cupric sulfate pentadeuterate to trideuterate, of strontium chloride hexadeuterate to dideuterate and dideuterate to monodeuterate. These values are compared with the corresponding values in ordinary water.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Stability of Solutions of Trivalent Columbium in Sulfuric Acid

BY SAMUEL J. KIEHL, ROBERT L. FOX AND HENRY B. HARDT

The reduction of pentavalent columbium to trivalent columbium furnishes the basis for a number of analytical methods[1] for the determination of columbium. In these methods complete reductions were accomplished in various ways and the amounts of columbium determined by an oxidimetric titration. A complete reduction was secured electrolytically at a mercury cathode[2] and the oxidation–reduction potentials of the oxidant–reductant system determined.[2] In the course of these reductions, moreover, depending upon the concentration of sulfuric acid, the color of the solutions varied from a light blue to a reddish-brown, to a brown. From such solutions many attempts have been made to separate compounds, among the most successful of which were those of Ott,[3] who prepared a red crystalline substance to which the possible formula, $Cb_2(SO_4)_3\cdot(NH_4)_2SO_4\cdot H_2SO_4\cdot 6H_2O$, was given. It, moreover, was shown that the color disappeared upon dilution and that in the colored solutions the columbium was upon an oxidation level of three.[2] During attempts to separate compounds, it was discovered that the colored solutions became clear upon standing in an atmosphere of hydrogen sometimes with and sometimes without a deposit of the white hydrated columbic oxide. All the reduced solutions are unstable. Hydrogen is evolved during the change.

An account of a study of the conditions which affect the stability of the solutions and of pressure developed during the change, at constant volume and constant temperature of the gas hydrogen, which was confirmed by test and analysis, is given below.

Preparation of Materials

Columbic Oxide Solutions.—Columbic oxide of a very high degree of purity was dissolved in hot concentrated sulfuric acid. This solution, upon cooling, was diluted to 1 *M* with respect to sulfuric acid and heated at 100° for twelve hours. During this treatment, a white flocculent precipitate of hydrated columbic oxide formed, which was separated and washed by centrifuging. The purified oxide was then dissolved in concentrated sulfuric acid and diluted to the desired acid and columbium concentrations. During the dilution, the temperature was not allowed to rise above 20°.

Mercury.—The mercury was distilled as recommended by Hulett,[4] washed in a tower containing dilute nitric acid according to the method of Hildebrand[5] and finally in a tower of distilled water.

Hydrogen.—Commercial electrolytic hydrogen was used. Whatever impurities it contained were removed so far as possible by passing it successively over heated copper gauze, through soda lime, cotton, and finally through 9 *M* sulfuric acid. To avoid contamination with oxygen, all joints were glass seals except the rubber tubing connecting the bottles containing the solutions, the piece in the pressure apparatus and two pieces near the reduction apparatus, where flexibility was required. Pressure rubber tubing treated with castor oil, and covered with either "Picëin" a commercial wax, or shellac was used.

Nitrogen.—The purification of the nitrogen was accomplished by two Van Brunt[6] towers, modified as described by Cowperthwaite and La Mer,[7] in one the nitrogen was passed over closely packed spirals made of copper wire, wet with an ammoniacal solution of ammonium carbonate; in the other, over pieces of glass wet with sulfuric acid. Finally the gas was passed through a tube loosely packed with cotton.

The other chemicals used—the sulfuric acid, potassium permanganate, ferrous ammonium sulfate, the potassium bisulfate, ammonium hydroxide, acetone, and ether—were of the highest purity obtainable.

Apparatus

Baths.—To maintain constant temperatures of 30, 45 and 60°, three thermo-regulated[8] baths were employed, the one at 30° within ± 0.01°, the next at 45° within ±0.05°, and the last, which was filled with oil, at 60° well within ±0.5°.

Reduction Apparatus.—Figure 1, A, B, C, shows a modification of the apparatus used by Kiehl and Hart.[2] There are three parts, A, B, C, all united by means of

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[1] Osborne, *Am. J. Sci.*, [3] **30**, 328 (1885); Levy, *Analyst*, **40**, 204 (1905); Giles, *Chem. News*, **95**, 1 (1907); **99**, 1 (1909); Metzger and Taylor, *J. Soc. Chem. Ind.*, **28**, 818 (1909); Schwartz, *Z. angew. Chem.*, **46**, 552 (1933).

