I. The Free Energy of Antimony Trioxide and the Reduction Potential of Antimony

II. The Activity of Perchloric Acid in Aqueous Solution

III. The Free Energy and Heat Content of Arsenic Trioxide and the Reduction Potential of Arsenic

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By Reinhardt Schuhmann

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THE FREE ENERGY AND HEAT CONTENT OF ARSENIC TRIOXIDE AND THE REDUCTION POTENTIAL OF ARSENIC

BY REINHARDT SCHUHMANN

RECEIVED APRIL 10, 1924

Purpose of the Research

In a previous article[1] a research was described in which the free energy of antimonous oxide and the reduction potential of antimony were determined with the aid of electromotive-force measurements. The object of the present investigation is to determine in a similar way (1) the change in free energy and heat content of arsenic trioxide when it is formed from its elements, and (2) the reduction potential of arsenic. These quantities were derived from measurements at 25° and 45° of the electromotive force of the cell, As (s) + As_2O_3 (s), $HClO_4$ (0.22–0.94 *M*), H_2 (g). No data are available in the literature relating to arsenic, except the doubtful value of the electrode potential determined by Neumann[2] in 1894.

This investigation was undertaken at the suggestion of Professor A. A. Noyes, to whom I wish to express my indebtedness for many valuable suggestions. It was aided on the financial side from a grant made to him by the Carnegie Institution of Washington.

Preparation of the Materials and of the Arsenic Electrode

The metallic arsenic was prepared by subliming a chemically pure Kahlbaum product in an atmosphere of nitrogen, and condensing the vapors. An electrically heated, horizontal, cylindrical furnace about 30cm. long, open at both ends, was used. A glass tube 15 mm. in diameter was placed in the furnace so as to extend a little beyond it at both ends. A combustion boat containing powdered arsenic was placed in this tube just outside the furnace. While a current of nitrogen was passing the arsenic was heated with a gas burner. The furnace was kept at 305–360°. The current of nitrogen carried the vapors into the furnace; and the metallic arsenic deposited on the walls of the glass tube inside the furnace. After cooling, the arsenic was removed from the walls, finely ground, and placed in a desiccator.

In the case of the arsenic it is important to use some definite allotropic form. Arsenic may be prepared by reduction of the arsenic trioxide by means of reducing agents, or by electrolysis of a fluoride solution; but the product obtained in these ways is not the common metallic form of the element stable at room temperature. Moreover, even when sublimation is employed, the particular form obtained depends on the temperature

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[1] Schuhmann, THIS JOURNAL, **46**, 52 (1924).

[2] Neumann, *Z. physik. Chem.*, **14**, 193 (1894).

of condensation. The metallic arsenic used in this investigation was prepared by condensing the sublimed arsenic vapors at temperatures between 305° and 360°.

The electrode was of spiral form like that used previously in the case of antimony.[3] It was prepared as follows. The glass tube holding the electrode was wrapped with asbestos paper, and inserted by means of a cork stopper within a large test-tube containing some powdered arsenic, so that the spiral was near the bottom of the tube. Nitrogen was passed in through a side arm near the bottom of the tube, and the powdered arsenic was vaporized by heating with a gas burner, so that it deposited on the spiral. By this procedure it is obtained in the metallic form, with a white silvery appearance. The electrode was then placed in the furnace described above, and heated to 310° in a current of nitrogen, as recommended by Kohlschütter,[4] so as to change any small amount of amorphous arsenic deposited on the electrode into the metallic form. The furnace was finally allowed to cool slowly, so as to prevent strains in the deposited arsenic; for otherwise reproducible electromotive forces were not obtained.

In the measurement of the electromotive force of the cell it was found that coating the platinum spiral with metallic arsenic was not sufficient to give a constant reproducible value, but that it was essential that there be also present in the cell finely powdered metallic arsenic. This was also found true in the case of antimony.

The arsenic trioxide was in the octahedral form, which is stable at ordinary temperatures, and was prepared by recrystallizing a pure Kahlbaum product from hydrochloric acid in the manner described by Anderson and Story.[5] After very careful washing to free it from chlorides, it was dried for at least a week in a vacuum desiccator.

The perchloric acid used was obtained from the same source as in the previous investigation,[6] and the solutions were prepared in the same manner. All concentrations are expressed in moles per 1000 g. of water. No density determinations of the perchloric acid solutions were made in this investigation, but the densities may be obtained from the previous values by interpolation.

Apparatus and Methods of Measurement

The apparatus used in measuring the electromotive force of the cell was the same as that used in the investigation on the free energy of antimony trioxide.[3]

The cell was only slightly different from the one used before. Since it was found impossible to get constant and reproducible results when the metallic arsenic was stirred,

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[3] Ref. 1, p. 54.

