150. *Studies on Some Metal Electrodes. Part V. The Amphoteric Properties of Antimony Tri- and Pent-oxide.*

By A. Riad Tourky and A. A. Mousa.

In connection with a study of the behaviour of the antimony electrode, the solubility and amphoteric properties of highly purified antimony tri- and pent-oxide were examined. The solubilities in water at 35° were found to be $4{\cdot}48 \times 10^{-5}$ and $2{\cdot}71 \times 10^{-4}$ g.-mol. per l., respectively.

From solubility determinations in alkali hydroxide and in acid solutions, the isoelectric point of antimony trioxide was found to lie at pH 8·6, whereas that of the pentoxide was within the acid range 1·05—2N-hydrochloric acid. Below and above its isoelectric point the trioxide was found to behave in solution as an ortho-base and as a meta-acid respectively. The pentoxide, on the other hand, was found to behave above the zone of its isoelectric point as a meta-acid only.

In applying macro-methods for the determination of antimony in small quantities, it was found that, whereas the potentiometric bromate method did not yield reproducible results, the ordinary bromate method, as well as the potentiometric permanganate method for the determination of Sb^{3+} and the potentiometric titration of Sb^{5+} with chromous chloride yielded highly satisfactory results: quantities as small as $1{\cdot}96 \times 10^{-5}$, $2{\cdot}07 \times 10^{-5}$, and $1{\cdot}96 \times 10^{-4}$ g.-atom/l. could be determined by the last three methods respectively.

In discussing the formation of acids and bases from the standpoint of the atomic theory, Kossel (*Ann. Physik*, 1916, **49**, 303) inferred that a hydroxy-compound ROH would behave as an ideal ampholyte if the work of separation into the ions H^+ and RO^- does not differ from the work of separation into R^+ and OH^-. In extreme cases at maximum differences, the compound behaves either as a strong acid or as a strong base. Kossel's conclusions, as based on considerations of the hydroxy-compounds of elements in the second short period of the Periodic Table, were in conformity with known facts, though his calculations were based on purely electrostatic grounds and no account was taken of the deformation or hydration energies of the ions concerned. It is possible, however, that these energies, though affecting the single values, do not affect the general picture which one obtains when comparing successive elements in the Periodic Table. Laue (*Z. anorg. Chem.*, 1927, **165**, 325) extended Kossel's calculations in a somewhat modified manner to other elements in the table. According to his views, antimonic acid should be more acid than plumbic, and still more so than stannic acid, and since the acid properties of these compounds are much more pronounced than their basic properties (Töpelmann, *J. pr. Chem.*, 1929, **121**, 320; Collins and Wood, *J.*, 1922, **121**, 441), one can safely conclude that if antimonic acid behaved as an ampholyte, its isoelectric point should be on the acid side of pH 7. As to antimony trioxide, it is probable that, like other tervalent metal oxides, it is more a base than an acid (Lea and Wood, *J.*, 1923, **123**, 259), with its isoelectric point above pH 7. As will be seen below, both predictions are confirmed by experiment.

In addition to the above oxides, the intermediate tetroxide may be formed on the metal at ordinary temperatures. There is evidence, however, that the only ions capable of existence in solution are the ter- and quinque-valent ions (Van Vleck, *Chem. Reviews*, 1928, **5**, 501; Asmussen, *Z. Elektrochem.*, 1939, **45**, 698).

EXPERIMENTAL.

Antimony Trioxide.—Chemically pure antimony trichloride was dissolved in the minimum amount of concentrated hydrochloric acid, the solution distilled in all-Pyrex apparatus, and the distillate discarded until a test drop solidified on a cold glass surface. The product was then poured into 15 volumes of redistilled water and kept overnight at 80°. The initial voluminous flocculent precipitate of basic chloride settled readily. It was washed with redistilled water, digested for 18 hours with a concentrated solution of sodium carbonate, and washed with hot redistilled water four times daily for 8 days. The supernatant liquid then had a constant conductivity, and portions of the precipitate did not afford hydrogen chloride when distilled with concentrated sulphuric acid. The oxide was then collected, dried at 100°, finely powdered, and kept in a dark glass bottle.