[2] (a) Kiehl and Hart, THIS JOURNAL, **50**, 1608 (1928); (b) Kiehl and Hart, *ibid.*, **50**, 2337 (1928).

[3] Ott, *Z. Elektrochem.*, **18**, 349 (1912).

[4] Hulett, *Z. physik. Chem.*, **33**, 611 (1900).

[5] Hildebrand, THIS JOURNAL, **30**, 1672 (1908).

[6] Van Brunt, *ibid.*, **36**, 1448 (1914).

[7] Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

[8] D. J. and J. J. Beaver, *Ind. Eng. Chem.*, **115**, 359 (1923).

ground glass connections. Part A, with a capacity of 1200 cc., was the cathode compartment. There was a large cross sectional area to afford a mercury cathode surface of about 180 sq. cm. A tungsten wire of large capacity was sealed into the tube at the bottom. This tube, provided with a stopcock, served to drain the mercury, and to collect the crystals that settled to the bottom of the solution during some of the experiments. Through the ground-glass stopper, which fitted the top of the cell, were two tubes, one to admit hydrogen or to liberate the excess through a water seal, the other to deliver the reduced solution to a buret by the pressure.

Part C acted as a bridge to connect A with B, the anode compartment. At each end of C was sealed a "Fritted Glass" plate, 3 cm. in diameter and of No. 5 porosity. C was provided with a ground-glass stopper for filling the compartment and liberating gas bubbles.

Part B, the anode compartment, was 4 cm. in diameter and had a capacity of 235 cc. The anode was a platinum gauze.

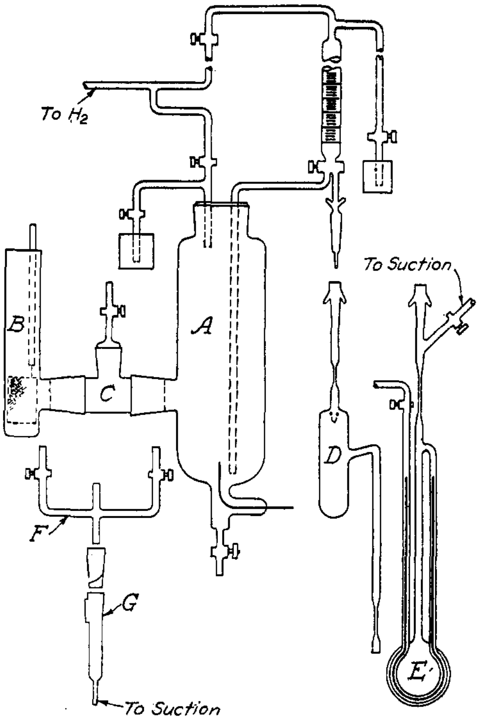

Fig. 1.

The Individual Reaction Cells.—These cells, Fig. 1, D. were made to contain aliquot parts of the reduced solution. Two glass tubes, one to connect to the buret, the other to a water seal, were sealed to the cell. These tubes were constricted for sealing near their ends.

Vessels for Measuring Pressure of Gas Generated at Constant Volume.—This apparatus, Fig. 1, E, was a 125-cc. round-bottomed flask, to which was sealed a mercury-filled capillary differential manometer and tubing for buret and suction connections.

Weighing Bottles.—A Jena Glass Microfilter, type 12G4, with a "Fritted Glass" disk 10 mm. in diameter, was adapted to serve as a weighing bottle, Fig. 1, G. In order to keep the substance in an atmosphere of hydrogen, a ground glass connection was constructed to fulfill the double purpose—as stopper and a stopcock.

Method of Procedure.—The solutions of trivalent columbium were prepared in the reduction apparatus (Fig. 1, A, B, C). Parts A and C contained the solution of columbium pentoxide in sulfuric acid. Sulfuric acid of the same concentration as in A and C filled B to the same level as A. Mercury filled the bottom of A to a point of maximum diameter. A current density of 12.5 m. a./sq. cm. was maintained in all reductions. Aliquot portions of the solution after reduction were measured by the attached buret into the individual reaction cells (Fig. 1, D), which were swept by hydrogen. The cells were then sealed with a small flame at the constrictions in the arms, and seven or more placed in each bath. Analyses for total columbium in the reduced solutions were made in the following manner.