[4] Kohlschütter, *Ann.*, **400**, 283 (1913). Also Erdmann and Reppert, *Ann.*, **361**, 23 (1908).

[5] Anderson and Story, THIS JOURNAL, **45**, 1102 (1923).

[6] Ref. 1, p. 53.

the stirrer was eliminated from the arsenic half-cell. The hydrogen half-cell and hydrogen generator were the same as those used before.

The solution for the arsenic half-cell was prepared by rotating for 48 hours a mixture of perchloric acid, arsenic trioxide, and finely ground arsenic, at the temperature at which the cell was to be measured. The half-cell itself was prepared as follows. The electrode was placed in position in the bottom of the cell, and was covered with finely ground arsenic. The air in the half-cell was then displaced with nitrogen, and the half-cell was completely filled with the rotated mixture and sealed. The hydrogen half-cell was filled with the same perchloric acid solution as was used in preparing the mixture above. Such cells became constant within 36 hours and remained constant for 18 to 24 hours with variations of less than 0.1 millivolt.

The Measured Electromotive Forces

The electromotive forces measured at 25° and 45° are listed in Table I. The hydrogen pressure given in the table was obtained by subtracting from the corrected barometric reading the vapor pressure of the solution at that temperature. This vapor pressure for all the solutions was taken equal to that of pure water at the same temperatures, namely, 24 mm. at 25° and 71 mm. at 45°.

Table I

Electromotive Forces of the Cell As(s) + As_2O_3(s), $HClO_4$ (*c M*), H_2(g)

Temperature	Molality *c* of $HClO_4$	Pressure of hydrogen	E.m.f. observed	E.m.f. for H_2 at 1 atm.
25°	0.9450	718	−0.2331	−0.2338
		715	− .2335	− .2342
		717	− .2334	− .2341
	.5588	717	− .2335	− .2342
		715	− .2332	− .2339
		723	− .2331	− .2338
	.2162	720	− .2333	− .2340
			Mean	− .2340
45°	.5588	669	− .2235	− .2251
		671	− .2235	− .2251
	.4438	672	− .2235	− .2251
	.2162	673	− .2232	− .2248
			Mean	− .2250

Free Energy and Heat Content of Arsenic Trioxide

By multiplying the mean values of the electromotive force of the cell at each temperature by 6 × 96,500 and dividing by 4.182 the free-energy decreases were calculated for the cell reaction to be those expressed by the equation, $2As(s) + 3H_2O\ (l) = As_2O_3(s) + 3H_2(g) - 32{,}400$ cal. at 25°; or —31,150 cal. at 45°.

The equation expressing the free energy of formation of water at 25° is, $3H_2(g) + \frac{3}{2}O_2(g) = 3H_2O(l) + 169{,}680$ cal. Adding this equation to the preceding one we get, $2As(s) + \frac{3}{2}O_2(g) = As_2O_3 + 137{,}280$ cal. at 25°. That is, the free energy of formation of octahedral arsenic trioxide ($1As_2O_3$) from metallic arsenic and oxygen at 25° is —137,300 cal.

We may substitute the two free energy values just calculated for the cell reaction and the respective temperatures in the Gibbs-Helmholtz equation integrated under the assumption that the heat-content change ΔH is constant for this temperature interval.

$$\frac{-\Delta F_2}{T_2} - \frac{-\Delta F_1}{T_1} = \Delta H \left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

We thus find the heat-content decrease, $-\Delta H$, to be —51,000 cal. for the cell reaction at 35°.

If it be assumed that there is an error in each of the final electromotive-force values equal to the maximum variation (0.2 mv.) of the separate values from the mean, and that this error lies in opposite directions at the two temperatures, there would result an error in the heat-content change for the cell reaction of about ±850 cal. The probable error is, of course, much smaller than this.

Combining this heat content with that of $3H_2O$(l) at 25°, for which Lewis and Randall[7] give the value, $-3 \times 68{,}270$, the heat content of $1As_2O_3$ (octahedral) is found to be —153,800 cal. Thomsen[8] by an indirect method obtained —154,700 cal., while the value of Berthelot[9] for the same reaction is —156,400 cal. The value here obtained is in fair agreement with that derived by Thomsen.