Antimony Pentoxide.—Pure antimony pentoxide was prepared by a method similar to that of Willard and McAlpine (*J. Amer. Chem. Soc.*, 1921, **43**, 797), *viz.*, by saturating a solution of the pure trioxide in moderately concentated hydrochloric acid with chlorine prepared as recommended by Archibald ("Preparation of Pure Inorganic Compounds," 1932, p. 317) for at least 2 hours. The yellowish-green solution was then evaporated to a small volume, cooled with ice, and saturated with pure hydrogen chloride, whereupon the compound $HSbCl_6,4\frac{1}{2}H_2O$ separated. After five recrystallisations by the last process, the crystals were redissolved and poured into much hot water, whereupon antimonic oxide separated. As this tended to peptise on repeated washing with hot redistilled water, it was purified by dialysis through a parchment membrane, the wash water being renewed twice daily until it failed to give a test for chloride (about one week). Distillation of a sample of the suspension with concentrated sulphuric acid, however, still afforded traces of chloride, so portions were placed in a Pauli's electrodialysis apparatus provided with platinum and copper wire gauze as anode and cathode respectively. On application of a current of 45 milliamps. at 100—150 volts, the specific conductivity of the liquid in the outer compartment decreased rapidly during the first 80 hours from an initial value of 2×10^{-5} to 5×10^{-6} and then remained practically constant during the next 220 hours at an average value of $4{\cdot}1 \times 10^{-6}$ after correction for the conductivity of water at 25°. The sulphuric acid distillate then gave a negative chloride test, and the product was dried at 90°, finely powdered, and stored in a dark glass bottle.

Determination of Small Quantities of Antimony in Solution.—Comparatively little work has been done on the microchemical determination of antimony in solution. The potentiometric bromate method seems to have been the only one applied to solutions as dilute as 0·0001N (Zintl and Betz, *Z. anal. Chem.*, 1928, **74**, 330). As the method in our hands did not yield reliable results, trials were made to find out whether other macro-methods could be adapted for this purpose.

(a) *Determination of* Sb^{3+} *with potassium bromate.* Unlike the electrometric method, Győry's ordinary bromate method (*Z. anal. Chem.*, 1893, **32**, 415) led to highly accurate results. The process worked well in the presence of 10% hydrochloric acid, with a 0·05% solution of methyl-orange as indicator. Blank experiments were always carried out: this precaution was essential when titrating with bromate solutions as dilute as 0·01N, especially at high hydrochloric acid concentrations. When the titration was carried out at 60°, the end-point was very sharp, and solutions 0·0001N with respect to Sb^{3+} could be accurately determined.

(b) *Potentiometric determination of* Sb^{3+} *with potassium permanganate.* In applying this method (Pugh, *J.*, 1933, 1) it was found that only sufficient hydrochloric acid should be added to prevent formation of any basic salts, and that higher concentrations of sulphuric acid improved the results considerably. The best electrode was a perforated platinum sheet 2 × 3 cm. When titration was carried out at 80°, the potentials very rapidly assumed a steady value over the whole titration range. At the equivalence point the fall was sharp, being 300 mv.

(c) *Determination of* Sb^{5+} *with chromous chloride.* Chromous chloride solutions were prepared and standardised electrometrically as recommended by Zintl and Reinäcker (*Z. anorg. Chem.*, 1927, **161**, 374) against copper sulphate solutions, the copper content of which was checked by electrodeposition. When the solutions were too dilute (down to $1{\cdot}73 \times 10^{-4}$ g.-atom/l.) equilibria were only readily attained in the presence of 20% hydrochloric acid at 80—90°. With an indicator electrode consisting of a platinum rod 12 cm. long and 1·5 mm. in diameter, the satisfactory establishment of equilibria required that, before every titration, the rod be cleaned with hot chromic–sulphuric acid, washed thoroughly, and then ignited. The solutions of quinquevalent antimony were prepared by volumetric dilution from different stock solutions of potassium antimonate, the antimony content of which was determined by Henz's method (Mellor, "A Treatise on Quantitative Inorganic Analysis," London, 1938, 297). The titrations with chromium chloride were carried out in 20% hydrochloric acid at 80—85° in the absence of atmospheric oxygen in a manner similar to that adopted by Brintzinger and Rodis (*Z. anorg. Chem.*, 1927, **166**, 53). Zintl's storage and titration equipment was used after it had been modified by inserting a calibrated 10 c.c. micro-burette graduated to 0·02 c.c. parallel to the calibrated 50 c.c. burette. With the help of a three-way tap, the solution could be delivered from either burette. The common burette tip was made so fine as to allow the delivery of 50 drops per c.c. It was found that solutions of chromous chloride as dilute as 0·0431N could, by careful manipulation, be used as reagent for titrating the more dilute antimony solutions. Still more dilute chromous chloride solutions could not be readily standardised, were unstable, and yielded titration curves with inflexions not sharp enough to define accurately the equivalence points.