Analysis for Total Columbium.—A measured sample of the reduced solution was oxidized with hydrogen peroxide and evaporated almost to dryness at 110°. This solution was then diluted and the hydrated columbic oxide precipitated with ammonium hydroxide and transferred to a Gooch crucible, where it was washed, ignited and weighed as Cb_2O_5.

Analysis for Trivalent Columbium. (A) To Determine the Extent of Reduction.—A sample of the reduced solution was measured into a bottle containing a known volume of an acidified standard solution of potassium permanganate, through which nitrogen had been bubbled. An excess of standard solution of ferrous ammonium sulfate was then added, and the surplus determined with the standard solution of potassium permanganate.

(B) To Determine Progress of Oxidation.—At intervals of several days, an individual reaction cell was removed from a bath, the tip of the lower arm broken beneath the surface of a portion of the standard solution of potassium permanganate which was drawn in excess into the cell by suction applied through the upper arm, the tip of which had been broken under reduced pressure. The solutions were then washed into a beaker and ferrous ammonium sulfate added, the excess of which was determined as before.

The Measurement of the Pressure of the System at Constant Volume.—The pressure apparatus, Fig. 1, E, contained a small piece of platinum with a deposit of platinum black. It was covered with sulfuric acid of the same concentration as that in the reduced solution. The system was evacuated and filled with hydrogen several times, and again evacuated and a measured volume of the reduced solution added. The apparatus was then sealed at the constriction, and placed in the bath. The progress of the oxidation was ascertained at intervals of several days by connecting it to a manometer and measuring the pressure necessary to maintain constant volume. At the completion of the reaction, the volume occupied by the gas was determined by weighing the distilled water required to fill the apparatus.

Analysis of the Crystals Containing the Reduced Columbium.—The crystals which appeared upon the surface of the mercury during the reduction of some of the solutions, were drained into the suitably prepared weighing bottle, Fig. 1, G, after the removal of the mercury. The supernatant solution was removed by suction and the crystals were washed with a mixture of acetone and sulfuric acid of the same concentration as the reduced solution, and then with several portions each of acetone and of ether. Throughout the complete operation, a slight pressure of hydrogen was maintained on one side and suction on the other. After the crystals had been dried in a stream of hydrogen, the weighing bottle was closed, removed and weighed. The weight of the bottle filled with hydrogen was known, so that the weight of the crystals could be ascertained. Both trivalent columbium and total columbium in the crystals were determined as previously described. The filtrates from the total columbium determinations were analyzed for both potassium and sulfate. Potassium was determined by evaporating the filtrate and weighing the residue as K_2SO_4 by the method described by Treadwell and Hall.[9]

Experimental Data

In determining the stability of solutions of trivalent columbium in sulfuric acid it was deemed unnecessary to attain complete reduction. The extent to which the pentavalent columbium had been reduced was determined in each case so that the effect at different stages of reduction could be ascertained. The rate of reaction was taken as a criterion of stability when solutions differing in concentration in respect both to columbium and to sulfuric acid were caused to remain in the bottles at temperatures of 30, 45 and 60°.