If the heat capacities of arsenic and arsenic trioxide are assumed constant for temperatures ranging from 0° to 100° and equal to the values determined by Russell[10] for arsenic trioxide and by Bettendorff and Wüllner[11] for arsenic, the free energy and heat contents of arsenic trioxide may be expressed as temperature functions. These authors found, respectively, the heat capacity C_p of $1As_2O_3$ (octahedral) to be 23.83 cal. between 3° and 41°, and that of 2As (metallic) to be 12.44 (between 22° and 68°). For $\frac{3}{2}O_2$ Lewis and Randall[12] give $9.75 + 0.0015\ T$. These values give $\Delta C_p = 1.64 + 0.0015\ T$; and this leads to the following expressions for the increase in heat content and in free energy accompanying the formation of $1As_2O_3$ from its elements for the temperature range of 0–100°: $\Delta H = -154{,}200 + 1.64\ T - 0.00075\ T^2$, and $\Delta F = -154{,}200 - 1.64\ T \ln T + 0.00075\ T^2 + 65.8\ T$.

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[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., **1923**, p. 485.

[8] Thomsen, "Thermochemistry" (translated by Burke), Longmans, Green and Co., London, **1920**, p. 227.

[9] Berthelot, "Thermochimie," **2**, 117 (1897).

[10] Russell, *Physik. Z.*, **13**, 60 (1912).

[11] Bettendorff and Wüllner, *Pogg. Ann.*, **133**, 293 (1868). Wigand [*Ann. Physik*, [4] **22**, 91 (1907)] found the nearly identical value, 12.34, between 0° and 100°. Ewald [*ibid.*, [4] **44**, 1216 (1914)] found, to be sure, a considerably lower value, 11.58, between 1° and 55°.

[12] Ref. 8, p. 80.

It is reasonable to expect that these expressions will be approximately valid up to temperatures where the vapor pressure of arsenic trioxide is known,[13] thus making it possible to extend the free-energy equation to the gaseous substance.

The Molal Reduction-Potential of Arsenic

In order to express the molal reduction-potential of arsenic it is necessary to know in what form the arsenic mainly exists in solution. Previous researches have, however, established this. Moreover, new measurements of its solubility in perchloric acid here communicated have confirmed the conclusion that up to hydrogen-ion concentrations of at least 1 *M* arsenious oxide does not show basic properties.

Freezing-point determinations were made by Raoult[14] and boiling-point determinations by Zawidski,[15] which show that one molecule is present in water solution for every atom of arsenic dissolved. This shows that the formula of the solute is $HAsO_2$ or some hydrate of it. Zawidski derived the ionization constant of arsenious acid from conductivity measurements and found it to be 210×10^{-10}. Woods[16] determined this constant by saponification experiments to be 6.3×10^{-10}, and by conductivity measurements to be 26.5×10^{-10}. These results show that the degree of ionization is extremely small.

The solubility of arsenic trioxide in water at 25°, as determined by Zawidski and confirmed by Anderson and Story[17] is 0.2067 mole of arsenious acid ($HAsO_2$) per 1000 g. of water. New determinations were made of its solubility in perchloric acid solutions. The procedure consisted in removing by means of a pipet some of the arsenic half-cell solution, weighing it, adding just enough carbonate solution to neutralize the acid and leave the carbonate as bicarbonate, adding an excess of bicarbonate, and titrating the arsenic with standard iodine solution.

The solubility values so determined (together with that in pure water found by Zawidski and by Anderson and Story) are as follows.

	Moles per 1000 g. of water			
$HClO_4$	0.0000	0.2162	0.5588	0.9450
$HAsO_2$	.2067	.1963	.1900	.1770

These results show a small gradual decrease in solubility with increasing acid concentration, instead of the large increase which would occur if arsenious perchlorate were being formed in considerable proportion. The

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[13] Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, **1923**, p. 1341; see also Smellie, *J. Soc. Chem. Ind.*, **42**, 466 (1923).

[14] Raoult, *Ann. chim. phys.*, [6] **2**, 84 (1884).

[15] Zawidski, *Ber.*, **36**, 1434 (1903).

[16] Woods, *J. Chem. Soc.*, **93**, 411 (1908).

[17] Ref. 5, p. 1104.

solubilities in the presence of hydrochloric acid, as determined by Woods[18] show up to 3.2 *M* acid an entirely similar behavior. The solubility decrease observed in both cases is presumably due to a decrease in the hydration of the arsenious hydroxide or to a salting-out effect arising from other changes in the solvent medium.

