Ammonium hexafluorozirconate was prepared by adding the theoretical quantity of ammonium fluoride solution to a solution of oxide in hydrofluoric acid and evaporating to incipient crystallization.

Anal. Calcd. for $(NH_4)_2ZrF_6$: NH_4, 14.93; Zr, 37.80. Found: NH_4, 14.75, 14.84; Zr, 37.39, 37.78, 37.80.

The first decomposition product from the 515 mm. run was analyzed. Found: NH_4, 14.35, 14.05; Zr, 37.70, 37.97.

Ammonium pentafluorozirconate was prepared by adding 75% of the theoretical quantity of ammonium fluoride solution to a solution of the oxide in hydrofluoric acid and allowing the solution to crystallize slowly.

Anal. Calcd. for NH_4ZrF_5: NH_4, 8.82; Zr, 44.56. Found: NH_4, 8.58, 8.63, 8.67; Zr, 44.63, 44.13.

The product from the second decomposition at 515 mm. was analyzed. Found: NH_4, 8.80, 8.74, 8.74; Zr, 43.90, 43.95.

The zirconium(IV) fluoride used for comparison with the end product was prepared by fluorination of zirconium metal at 550°.

DURHAM, NEW HAMPSHIRE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Equilibria of Antimonous Oxide (Rhombic) in Dilute Solutions of Hydrochloric Acid and Sodium Hydroxide at 25°

BY KARL H. GAYER[1] AND A. B. GARRETT

The solubility of antimonous oxide has been determined in water and in dilute solutions of sodium hydroxide and hydrochloric acid. The equilibria in sodium hydroxide and in hydrochloric acid solutions indicate that the antimony is present in both cases as a monovalent ion. Values of the solubility of antimony oxide in water and for the acid and base constants of antimony trioxide have been obtained.

The purpose of this investigation was to obtain data on the equilibria of antimonous oxide in dilute hydrochloric acid and sodium hydroxide solutions. Previous work on antimonous oxide is incomplete in regard to solubility and equilibria values. The earliest reported work on the reactions of antimony was made by Terriel[2] who prepared sodium antimonite and studied some of its properties. Schulze[3] determined the solubilities of antimony trioxide in water at 15 and 100° and found them to be 5.5×10^{-5} and 3.4×10^{-4} mole per 1000 g. of water, respectively. Schuhmann[4] measured the solubility of antimony trioxide (probably the rhombic form) in several solutions of various concentrations of perchloric acid, and found a fairly constant value for the ratio of hydrogen ion concentration to antimony concentration, which led him to conclude that the SbO^+ ion exists in acid solutions.

Procedure

The general procedure was similar to that of Garrett and Heiks.[5]

Water.—Triply distilled water was boiled to free it from dissolved gases and then stored under nitrogen.

Antimony Trichloride.—Baker and Adamson Reagent antimony trichloride was used to prepare the rhombic antimonous oxide.

Antimony Metal.—Baker and Adamson Reagent antimony was used to prepare the colorimetric standards.

Sodium Carbonate.—Mallinckrodt anhydrous Analytical Reagent was used to precipitate the oxide.

Hydrochloric Acid.—Standard solutions for analysis and for the solubility measurements were prepared from C.P. hydrochloric acid and standardized gravimetrically.

Rhodamine B.—Eastman Kodak Co. practical grade was used to prepare the 0.2% water solution.

Rhombic Antimonous Oxide.—The antimonous oxide was prepared in an atmosphere of nitrogen. To a solution containing 30 g. of antimony trichloride per liter of water was added a saturated solution of sodium carbonate to precipitate the antimony oxide. The oxide was then washed with triple-distilled, boiled water until free of chloride and sodium ions. Fifteen one-liter washings sufficed. The identity of the rhombic form was obtained by X-ray analysis.[6]

Equilibration.—Two 180-ml. samples of the equilibrating mixture, contained in 200-ml. round bottom flasks, were prepared at each concentration of alkali or acid. One sample was agitated in a thermostat at 35° for a period of 5 to 7 days, then transferred to a thermostat at 25 ± 0.02° for an additional agitation period of seven days. The other one of each pair was placed directly in the 25° thermostat and agitated for seven days. By this means, equilibrium was approached from supersaturation and undersaturation. Both values were found to check within experimental limits.

Sedimentation.—After the completion of the agitation period, the flasks were clamped in an upright position in the 25° thermostat, and the oxide allowed to settle for seven days.

Filtration.—The flasks were opened and contents removed under an atmosphere of nitrogen through a covered, sintered glass funnel, and into a glass-stoppered bottle.