TABLE I

THE EFFECT OF CONCENTRATION OF TRIVALENT COLUMBIUM IN SOLUTIONS OF SULFURIC ACID ON THE REACTION AT 30, 45 AND 60°

H_2SO_4, *M*	°C.	Total Cb_2O_5, *M*	Change Cb^{III} to Cb^{V}, %	Time, days
2.96	30	0.00452	81.3–76.4	69
2.43		.00676	78.0–73.4	69
2.96	45	.00452	81.3–70.5	69
2.43		.00676	78.0–69.6	69
2.96	60	.00452	83.6–58.7	69
2.43		.00676	78.0–54.4	69
5.16	30	.00288	95.0–87.6	69
5.91		.00518	96.5–86.8	69
5.79		.00741	88.4–81.0	69
5.16	45	.00288	95.0–84.0	69
5.91		.00518	100.0–88.0	69
5.79		.00741	100.0–90.0	69
5.16	60	.00288	95.0–67.6	69
5.79		.00741	88.3–60.8	69
5.86		.01137	100.0–72.8	69
7.90	30	.00414	96.6–71.0	69
9.29		.00605	55.1–50.8	69
9.11		.01255	66.2–59.2	69
7.90	45	.00414	96.6–57.0	69
9.29		.00605	46.8–38.8	69
9.11		.01255	67.0–51.0	69
8.95	60	.00467	82.1–26.4	69
8.91		.00732	93.3–37.0	69
8.40		.01588	74.0–43.7	69

TABLE II

THE EFFECT OF PLATINUM BLACK AS A CATALYST, OF TEMPERATURE, AND OF CONCENTRATION OF SULFURIC ACID ON THE OXIDATION OF SOLUTIONS OF TRIVALENT COLUMBIUM IN SULFURIC ACID BY HYDROGEN ION

Approx.			Catalyzed	Uncatalyzed
3 *M* H_2SO_4	45°	46% Theoretical change	4.6 days	213 days
9 *M* H_2SO_4	60°		2.0 days	14 days

TABLE III

STUDY OF THE EVOLUTION OF HYDROGEN BY MEASURING PRESSURE DEVELOPED AT CONSTANT VOLUME

Sample No. 1

Approx. 3 *M* H_2SO_4 45°
0.0585 g. Cb^{III} in 77.58 cc.
25.91 cc. constant gas volume
0.0585 g. Cb^{III} ≡ 15.36 cc. H_2 at 22.5°
751 mm. pressure.

Days	Pressure at 22.5°, mm.	Calcd. vol. increase, cc.	Theor. complete vol., %
0	751	0	0
5	854	3.6	23.1
10	981	7.9	51.7
14	1099	12.0	78.1
22	1177	14.7	95.6
27	1157	14.0	91.2
31	1170	14.5	94.1

Sample No. 2

Approx. 3 *M* H_2SO_4 45°
0.0577 g. Cb^{III} in 76.58 cc.
32.23 cc. constant gas volume.
0.0577 g. Cb^{III} ≡ 10.66 cc. at 25.5°, 767 mm. pressure.

	At 25.5°, mm.		
0	767	0	0
4	918	6.3	42.2
9	1045	11.7	77.7
13	1081	13.2	87.6
31	1079	13.1	87.6

Sample No. 3

Approx. 3*M* H_2SO_4 60°
0.0584 g. Cb^{III} in 77.50 cc.
37.1 cc. constant gas volume
0.0584 g. Cb^{III} ≡ 15.04 cc. H_2 at 28°, 781 mm. pressure.

	At 24°, mm.		
0	773	0	0
2	995	10.6	71.0
4	1017	11.3	75.2

Sample No. 4

Approx. 9 *M* H_2SO_4 60°
0.474 g. Cb^{III} in 77.6 cc.
36.71 cc. constant gas volume
0.474 g. Cb^{III} ≡ 123.3 cc. H_2 at 25°, 766 mm. pressure.

	At 25.0°, mm.		
0	766	0	0
1	1516	35.9	29.1
2	1784	48.8	39.2
3	2515	83.7	67.7

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[9] Treadwell and Hall, "Analytical Chemistry," Vol. II, J. Wiley and Sons, Inc., New York, 1928, p. 57.

A summary of the results, a complete tabulation of which may be found elsewhere,[10] obtained by graphical interpolation for a period, in each case of sixty-nine days, is given in Table I. In Table II the effect of platinum black is compared with the effect when the reaction is uncatalyzed. Table III contains pressures developed by the evolution of hydrogen. Analytical data determined for compounds are to be found elsewhere.[10]

Qualitative migration experiments were performed to determine the charge on the colored radical in the variously colored solutions of trivalent columbium in 3, 6, and 9 *M* sulfuric acid. In all cases the colored radical migrated toward the anode.