In view of all these facts, we are justified in assuming that all the arsenic in neutral or moderately acid solutions is in the form of $HAsO_2$ (or a hydrate of it), and that the electrode reactions may be expressed by the following equations: $As + 2H_2O + 3\oplus = HAsO_2 + 3H^+$; and $3H^+ = \frac{3}{2}H_2(g) + 3\oplus$. The relation of the electrode potential E of arsenic to its molal potential E_0 may therefore be expressed in correspondence with this electrode reaction as follows.

$$E = E_0 - \frac{RT}{3F} ln\ (HAsO_2)\ (H^+)^3 = E_0 - 0.01971 \log\ (HAsO_2)\ (H^+)^3$$

With the aid of this equation the molal electrode-potential may be calculated from the electromotive force (—0.2340 volt) of the cells with arsenic trioxide present as solid phase by placing ($HAsO_2$) equal to its solubility in water (0.2067 *M*) and (H^+) equal to unity. Its value is thus found to be **—0.2375** volt.

Summary

The electromotive force of the cell $As(s) + As_2O_3(s)$, $HClO_4(0.22–0.94)$, H_2 (1 atm.) was measured at 25° and 45°, and the respective values were found to be —0.2340 and —0.2250 volt. The free energy at 25° of arsenic trioxide $1As_2O_3$ (octahedral) referred to crystalline metallic arsenic was computed from the first of these values, and found to be —137,300 cal. Its heat-content, as derived from the cell measurements at the two temperatures, was found to be —153,800 cal.

By considering all the arsenic in solution to be in the form $HAsO_2$, the molal electrode or reduction potential of arsenic calculated for the oxidation reaction, $As + 2H_2O + 3\oplus = HAsO_2 + 3H^+$, was found to be **—0.2375** volt.

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[18] Ref. 16, p. 413.

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THE FREE ENERGY OF ANTIMONY TRIOXIDE AND THE REDUCTION POTENTIAL OF ANTIMONY

BY REINHARDT SCHUHMANN[1]

RECEIVED OCTOBER 23, 1923

Purpose of the Research

Little reliable information is available about the free energy of formation of any compound of antimony. Its molal electrode potential is also very uncertain: it is given as —0.1 volt by Abegg, Auerbach and Luther,[2] this value being taken from the results obtained by Neumann[3] in 1894. Lewis and Randall[4] point out the lack of information about the free energies of the compounds of a number of non-metallic elements, and antimony is included in the list.

The object of the present investigation was to determine (1) the free energy of formation of antimony trioxide, and (2) the molal electrode potential of antimony. These quantities were determined by measuring the electromotive force of cells of the type: $Sb(s) + Sb_2O_3(s), HClO_4$

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[1] DuPont Fellow at the California Institute of Technology.

[2] Abegg, Auerbach and Luther, "Elektromotorische Kräfte, Ergänzungsheft," Wilhelm Knapp, Halle, **1915**, p. 48.

[3] Neumann, *Z. physik. Chem.*, **14**, 193 (1894).

[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, p. 466.

(c_Am.), $H_2(g)$. After the conditions had been found under which such cells gave constant and reproducible electromotive forces, measurements were made at three different concentrations of perchloric acid lying between about 0.1 and 1.0 *M*.

The solubility of antimony trioxide at 25° in four concentrations of perchloric acid was also determined, in order to enable the molal electrode potential of antimony to be calculated from the electromotive-force measurements.

This investigation was carried on under the general direction of Professor A. A. Noyes; to him the writer wishes to express his indebtedness for assistance in the prosecution of the work and in the preparation of the manuscript for publication.

Preparation of Materials and Solutions

The metallic antimony was prepared by electrolysis of a solution of antimony fluoride containing a slight excess of hydrofluoric acid,[1] as described by Cohen, Collins and Strengers.[5] A pure, imported antimony trioxide was dissolved in a platinum dish in a slight excess of pure 48% hydrofluoric acid, and the solution was diluted with water to approximately eight times its volume. The dish was made the anode; and a small piece of platinum foil, about 1.5 sq. cm. in area, was used as cathode. A current of 4 to 6 amperes was passed through the solution. The metallic antimony was deposited on the cathode in a very finely divided form; and by gently tapping the cathode, it fell into the platinum dish. The material thus collected was washed repeatedly with distilled water in the dish by decantation. It was then filtered, washed with a large amount of hot water and dried in a vacuum desiccator.

The antimony trioxide used in the cell was prepared by purifying the imported product, which contained a trace of iron and a little antimony pentoxide. The original material was dissolved by adding just enough dil. hydrochloric acid; the solution was then filtered to remove traces of solid substances, and 6 volumes of water were added. This precipitated a basic antimonous chloride, which was free from iron and antimony pentoxide (as shown by dissolving it in hydrochloric acid and adding potassium iodide). This basic salt was redissolved in the same manner as the original oxide, and the solution was slowly stirred into a boiling solution of sodium carbonate, used in slight excess over that required to neutralize the total acidity in the antimony solution. The precipitated oxide was filtered off and washed with hot water. As it still contained a little chloride, this was removed by boiling the solid with water and filtering, repeating these operations until the filtrate gave no test for chloride. The product was dried in a vacuum desiccator.