In determining the amount of antimony in solution, an oxidation followed by a reduction method or *vice versa* was generally applied to one and the same sample. In reducing Sb^{5+} a method similar to that adopted by Kurtenacker and Fürstenau (*Z. anorg. Chem.*, 1933, **212**, 289) was applied. Sulphur dioxide was bubbled through the solution containing 10% of hydrochloric acid, first in the cold and then at 50°, at a rate of 3 bubbles per second for 20—25 minutes, and the solution was then boiled. In all cases the results were not materially affected in the presence of salt solutions of the same ionic strength as usually met with when determining the amphoteric properties in the presence of sodium hydroxide. Table I contains some representative results obtained by the different methods.

TABLE I.

	Sb, g.-atom/l. × 10^4.	Sb found * (g.-atom/l. × 10^7) by method : (c).	(a).	(b).	
Sb^V	346	346			
	34·6	34·7			
	3·46	3·41			
	1·73	1·96			
			346 *	347 *	
			34·8 *	34·8 *	
			3·48 *	3·50 *	
			1·84	1·96 *	
Sb^{III}	275		276	275	276 †
	27·7		27·8	27·7	27·9 †
	2·84		2·86	2·80	2·84 †
	1·42		1·57	1·58	1·53 †
	0·710		0·727	0·733	0·722 †
	0·355		0·368	0·378	0·371 †
	0·178		0·196	0·207	0·191 †

* Values denoted by an asterisk were obtained after reduction of the antimonic solutions.
† Values so indicated were obtained by method (a) after reduction of the titrated solutions.

(A) *Solubilities of Antimony Tri- and Pent-oxide in Water at* 35°.—The only values reported for the solubility of the trioxide in water are those of Schulze (*J. pr. Chem.*, 1883, **27**, 320), *viz.*, that 100 parts of water dissolve 0·0016 part of the oxide at 15° and 0·01 part at 100°. The solubility of the pentoxide in water is 1·717 g. per 250 c.c. after ¼ hour's shaking at 100° (Glixelli and Przyszczypkowski, *Rocz. Chem.*, 1934, **14**, 474; *Chem. Abst.*, 1935, 2424). In neither case, however, were details given of methods of preparation or purification or of solubility determinations. Our procedure for determining the solubilities was as follows. Portions of the products, prepared and purified as above, were introduced into a 1-l., flat-bottomed Pyrex-glass flask two-thirds filled with previously boiled redistilled water. The flask was furnished with a mercury seal connected to an efficient motor-stirrer. Stirring was carried out in a water thermostat at 35° ± 0·05° for periods ranging from 5 to 24 hours, which always secured equilibrium, the laboratory temperature being 32—34°. The mixture was then filtered with the aid of a high-pressure ultra-filtration apparatus under about 14 atm. The filters used were Zsigmondy membrane filters impermeable to Congo-red. Measured volumes were then analysed, at least in duplicate, for their antimony content. Tables II and III express the results obtained for the two oxides, the method of analysis used being shown.

TABLE II.

Solubility of Sb_2O_3 (g.-mol./l. × 10^5) at 35°.

Time of stirring, hrs.	Method (a).	Method (b).
5	4·53	4·76
10	4·36	—
20	4·56	4·76

TABLE III.

Solubility of Sb_2O_5 (g.-mol./l. × 10^4) at 35°.

Time of stirring, hrs.	Direct : Method (c).	After reduction : Method (a).	After reduction : Method (b).
5	2·64	2·66	2·82
8	2·85	2·73	2·86
15	—	2·71	2·91
20	2·66	2·88	2·74

Results and Discussion.—From the curve in Fig. 1 it can be seen that the solubility of the trioxide decreases with increasing alkali hydroxide concentration up to a certain stage, after which it increases. Extrapolation of the main slopes on each side of the minimum (dotted lines) gives the isoelectric point as equivalent to an alkali concentration of 1·1 × 10^{-5}N. As pK_w is 13·59 at 35°, the pH value corresponding to the isoelectric point of the trioxide is 8·63. At lower pH values the oxide in solution dissociates mainly as a base which may be either $Sb(OH)_3$ or SbO(OH). From the solubility data in solutions of different pH below the isoelectric point, one can obtain information as to the most probable form which prevails in solution. A reaction to completion between the ortho-base of a tervalent metal and an acid implies that $[M^{3+}]$ in solution should be proportional to $[H^+]^3$, but with the meta-base $[MO^+]$ should be directly proportional to $[H^+]$. Now the solubilities in 0·991, 1·400, and 3·105N-acid solutions were respectively 7·1, 37·5, and 1212·5 × 10^{-4} g.-mol./l., *i.e.*, in the process of neutralisation more than three hydrogen ions per molecule of the ortho-base are required. This implies that in addition to the neutralisation reaction more acid is utilised in the formation of complexes of the type H_nSbCl_{3-n}. The solubilities in the acid ranges 0·991—1·400N and 1·400—3·105N are found to be proportional to $[H^+]^4$ and to $[H^+]^5$ respectively, *i.e.*, we have an increasing tendency for complex formation with increase of acidity.