Measurement of Hydrogen Ion Concentration.—The *p*H values of the equilibrated samples were obtained by using a Beckman portable *p*H meter. The meter was calibrated with potassium acid phthalate–sodium hydroxide buffer at *p*H 4, and with boric acid–sodium hydroxide buffer at *p*H 10.

Analysis of Antimony.—The antimony analysis on the equilibrated samples was made with a Lumetron spectrophotometer using rhodamine B to produce the colored complex. The procedure for analysis was a modification of that described by Maren.[7] The analyses were reproducible to ± 3%.

The data are collected in Tables I and II and are shown graphically in Fig. 1. The rhombic form of

TABLE I

SOLUBILITY OF RHOMBIC Sb_2O_3 IN NaOH SOLUTIONS AT 25°

Initial mole NaOH/1000 g. H_2O	Gram atom of Sb/1000 g. H_2O $\times 10^5$	$K \times 10^3$
0.000	5.8	
.00505	9.8	7.9
.0101	14.8	8.9
.0202	23.8	8.9
.0404	42.8	9.2
.0400	37.8	8.0
.0749	75.8	9.3
.0998	99.8	9.4
		Av. 8.8

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[2] M. A. Terriel, *Ann. chim. phys.*, [4] **7**, 350 (1866).

[3] H. Schulze, *J. prakt. Chem.*, [2] **27**, 320 (1883).

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

[5] A. B. Garrett and R. E. Heiks, *ibid.*, **61**, 367 (1939).

[6] We are indebted to Dr. D. A. Vaughan of the Battelle Memorial Institute for the X-ray analysis of these samples.

[7] T. H. Maren, *Ind. Eng. Chem., Anal. Ed.*, **19**, 487 (1947).

TABLE II

SOLUBILITY RHOMBIC Sb_2O_3 IN HCl SOLUTIONS AT 25°

Initial mole, HCl/1000 g. H_2O	Gram atom of Sb/1000 g. $H_2O \times 10^5$	Mole H^+/1000 g. H_2O from *p*H values	$K_2 \times 10^4$
0.005	2.1	5.2×10^{-3}	
.010	2.6	1.0×10^{-2}	6.0
.020	3.4	2.2×10^{-2}	7.0
.030	4.5	3.1×10^{-2}	8.3
.050	6.1	5.8×10^{-2}	8.2
.075	8.2	6.9×10^{-2}	8.3
.100	10.2	1.3×10^{-1}	8.2
		Av.	7.7

antimony oxide was used throughout. It is reported to be unstable at room temperature, but apparently the rhombic modification is formed on precipitation and changes over to the cubic only very slowly. No evidence of the cubic form was found in any of our samples. Since the rhombic form is the less stable form at room temperature, it will have a higher solubility than the cubic form.

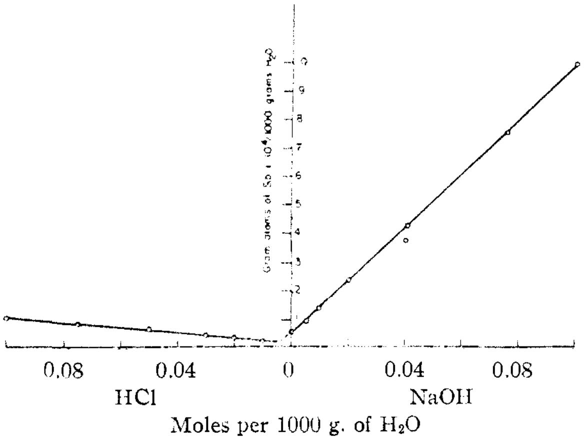

Fig. 1.—Solubility of Sb_2O_3 (in gram atoms Sb) in dilute acid and base.

In general, we can assume that the equilibria of antimony trioxide in neutral, acidic and basic solutions may be represented by equations 1 to 5.

$$Sb_2O_3(s) + 3H_2O \rightleftarrows 2Sb(OH)_3 \quad (1)$$

$${}^1/_2Sb_2O_3(s) + H^+ \rightleftarrows SbO^+ + {}^1/_2H_2O \quad (2)$$

$$ {}^1/_2Sb_2O_3(s) + OH^- \rightleftarrows SbO_2^- + {}^1/_2H_2O \quad (3)$$

$$ {}^1/_2Sb_2O_3(s) + {}^1/_2H_2O \rightleftarrows SbO_2^- + H^+ \quad (4)$$

$$ {}^1/_2Sb_2O_3(s) + {}^1/_2H_2O \rightleftarrows SbO^+ + OH^- \quad (5)$$

The Solubility of Rhombic Antimonous Oxide in Water.—The solubility of antimonous oxide in water was found to be $5.2 \times 10^{-5} \pm 1 \times 10^{-5}$ gram atom of Sb per 1000 g. of water from an average of five determinations ranging from 5.6×10^{-5} to 5.0×10^{-5}. It was also found, from extrapolation (large scale) of the solubility of antimony oxide in alkaline solutions, to be $6.5 \times 10^{-5} \pm 1 \times 10^{-5}$. An average of the values is probably the most reasonable value giving 5.8×10^{-5} gram atom of antimony (Sb) per 1000 g. of water or 2.9×10^{-5} mole of Sb_2O_3 per 1000 g. of water.