The perchloric acid used was a 60% product obtained from a domestic source. It gave no test for chloride, sulfate, barium or oxidizing substance. One perchloric acid solution was standardized by means of an imported sodium carbonate, purified by precipitation with carbon dioxide and ignition. The others were standardized against a sodium hydroxide solution which had itself been standardized by means of the first perchloric acid solution. The concentrations are given in moles per 1000 g. of water; but density determinations were made, to enable volume concentrations also to be computed. Each solution was boiled to remove air before it was standardized, and then was kept under an atmosphere of nitrogen.

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[5] Cohen, Collins and Strengers, *Z. physik. Chem.*, **50**, 307 (1905).

Apparatus and Methods of Measurement

The electromotive force of the cell was measured by means of a commercial potentiometer of the latest type against a standard Weston cell. The standard cell was checked against another one of the same type.

The hydrogen half-cell was constructed as shown in Fig. 1. It contained two platinized platinum electrodes. The hydrogen, made by electrolysis of a potassium hydrogen sulfate solution, was passed first through a tube containing an electrically heated platinum coil (to free it from oxygen), and then through a saturator (shown at the right-hand side of the figure) containing the same solution as the electrode compartment. The antimony half-cell was constructed as shown in Fig. 2. It contained a small spiral platinum electrode and a mercury-sealed glass stirrer. The electrode had been plated electrolytically with antimony from a weak hydrogen fluoride solution at low current density (about 0.005 amperes per sq. cm.). The two half-cells were sealed to a connecting part of the apparatus, which was provided with stopcocks to permit separate filling of the half-cells and to prevent diffusion from one half-cell to the other. The stopcocks were opened only while readings were being taken.

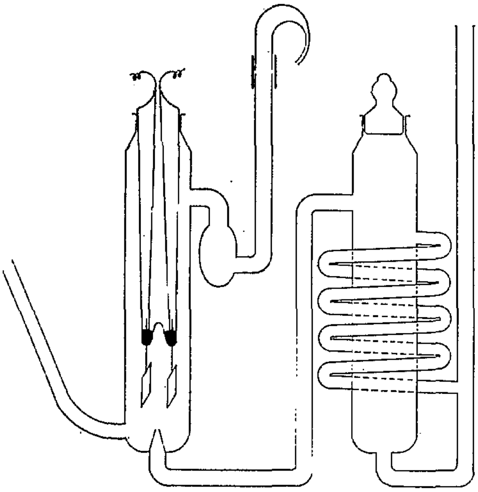

Fig. 1

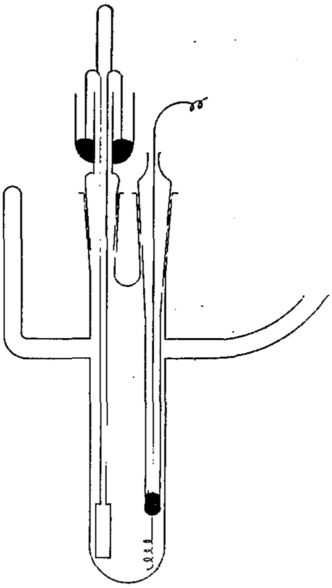

Fig. 2

The antimony half-cell was sealed air-tight, so that no surging of the liquids could take place even when the stopcocks were open. The plated electrode in the bottom was nearly covered with several cubic centimeters of finely divided antimony. The air was then displaced with nitrogen, and the cell was completely filled with a mixture of perchloric acid solution, antimony trioxide, and finely divided metallic antimony, which had been rotated in the thermostat for several days. The hydrogen half-cell was filled with just the same perchloric acid solution that was used for preparing the mixture in the antimony half-cell.

The whole apparatus was kept at 25° in an electrically-heated thermostat. The heating current was momentarily turned off when the potentiometer readings were taken.

The Measured Electromotive Forces

The results of the separate electromotive force measurements expressed in millivolts are given in Table I. Only those readings are included which were taken at approximately 12-hour intervals (or 24-hour intervals in the case of Cell 3). During the measurements the barometer varied only between the limits 735 and 739 mm., so that the pressure could have had scarcely any effect on the constancy of the results.