Discussion of Errors

1. The errors in sampling and analyzing the reduced solutions, determined by results from several analyses of the same solution, were not greater than plus or minus two parts per hundred. This is the largest error involved in all analytical operations which were used to determine the extent of reduction and subsequent oxidation. The precision in weighing and titrating is much greater.

2. A comparison of the results of pressure measurements on duplicate samples of the same reduced solution indicated an error of plus or minus five parts per hundred. It is believed that the effectiveness of the platinum black was inhibited by the deposit of columbic oxide which was formed upon it during the reaction.

3. In determining the composition of the crystals, the average deviation in the determination of trivalent columbium in six analyses was 0.7 part in 100; in the determination of total columbium in twelve analyses, 2.5 parts in 100; in the determination of potassium in 8 analyses, 2 parts in 100; in the determination of sulfate in 5 analyses, 2.5 parts in 100; in the determination of water in 2 analyses, 2 parts in 100. Therefore, the greatest error involved was plus or minus 2.5 per cent. The deviation based upon the empirical formulas obtained from the oxides was 2% below the theoretical value.

Discussion

The instability of trivalent columbium in sulfuric acid solutions in an atmosphere of nitrogen is indicated by a loss of color and at times a deposit of columbic oxide. The change is accompanied by an evolution of hydrogen. Samples of this gas when mixed with oxygen exploded upon ignition and failed to show the presence of hydrogen sulfide or sulfur dioxide, reduction products of sulfuric acid. Consequently by elimination and confirmatory tests hydrogen ion is the oxidizing agent and the reaction may be expressed by the equation

$$\mathrm{Cb^{III}} + 2\mathrm{H^+} \rightleftarrows \mathrm{Cb^{V}} + \mathrm{H_2}$$

Examples of similar reactions found in the literature, in which hydrogen ion acts as an oxidizing agent, are

$$2\mathrm{Cr^{+++}} + 2\mathrm{H^+} \rightleftarrows 2\mathrm{Cr^{+++}} + \mathrm{H_2}$$
$$2\mathrm{Co(CN)_6^{----}} + 2\mathrm{H^+} \rightleftarrows 2\mathrm{Co(CN)_6^{---}} + \mathrm{H_2},$$

the catalytic effect of platinum black upon which was studied by Jablczynski[11] and Manchot and Hertzog,[12] respectively.

The oxidation-reduction potentials of $\mathrm{Cb^V/Cb^{III}}$ from which the molar potentials were calculated, were determined by Hart and one of us.[2] In the different concentrations of sulfuric acid, they are as follows:

H_2SO_4, *M*	E_0 (Molar potential), v.
3.14	−0.3733
5.91	− .3851
9.87	− .4260

In any oxidation-reduction reaction, the oxidizing agent is the one whose oxidation-reduction potential is the more positive. Therefore, since the potential for the $\mathrm{Cb^V/Cb^{III}}$ was determined with respect to the potential for $2\mathrm{H^+/H_2}$ as zero, and since it is negative, it is natural that as a consequence hydrogen ion would serve as the oxidizing agent and that the molecular hydrogen would be liberated. Since also the increase in the concentration of sulfuric acid causes the molar potentials to become more negative, and since the molar potential is the most negative in the 9 *M* solutions of sulfuric acid, the reaction of $\mathrm{Cb^{III}} + 2\mathrm{H^+} \rightleftarrows \mathrm{Cb^V} + \mathrm{H_2}$ will proceed more rapidly as the concentration of sulfuric acid increases.

The oxidation of trivalent columbium by hydrogen ion is a very slow reaction. It is influenced by concentration of trivalent columbium, temperature, catalysis, and concentration of sulfuric acid. According to Hammett[13] and Hammett and Lorch[14] the system $2\mathrm{H^+/H_2}$

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[10] R. L. Fox, Dissertation, submitted in partial fulfilment of the requirements for the degree of doctor of philosophy in the faculty of Pure Science of Columbia University.

[11] Jablczynski, *Z. physik. Chem.*, **64**, 748 (1908).

[12] Manchot and Hertzog, *Ber.*, **33**, 1742 (1900).

[13] Hammett, "Solutions of Electrolytes," McGraw-Hill Book Co., Inc., N. Y., 1929, p. 160; *Trans. Faraday Soc.*, **29**, 7 (1933).