The Equilibria in Basic Solutions.—The constancy of the values of K_3 is evidence that the reaction indicated by Equation (3) accounts for the solubility of antimony oxide over this range of concentration of alkali.

$$ {}^1/_2Sb_2O_3(s) + OH^- \longrightarrow SbO_2^- + {}^1/_2HOH \quad (3)$$

The equilibrium constant

$$K_3 = m_{SbO_2^-}\gamma_{SbO_2^-}/m_{OH^-}\gamma_{OH^-}$$

The ratio $\gamma_{SbO_2^-}/\gamma_{OH^-}$ can be assumed to be unity over the concentration range studied. The value of $m_{SbO_2^-}$ = total antimony − undissociated antimony hydroxide. Since antimony hydroxide is a weak acid the undissociated antimony hydroxide can be determined by extrapolating the solubility curve for antimony oxide in base to $m_{OH^-} = 0$; this is the water solubility value which is determined to be 5.8×10^{-5}. The value of K_3 is $8.8 \times 10^{-3} \pm 1.0 \times 10^{-3}$ and $\Delta F^0 = 2800$ cal.

Further evidence for the monobasic character of the ions comes from the work of Terriel[2] who isolated sodium antimonite, $NaSbO_2$. There is no indication of the type of polymer formation found in the arsenious oxide–alkali system studied by Garrett, Holmes and Laube.[8]

Using the value for K_3 and the ion product of water K_w, the acid dissociation constant K_4 for the reaction was calculated

$$ {}^1/_2Sb_2O_3(s) + {}^1/_2H_2O \longrightarrow H^+ + SbO_2^- \quad (4)$$

$$K_4 = m_{SbO_2^-}\gamma_{SbO_2^-}\ m_{H^+}\gamma_{H^+} = K_wK_3$$

$$K_4 = 8.8 \times 10^{-17}$$

$$\Delta F^\circ = 22{,}000 \text{ cal.}$$

Equilibria in Acid Solution.—That the solubility of antimony trioxide in dilute hydrochloric acid solution can be accounted for by the reaction

$$ {}^1/_2Sb_2O_3(s) + H^+ \longrightarrow SbO^+ + {}^1/_2H_2O \quad (2)$$

can be shown by the constancy of the values of K_2. Similar conclusions were drawn by Schuhmann[4] from the solubility of antimony trioxide in perchloric acid.

Using the data of Table II the equilibrium constant K_2 for the above reaction was calculated

$$K_2 = m_{SbO^+}\gamma_{SbO^+}/m_{H^+}\gamma_{H^+} = 7.7 \times 10^{-4}$$

$$\Delta F^\circ = 4{,}300 \text{ cal.}$$

The ratio of $\gamma_{SbO^+}/\gamma_{OH^-}$ can be assumed to be unity over the concentration range studied. The value for m_{SbO^+} is obtained from the relationship

$$m_{SbO^+} = \text{total antimony concentration} - \text{the undissociated (antimony hydroxide)}$$

The value of undissociated hydroxide is found to be 2×10^{-5} from an extrapolation of the solubility in acid solution to $m_{HCl} = 0$. The above value of K_2 agrees well with that obtained by Schuhmann[4] (9.38×10^{-4}) using perchloric acid.

Using the above value for K_2 and $\cdot K_w$, the ion constant for water, equilibrium constant for the reaction can be obtained

$$ {}^1/_2Sb_2O_3(s) + {}^1/_2H_2O \longrightarrow SbO^+ + OH^- \quad (5)$$

$$K_5 = a_{SbO^+}\ a_{OH^-} = K_2K_w = 7.7 \times 10^{-18}$$

$$\Delta F^\circ = 23{,}000 \text{ cal.}$$

The above values agree with the value of 1×10^{-17} calculated by Latimer[9] from free energy values.

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[8] A. B. Garrett, O. Holmes and A. Laube, THIS JOURNAL, **62**, 2024 (1940).

[9] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1939, p. 109.