TABLE I

OBSERVED ELECTROMOTIVE FORCES OF THE CELL

H_2 (714 MM.), $HClO_4$ IN H_2O, Sb_2O_3 (s) + Sb, AT 25°

$HClO_4$, 0.4970 moles per 1000 g. of water				$HClO_4$, 1.1330 moles per 1000 g. of water			$HClO_4$, 0.2312 moles
1	2	3	4	5	6	7	8
151.5	150.0	152.4	149.4	155.2	154.8	155.6	154.0
150.7	149.5	152.8	149.2	153.3	154.5	154.7	153.1
150.4	149.7	153.3	149.0	153.4	154.6	154.4	152.4
150.1	149.5	153.4	149.7	153.4	154.7	154.1	152.1
149.7	149.4	151.8	149.2	153.4	...	154.2	151.7
149.7	149.4	150.2	148.8	...	154.6	...	151.5
149.6	...	149.7	...	...	...	...	151.0
149.7	...	149.7	...	...	154.5	...	151.1
149.7	...	...	...	...	...	...	151.2
...	...	...	...	...	...	...	151.0

The values finally adopted are given in Table II. These numbers are those best corresponding to the experimental values given in Table I, increased by 0.0008 volt to correct the hydrogen pressure to 760 mm. from that (714 mm.) corresponding to the barometric pressure (737 mm.) diminished by the vapor-pressure of the solutions (taken as 23 mm.). The weighings were not corrected for air buoyancy.

TABLE II

FINAL VALUES OF THE ELECTROMOTIVE FORCE OF THE CELL

H_2 (1 ATM.), $HClO_4$ IN H_2O, Sb_2O_3(s) + Sb(s), AT 25°

Molality of $HClO_4$	Density of $HClO_4$ at 25°		Corrected e.m.f.
0.2312	1.0096		0.1519
0.4970	1.0238		0.1504
1.1330	1.0554		0.1549
		Mean	0.1524

It will be seen that the two cells with the more dilute acid solutions give final values of the electromotive force that differ by only 1.5 mv., an amount which is within the experimental error. The cell with 1.133 *M* perchloric acid solution has, however, an electromotive force 4 mv. greater than the mean of the other two. This is also probably due to error, since the other effects that might come into consideration can hardly be of this magnitude. Thus, even if it were assumed that the vapor pressure of water in 1.1330 *M* perchloric acid solution were even 8% less than that of pure water, this would correspond to an increase of only 1 mv. in the electromotive force. In none of the solutions, according to the solubility results presented below, is more than 0.1% of the perchloric acid neutralized by the dissolved antimony, so that an appreciable effect on the electromotive force could not result from diminution of the hydrogen-ion concentration.

In interpreting the results the character of the solid phases is, of course, of much importance. That the antimony trioxide was really the anhydrous substance was confirmed by igniting portions of the substance that had been prepared as described above and had been dried for several days in a vacuum desiccator over sulfuric acid. Before ignition the substance was treated in the crucible with 16 N nitric acid. Weights of antimony tetra-oxide, Sb_2O_4, were obtained less than those that would have resulted from anhydrous antimony trioxide by only 0.2–0.4%. The metallic antimony used was doubtless the ordinary stable form, since it has been shown by Cohen, Collins and Strengers[5] that the electrolytic precipitate from hydrofluoric acid solutions is of this character. The long rotation with the solution would further tend to ensure this.

The Computed Free Energy of Antimony Trioxide

Taking 0.152 as the best value of the electromotive force E of the cell, the free-energy decrease $-\Delta F$ attending the cell reaction, as calculated by the equation $-\Delta F = -6\,E \times 96{,}500/4.182$, is found to be that expressed by the following equation: $2\,Sb(s) + 3H_2O(l) = Sb_2O_3(s) + 3H_2(g)$ $-21{,}040$ cal. The equation for the free energy of formation of water[6] at 25° is: $3\,H_2(g) + {}^3/_2\,O_2(g) = 3H_2O(l) + 169{,}680$ cal. Adding these equations, we get: $2\,Sb(s) + {}^3/_2\,O_2(g) = Sb_2O_3(s) + 148{,}640$ cal. Hence $-148{,}600$ calories is the free energy of formation of one formula weight of solid antimony trioxide ($1Sb_2O_3$) from its elements at 25°.

Solubility of Antimony Trioxide in Perchloric Acid

The solubility of antimony trioxide in each of four concentrations of perchloric acid was determined as follows. A volume of perchloric acid, varying from 200 cc. to 400 cc., mixed with an excess of the reprecipitated antimony trioxide and some finely divided metallic antimony, was rotated in the thermostat at 25° for 48 to 72 hours. The mixture was rapidly filtered in air at approximately 25°, the bottle being kept in the thermostat as much as possible. The filtrate was then weighed, and the antimony precipitated with hydrogen sulfide. The precipitated sulfide was collected in a perforated crucible and dried in air at 110°. It was then dried in carbon dioxide at 200° until constant weight was obtained. The experimental values are given in the first five columns of Table III. Values were always obtained both from the undersaturated and from the supersaturated side, the latter being indicated by asterisks (*).