[14] Hammett and Lorch, THIS JOURNAL, **55**, 70 (1933).

reaches equilibrium very slowly unless it is catalyzed, by platinum black, for example. They also believe that this system may be resolved into the two partial equations

$$2H^+ + 2e \rightleftarrows 2H^0$$
$$2H^0 \longrightarrow H_2$$

of which the second is the slower reaction at low overvoltages and is one catalyzed by platinum black. Since it has been shown[2] that the system Cb^V/Cb^{III} reaches equilibrium rapidly, it would seem that the rate of the reaction $Cb^{III} + 2H^+ \rightleftarrows Cb^V + H_2$ is governed largely by the rate of the reaction $2H^0 \rightleftarrows H_2$ unless it is catalyzed. It is the fact that hydrogen ion is reduced more easily than pentavalent columbium at a platinum cathode that made it necessary for us to select mercury, upon which hydrogen has a high overvoltage, to serve as the cathode in the reduction cell.

The rate of the oxidation is greater the greater the percentage of trivalent columbium and over comparable ranges of the percentages of trivalent columbium present, the percentage of trivalent columbium oxidized in a given period of time is approximately the same under the same conditions of temperature and acid concentration.

A rise of temperature increases the rate of the reaction in all cases but comparably much greater in the 9 *M* sulfuric acid.

In comparing effects of varying concentrations of sulfuric acid, effect of change in rate during a variation from 6 molar to 9 molar acid was much more pronounced than the effect of change from 3 molar to 6 molar.

Moreover, marked changes occurred in the physical appearance of the solutions of 3, 6, and 9 *M* sulfuric acid during the reduction to or subsequent oxidation of, trivalent columbium, both as to color and the shape of the crystals that formed. It is believed that these changes in the appearance of the solution are indicative of the formation of different complex compounds in the different concentrations of sulfuric acid, and that the differences in the rates of reaction noticed is partially due to the fact that the complex formed in the 9 *M*, when greatly reduced, is less stable than the ones formed in the 3 and 6 *M* solutions of sulfuric acid.

In the 3 and 6 *M* solutions of sulfuric acid, where the solutions were more concentrated with respect to trivalent columbium, blue crystals appeared in small quantities after the solutions had stood for one hundred and nine days at 60°. Their shape and color were observed with the aid of a microscope. They were in the shape of blue needles and orthorhombic crystals. That they contained trivalent columbium was proved by the fact that in the presence of an excess of potassium permanganate solution, the solid phase became colorless. Migration experiments showed all the colored ions blue as well as brown to be negatively charged.

When solutions of sulfuric acid saturated with columbium pentoxide and potassium hydrogen sulfate were reduced at the mercury cathode, red crystals settled on the surface of the mercury. The crystals formed in the 6 *M* sulfuric acid solutions were hexagonal rods, in the 9 *M* sulfuric acid solution, they were hexagonal plates. The analyses of these crystals indicate that they have the following tentative empirical formulas

From 6 *M* H_2SO_4	$4K_2O{\cdot}2Cb_2O_3{\cdot}Cb_2O_5{\cdot}12H_2SO_4{\cdot}12H_2O$
From 9 *M* H_2SO_4	$4K_2O{\cdot}2Cb_2O_3{\cdot}Cb_2O_5{\cdot}13H_2SO_4{\cdot}16H_2O$

Summary

1. Trivalent columbium in solutions of sulfuric acid is oxidized slowly by hydrogen ion: $Cb^{III} + 2H^+ + \rightleftarrows Cb^V + H_2$.

2. The extent of the uncatalyzed reaction was determined by measuring at varying intervals the concentration of trivalent columbium. The catalytic effect of platinum black on the reaction was determined by measuring the pressure developed at constant volume.

3. Small amounts of two differently shaped blue crystals were observed to appear in the individual reaction cells from the most concentrated solutions of trivalent columbium in 3 and 6 *M* sulfuric acid. Two different forms of red crystals that appeared in sufficient quantities during the reduction of 6 and 9 *M* solutions of sulfuric acid saturated with columbic oxide and potassium hydrogen sulfate, were analyzed and the tentative empirical formulas assigned.

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