

adsorption by the method herein recorded. For kindly criticism and advice when in difficulties, we are likewise grateful.

Summary

1. A rapid method for measuring heats of adsorption of gases on metallic catalysts is described.

2. The integral value for the heat of adsorption of hydrogen on nickel varies from 13,500 to 20,500 calories depending upon the past history of the adsorbent. Corresponding values for the same samples are in good agreement.

3. The magnitude of the value shows that the phenomenon is not one of condensation in this case.

4. The differential values do not decrease with increasing partial pressure. In this respect the case is anomalous.

5. With copper as adsorbent of hydrogen more nearly concordant results are obtainable. The magnitude of the heat of adsorption is in this case 9600 calories. The case is therefore parallel to that of nickel.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 35]

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

BY REINHARDT SCHUHMAN¹

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 Neumann³ in 1894. Lewis and Randall⁴ 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: $\text{Sb}(s) + \text{Sb}_2\text{O}_3(s), \text{HClO}_4$

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,⁵ 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.

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

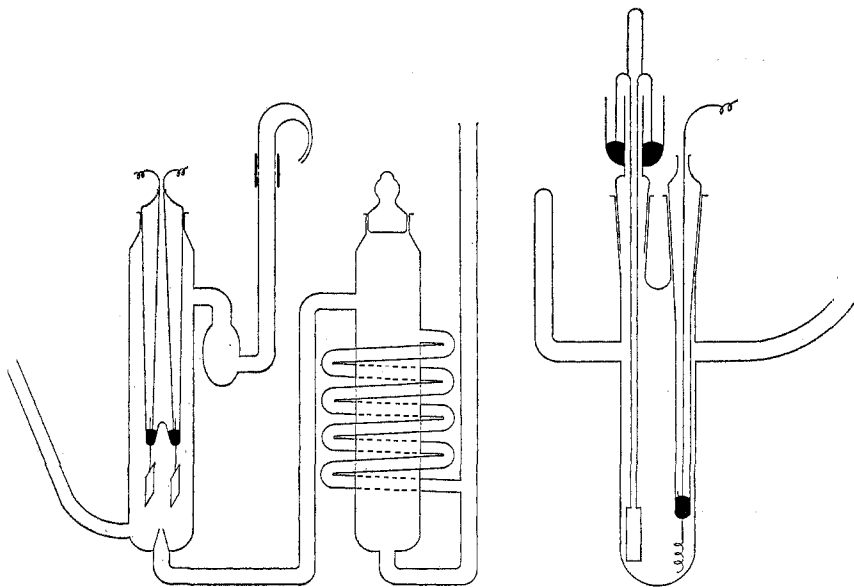


Fig. 1

Fig. 2

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.

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
H₂ (714 mm.), HClO₄ IN H₂O, Sb₂O₃ (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
H₂ (1 ATM.), HClO₄ IN H₂O, Sb₂O₃(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 Strengers⁶ 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 \mathcal{E} of the cell, the free-energy decrease $-\Delta F$ attending the cell reaction, as calculated by the equation $-\Delta F = -6 \mathcal{E} \times 96,500/4.182$, is found to be that expressed by the following equation: $2 \text{Sb}(s) + 3\text{H}_2\text{O}(l) = \text{Sb}_2\text{O}_3(s) + 3\text{H}_2(g) - 21,040 \text{ cal.}$ The equation for the free energy of formation of water⁶ at 25° is: $3 \text{H}_2(g) + \frac{3}{2} \text{O}_2(g) = 3\text{H}_2\text{O}(l) + 169,680 \text{ cal.}$ Adding these equations, we get: $2 \text{Sb}(s) + \frac{3}{2} \text{O}_2(g) = \text{Sb}_2\text{O}_3(s) + 148,640 \text{ cal.}$ Hence $-148,600$ calories is the free energy of formation of one formula weight of solid antimony trioxide ($1\text{Sb}_2\text{O}_3$) 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 super-saturated side, the latter being indicated by asterisks (*).

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 $(\text{H}^+)^3$ of the hydrogen-ion activity, or to its square $(\text{H}^+)^2$, 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 Randall⁷ were employed.

TABLE III

SOLUBILITY OF ANTIMONY TRIOXIDE IN PERCHLORIC ACID SOLUTIONS AT 25°

Molality of HClO_4	At. wts. of Sb (ΣSb) $\times 10^6$ per 1000 g. of water				Activity coefficient of HClO_4	Ratio of (ΣSb) $\times 10^4$ to (H^+) ³ , (H^+) ² , (H^+) ¹		
	I	II	III	Mean		(H^+) ³	(H^+) ²	(H^+) ¹
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 $(\Sigma\text{Sb})/(\text{H}^+)$ 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 \mathcal{E} of the cell (in which the reaction $\text{Sb}(s) + \text{H}_2\text{O} + \text{H}^+ = \text{SbO}^+ + \frac{3}{2} \text{H}_2(g)$ may be considered to take place), and from the data of Table III, this potential \mathcal{E} was calculated by the following equation, in which c_A represents the molality and α_A the activity coefficient of the perchloric acid: $\mathcal{E} = \mathcal{E} + \frac{RT}{3F} \ln \frac{(\Sigma\text{Sb})}{c_A \alpha_A}$.

The results are presented in the fourth column of Table IV. In the fifth and sixth columns are given for comparison the potentials corresponding

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 (SbO^+)	Molal electrode potential assuming ΣSb equals (SbOH^{++})	Molal electrode potential assuming ΣSb equals (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, $\text{Sb(s)} + \text{H}_2\text{O} + 3\oplus = \text{SbO}^+ + 2\text{H}^+$.

Summary

The electromotive force of the cell $\text{Sb(s)} + \text{Sb}_2\text{O}_3(\text{s}), \text{HClO}_4 (c_A \text{ m.}), \text{H}_2(\text{g}, 1 \text{ atm.})$ was measured at 25° , and was found to be -0.152 volt; and the free energy of antimony trioxide ($1 \text{ Sb}_2\text{O}_3$) 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 $\text{Sb(s)} + \text{H}_2\text{O} + 3\oplus = \text{SbO}^+ + 2\text{H}^+$ was found to be -0.212 .

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 36]

THE ACTIVITY OF PERCHLORIC ACID IN AQUEOUS SOLUTION

BY REINHARDT SCHUHMAN¹

RECEIVED OCTOBER 23, 1923

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 $\text{H}_2 (1 \text{ atm.}), \text{HClO}_4, \text{HCl}, \text{H}_2 (1 \text{ atm.}),$

¹ DuPont Fellow at the California Institute of Technology.