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[6] Ref. 4, p. 485.

According as the antimony exists in the solution in the form of Sb^{+++}, or of $SbOH^{++}$, or of SbO^+, the mass-action law evidently requires that the ratio of the total dissolved antimony (ΣSb) to the cube $(H^+)^3$ of the hydrogen-ion activity, or to its square $(H^+)^2$, or to its first power (H^+), respectively, remain constant when the acid concentration is varied. The values of these ratios are given in the last three columns of Table III. The values of (H^+) used were obtained by multiplying the molalities of the perchloric acid by its activity coefficients, which are shown in the following paper to be substantially equal to those for hydrochloric acid, for which the values summarized by Lewis and Randall[7] were employed.

TABLE III

SOLUBILITY OF ANTIMONY TRIOXIDE IN PERCHLORIC ACID SOLUTIONS AT 25°

	At. wts. of Sb (ΣSb) × 10^6 per 1000 g. of water					Ratio of (ΣSb) × 10^4 to		
Molality of $HClO_4$	I	II	III	Mean	Activity coefficient of $HClO_4$	(H^+)	$(H^+)^2$	$(H^+)^3$
0.2310	234*	238	236	236	0.778	12.96	71	392
0.4970	316*	318	...	317	.762	8.39	22	58
0.8610	576*	575	...	575	.798	8.37	12.2	18
1.1330	731*	749	775	752	.852	7.80	8.1	8

It will be seen that of the three ratios the ratio $(\Sigma Sb)/(H^+)$ is much more nearly constant. Indeed the constancy is entirely satisfactory except in the most dilute perchloric acid solution, where the experimental error is large (the weighed antimony sulfide from 400 g. of solution amounting to only about 16 mg.), and where the later stage of the hydrolysis (forming antimony trihydroxide) may well become appreciable. We may, therefore, conclude that at acid concentrations between 0.25 and 1.15 *M* the antimony exists mainly in the form of antimonyl ion, SbO^+.

The Molal Electrode Potential of Antimony

In view of the solubility results presented in the preceding section, it is most appropriate to compute a molal electrode potential of antimony for molal concentrations of hydrogen ion and of antimonyl ion, SbO^+. For the results indicate that in solutions of salts of oxyacids where complexes do not form, the concentration of the latter ion can apparently be regarded as approximately equal to that of the total antimony. From the mean value, —0.1524 volt, of the measured electromotive force E of the cell (in which the reaction $Sb(s) + H_2O + H^+ = SbO^+ + {}^3/_2\, H_2(g)$ may be considered to take place), and from the data of Table III, this potential $\mathbf{E}$ was calculated by the following equation, in which c_A represents the molality and α_A the activity coefficient of the perchloric acid: $\mathbf{E} = \mathrm{E} + \frac{RT}{3\mathrm{F}}\, ln\, \frac{(\Sigma Sb)}{c_A \alpha_A}$. The results are presented in the fourth column of Table IV. In the fifth and sixth columns are given for comparison the potentials corresponding

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[7] Ref. 4, pp. 336, 362.

to the assumptions that all the antimony exists as $SbOH^{++}$ or as Sb^{+++}, respectively (computed by introducing the square or cube of $c_A\alpha_A$ in place of its first power in the equation just given).

TABLE IV

THE MOLAL ELECTRODE POTENTIAL OF ANTIMONY

Molality of $HClO_4$	Act. coef. of $HClO_4$	Conc. of Sb (ΣSb)	Molal electrode potential assuming ΣSb equals (SbO^+)	($SbOH^{++}$)	(Sb^{+++})
0.2312	0.778	0.000236	−0.209	−0.197	−0.181
0.4970	.762	.000317	− .213	− .204	− .196
0.8610	.798	.000575	− .213	− .210	− .206
1.1330	.852	.000752	− .213	− .213	− .213
		Mean	− .212		

In view of these results we may evidently adopt **—0.212** as the molal electrode potential corresponding to the electrode reaction, $Sb(s) + H_2O + 3\oplus = SbO^+ + 2\,H^+$.

Summary

The electromotive force of the cell $Sb(s) + Sb_2O_3(s)$, $HClO_4$ (c_A m.), H_2(g, 1 atm.) was measured at 25°, and was found to be —0.152 volt; and the free energy of antimony trioxide (1 Sb_2O_3) was computed from this value to be —148,600 cal. with an error which probably does not exceed ±300 cal.

