
16	1.896	.133	1.789	.0724	.0005
17	1.920	.112	1.792	.0725	.0004
18	1.886	.117	1.763	.0713	.0016
19	1.965	.110	1.835	.0743	.0014
			Av.	0.0729	±0.0009

times the quantity of reagents used above. These were carried through the reductor and their final corrected titers divided by 5. This figure, called the reagent correction, was added to the indicator correction, the combined value of which was subtracted from the glass sand titers.

The numerical results secured by this method compare favorably with those obtained by the Bureau of Standards using the gravimetric method described in the certificate of standardization. The method possesses advantages of speed and low cost, due to the elimination of the precipitation of iron, and the fact that, working with 2-g. samples, it is possible to use 30-cc. crucibles in place of liter platinum dishes. For practical work it is possible to shorten the procedure still further by elimination of one ignition without sacrificing undue accuracy.

The authors are grateful to Dr. Orin W. Rees for coöperation and helpful suggestions and to Mr. L. D. McVickers for gravimetric standardization of the ferric ammonium sulfate solution.

Summary

1. An attempt to determine small quantities of iron by reduction with silver followed by titration with ceric sulfate revealed an error attributable to the formation of hydrogen peroxide in the reductor.

2. By conducting the reduction in an atmosphere of hydrogen, thereby decreasing the reductor correction, and applying a correction for the indicator, it was possible to determine quantities of iron of the order of 1.5 mg. with a high degree of accuracy.

3. The method was found to be relatively rapid and not to require the use of large platinum dishes, thus possessing advantages of practical value.

URBANA, ILLINOIS RECEIVED NOVEMBER 4, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Hydrogen Sulfide. The Heat Capacity and Vapor Pressure of Solid and Liquid. The Heat of Vaporization. A Comparison of Thermodynamic and Spectroscopic Values of the Entropy

BY W. F. GIAUQUE AND R. W. BLUE[1]

The entropy of hydrogen sulfide as determined by means of the third law of thermodynamics is of special interest since it has been shown[2] that the ordinary application of this method does not give the correct entropy for the analogous and important case of water. However, the low temperature calorimetric investigation reported here proves that the $\int_0^T C_p \, d \ln T$ does give the correct entropy for hydrogen sulfide. The correct value has been calculated by Cross[3] from the band spectrum data of this substance.

The calorimetric apparatus and methods were identical with those described in our paper[4] on nitrous oxide except that the amounts of hydrogen sulfide were measured by absorbing the gas in alkali and observing the increase in weight. This latter procedure is the same as that followed by Giauque and Wiebe.[5]

Preparation of Pure Hydrogen Sulfide.—Hydrogen sulfide was prepared by direct combination of the elements. Dry electrolytic hydrogen which had been freed from oxygen by means of a nickel catalyst and sulfur which was shown by analysis to contain no trace of selenium were used. The hydrogen was bubbled through liquid sulfur at 275–300°. This temperature range ensured the presence of a large excess of hydrogen in the resulting mixture. The mixed gases were passed over a nickel catalyst on pumice at 600°. The nickel catalyst may be superfluous but it was readily available and was included because of its effectiveness in the analogous reaction between hydrogen and oxygen. In the preliminary preparations the hydrogen sulfide contained considerable impurity which was undoubtedly hydrogen polysulfide. While this condition may have been due to faulty operation of the above system, it was very satisfactorily eliminated by passing the gas, prepared as above, through a quartz tube, filled with pumice, and heated to 800°. After the furnace temperatures became constant the gaseous mixture was passed through the preparation system for half an hour before any hydrogen sulfide was collected. A large trap in the preparation line was then cooled with liquid air[6] and the hydrogen sulfide was collected as the solid. About 200 cc. of liquid hydrogen sulfide was prepared in twenty-four hours. The effective length of the tube at 600° was about 100 cm., that at 800° was about 30 cm. and the diameters were roughly 2 cm.

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[1] Shell Research Fellow, Academic year 1931–1932.

[2] Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

[3] Cross, *J. Chem. Phys.*, **3**, 168 (1935).

[4] Blue and Giauque, THIS JOURNAL, **57**, 991 (1935).

[5] Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

[6] In condensing materials of this sort in glass containers immersed in liquid air we consider it advisable to surround the glass by a close fitting easily removable case of thin metal. This is to prevent the formation of a potentially explosive mixture in case of accidental glass breakage.