Above the isoelectric point the trioxide dissociates mainly as an acid which might be H_3SbO_3 or $HSbO_2$, in which cases the solubility in alkali hydroxide of different concentrations should be proportional to $[OH']^3$ and to $[OH']$ respectively. From the solubility data obtained (see Table IV), it is found that between 1990 and 42·4 × 10^{-3}N-alkali hydroxide the solubility is proportional to $[OH']$, indicating that in this range the prevailing form is the monobasic acid.

FIG. 1.

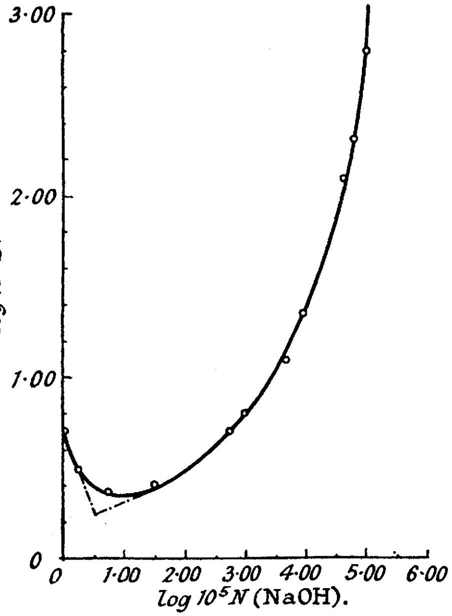

FIG. 2.

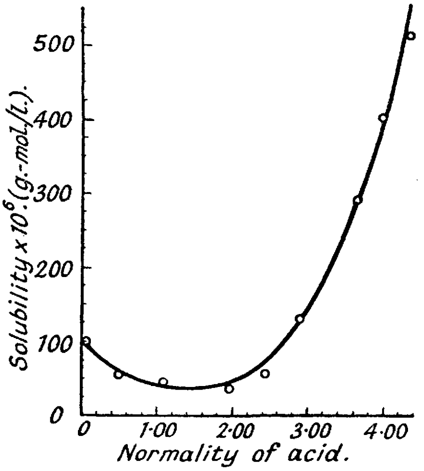

TABLE IV.

Alkali, N × 10^3.	Solubility of Sb_2O_3 : G./l.	Solubility of Sb_2O_3 : G.-mol./l. × 10^5.	Alkali, N × 10^3.	Solubility of Sb_2O_3 : G./l.	Solubility of Sb_2O_3 : G.-mol./l. × 10^5.
1990	1·8800	644·90	6·00	0·0141	4·84
702	0·6297	216·00	0·600	0·0099	3·39
458	0·3673	126·00	0·349	0·0070	2·40
91·5	0·0710	24·36	0·0600	0·0066	2·26
42·4	0·0403	12·82	0·01585	0·0089	3·05
10·3	0·0189	6·48	(H_2O)	0·0131	4·56

TABLE V.

Acid, N	0·050	0·100	0·516	1·064	1·981
Solubility of Sb_2O_5, g./l.	0·0327	0·0230	0·0184	0·0139	0·0113
,, ,, g.-mol./l. × 10^4	1·01	0·71	0·57	0·43	0·35
Acid, N	2·458	2·900	3·748	4·092	4·600
Solubility of Sb_2O_5, g./l.	0·0191	0·0405	0·0929	0·1204	0·1576
,, ,, g.-mol./l. × 10^4	0·59	1·25	2·87	3·72	4·87

From the curve in Fig. 2, which represents the solubility of antimony pentoxide in hydrochloric acid solutions of different concentrations, it can be seen that the isoelectric point corresponding to the minimum solubility of that oxide occurs within a wider limit of acidity; *viz.*, between 1 and 2N-acid. It is, therefore, difficult to define the exact position of that point on the curve. Below the isoelectric zone, on the acid side, antimony pentoxide, when dissolving, will dissociate mainly as a base which might be $Sb(OH)_5$, $SbO(OH)_3$, or $SbO_2(OH)$. The solubilities in different acid concentrations will, therefore, be proportional to $[H^+]^5$, $[H^+]^3$, or $[H^+]$ respectively. By considering the solubility data obtained (Table V), it is found that the most probable form prevailing within the acid range 2·458—4·600N is the tri-acid form; this does not, however, exclude the possibility that it might be $SbO_2(OH)$ and that the excess of acid has been utilised in formation of complexes.

FOUAD I UNIVERSITY, FACULTY OF SCIENCE,
ABBASSIA, CAIRO, EGYPT.

[*Received, April 2nd,* 1947.]