Solubility determinations of antimony trioxide in four concentrations of perchloric acid (0.2–1.1 *M*) were made. The results indicated that the dissolved antimony existed mainly in the form SbO^+ at these concentrations of perchloric acid. From the solubility values and the electromotive force of the cell the molal reduction potential corresponding to the electrode reaction $Sb(s) + H_2O + 3\,\oplus = SbO^+ + 2\,H^+$ was found to be —0.212.

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THE ACTIVITY OF PERCHLORIC ACID IN AQUEOUS SOLUTION

By Reinhardt Schuhmann[1]

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Plan of the Investigation

In the research on the molal reduction potential of antimony described in the preceding paper a knowledge of the activity of perchloric acid was required. Moreover, it is of general interest to ascertain the activity relations of this univalent oxyacid, the first one to be investigated. Its activity coefficient was therefore determined by measuring the electromotive force of cells of the type H_2 (1 atm.), $HClO_4$, HCl, H_2 (1 atm.),

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[1] DuPont Fellow at the California Institute of Technology.

the two acids being at the same or nearly the same concentration. The measurements were made at 25° at four concentrations of the acids lying between 0.1 and 1.0 *M*. The liquid potential between the two solutions is very small in the case of this cell, owing to the slight difference in the mobilities of perchlorate and chloride ions, and it can be estimated with sufficient accuracy to enable a correction for it to be made.

This research was undertaken at the suggestion of Professor A. A. Noyes, to whom I am indebted for many helpful comments.

Preparation of the Solutions and the Experimental Procedure

The perchloric acid solutions were prepared as described in the earlier paper. The four hydrochloric acid solutions were prepared by distilling a pure commercial acid and diluting the middle constant-boiling portion by weight. The concentrations of the solutions thus prepared were checked by titration with a standard alkali.

The apparatus was similar to that used in the investigation previously described. Two hydrogen half-cells, each containing two electrodes, were sealed to the two sides of the connecting part of that apparatus. The hydrogen was taken from the same generator and passed through the purifier, and then run through the two half-cells in parallel. The measurements were made with one of the stopcocks in the connecting part closed. Such cells after a few hours reached values constant within 0.03 millivolt.

The Observed and Corrected Electromotive Forces

Table I contains the final results of the measurements of the electromotive force at 25° in the direction from the perchloric to the hydrochloric acid solution. The concentrations are expressed as molalities, that is, in moles per 1000 g. of water. The headings are for the most part self-explanatory. The electromotive force ($\delta\,\mathrm{E}$) due to the unequal molalities, and that ($\mathrm{E_L}$) due to the liquid potential, were calculated by the equations,

$$\delta\mathrm{E} = -0.05915 \log \frac{C_{\mathrm{HClO_4}}}{C_{\mathrm{HCl}}}; \text{ and } \mathrm{E_L} = -0.05915 \log \frac{\Lambda_{\mathrm{H}} + \Lambda_{\mathrm{ClO_4}}}{\Lambda_{\mathrm{H}} + \Lambda_{\mathrm{Cl}}}$$

The values of the equivalent conductances at 0.05 *M* concentration were used, namely, 391.4 for perchloric acid[2] and 398.5 for hydrochloric acid,[3] since accurate data are not available for perchloric acid at lower concentrations; and the liquid potential was calculated to be +0.00047 volt.

TABLE I

THE OBSERVED AND CORRECTED ELECTROMOTIVE FORCES

Molality of		Observed	E.m.f. corrected for	
$HClO_4$	HCl	e.m.f.	unequal molalities	liquid potential also
0.1000	0.1005	0.00060	0.00047	±0.00000
0.2312	0.2334	.00071	.00048	+ .00001
0.5194	0.5194	.00056	.00056	+ .00009
1.1380	1.1382	.00030	.00030	− .00017

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[2] Smith, THIS JOURNAL, **45,** 360 (1923).

[3] Bray and Hunt, *ibid.*, **33,** 781 (1911).

The Activity Relations of Perchloric Acid. Summary

The corrected electromotive forces given in Table I are so small as to be negligible in determining the relative activities of the two acids at the same concentration. Thus the largest value (0.00017 volt) would correspond to a difference of only 0.7% in the value of the activity coefficient of the hydrogen ion. The conclusion may therefore be drawn that the activity coefficient of perchloric acid is substantially the same as that of hydrochloric acid up to 1.1 *M;* and the values derived for the latter acid (for example, as summarized by Lewis and Randall[4]) may therefore be employed in mass-action and thermodynamic expressions relating to perchloric acid.

This conclusion is of general interest, inasmuch as it indicates that the behavior of both these acids, including the pronounced minimum in their activity-coefficients in the neighborhood of 0.5 *M*, is primarily determined by the hydrogen ion; the effects of the two anions being apparently relatively small and nearly equal.

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[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, p. 362.