THE VAPOR PRESSURE OF ANTIMONY TRIOXIDE[1]

BY W. B. HINCKE[2]

During the past few years the Pacific Experiment Station of the U. S. Bureau of Mines has received many inquiries regarding the vapor pressure of antimony trioxide. The applicability of such information to the study and improvement of technical methods involved in lead softening, as well as the possible value of such data to the manufacturer of pigments and rubber fillers, has been the incentive in making the following measurements. This work also has an essential place in a general program of investigation being carried on by the Pacific Experiment Station of the Bureau, dealing with the determination of the thermodynamic properties of metallurgically important materials, such as oxides and sulfides.

Preliminary Measurements and Selection of Methods.—Solid antimony trioxide exists in two crystalline forms, cubic and orthorhombic, and has a transition temperature at $570 \pm 10°$ as determined by Roberts and Fenwick.[3] The cubic form is stable below the transition temperature, and the orthorhombic modification is stable from the transition temperature to the melting point, which has been given by Quercigh[4] as $656°$. Preliminary experiments showed that vapor pressures ranging from a fraction of a millimeter to a total of several centimeters prevail in the temperature range $500–800°$.

Two serious difficulties beset any attempt to measure vapor pressures of antimony trioxide. At very low total pressures, thermal dissociation of the oxide becomes apparent, and in fact it proved impossible to resublime even under moderate vacua without always producing small amounts of antimony metal. At higher temperatures, and especially in the case of the molten oxide, the material is an active slagging as well as oxidizing agent, preventing the extensive use of both vitreous and metallic containers.

After some testing of a variety of materials, silica glass was found usable below about $800°$, when the time of contact of liquid oxide and glass was not too great, although it was slowly and continuously slagged.

From these preliminary experiments it was apparent that the inert gas saturation method would be suitable for the determination of the vapor

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[3] Roberts and Fenwick, THIS JOURNAL, 50, 2125 (1928).

[4] Quercigh, *Atti Accad. Lincei*, [5] 21, 415 (1912).

pressures of the solid oxide, but that ordinary methods such as the "boiling point" method would be unsuitable for the liquid, both because of the order of magnitude of pressure involved, and because long contact and agitation were to be avoided to prevent excessive slagging. By the use of a special form of tensimeter the difficulties attendant upon measurements of the liquid oxide were overcome in sufficient degree to furnish adequate, if not completely satisfactory, vapor pressures. Experiments upon the solid oxide, by the inert gas method, and upon the liquid by the new method, will be described separately, and in order.

Part I. Sublimation Pressures of Solid Antimony Trioxide

Preparation of Materials.—Samples of cubic and orthorhombic crystals were prepared by repeated sublimation and condensation in vacuum, and finally in nitrogen, at a temperature at which only the desired crystalline form was stable. Since antimony trioxide readily absorbs oxygen at elevated temperatures, to give more stable higher oxides (tetroxide), great care was taken to prevent the presence of elemental oxygen both during preparation and measurement.

Method.—The inert gas saturation method used for the solid forms of oxide was practically identical with that used by Eastman and Duschak[5] and need not be again described. One essential modification which was made, however, consisted in the fitting of the apparatus with a condenser tube of very light mass (about 1 mm. bore) which could be weighed on the button balance. Experiments of long duration were unsatisfactory because of the slight corrosive action of antimony trioxide vapor on the weighing tube even at a few millimeters' partial pressure. It was better, therefore, to use a sensitive button balance to determine a few milligrams of condensed oxide rather than to attempt to secure equal accuracy from greater amounts of condensed oxide produced over longer sublimation periods.

The lower limit of pressures measurable by the saturation method was determined by the precision with which minute quantities of sublimate deposited in the gas outlet tube could be weighed. All other factors, such as the completeness of saturation and the accuracy of measurement of the volume of nitrogen and the temperature of the furnace, were so controlled as to produce negligible errors in comparison with the unavoidable variations of weights. By the use of the button balance the limit of the vapor pressure measurements was extended to a low range; in fact, weighings were made of samples of condensate as small as 0.00016 g., corresponding at 460° to a partial pressure of 0.0169 mm. of antimony trioxide vapor in the saturator.

At temperatures above 600° the corrosive action of the antimony trioxide vapor began to glaze the inside surface of the quartz saturation chamber as well as to attack the quartz outlet tube with considerable effect on the accuracy of weighing the deposited sample. This glazing action, although not completely disastrous to the method up to 640°, may account for the slight irregularity of the values in this range (see Fig. 2).

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[5] Eastman and Duschak, U. S. Bureau of Mines Technical Paper 225.

Results of Inert Gas Method.—In Table I are shown the results obtained by measurements on cubic crystals of antimony trioxide, and Table II shows similar figures for the orthorhombic form. In the calculation of vapor pressures, the mole of trioxide in the gas phase was taken as Sb_4O_6, in accordance with the results of V. Meyer and H. Mensching[6] and of Biltz.[7] The pressures are reduced to millimeters of mercury at $0°$.

The determined values in Tables I and II are shown as individual points in the chart of Fig. 2, where the logarithm of pressure is plotted against the reciprocal temperature in the conventional way.

TABLE I

VAPOR PRESSURE BY INERT GAS METHOD OF CUBIC CRYSTALS

Temp., °K.	Mole of N_2 (satd.)	Weight of Sb_2O_3 condensed, g.	Total press., mm. of Hg	Calcd. press. $(Sb_2O_3)_2$, mm. of Hg	Log p, (mm.)	$\dfrac{10^4}{T, °K.}$
742	0.01227	0.00016	758.4	0.0169	−1.7705	1348
755	.01543	.00038	758.2	.0319	−1.4955	1325
767	.01561	.00064	754.8	.0528	−1.2783	1305
780	.01676	.00104	754.0	.0802	−1.1060	1285
797	.01400	.00165	759.9	.1530	−0.8145	1255
816	.01423	.00350	759.3	.319	− .496	1226
827	.00917	.00358	757.3	.505	− .296	1210
839	.01041	.00566	756.1	.703	− .153	1191

TABLE II

VAPOR PRESSURE BY INERT GAS METHODS OF ORTHORHOMBIC CRYSTALS

Temp., °K.	Mole of N_2 (satd.)	Weight of Sb_2O_3 condensed, g.	Total press., mm. of Hg	Calcd. press. $(Sb_2O_3)_2$, mm. of Hg	Log p. mm.	$\dfrac{10^4}{T, °K.}$
742	0.01148	0.00019	758.9	0.0215	−1.668	1348
742	.01237	.00020	763.5	0.02108	−1.676	1348
862	.01625	.0198	762.8	1.585	0.205	1161
862	.01596	.0196	761.4	1.594	.203	1161
862	.01717	.0210	760.1	1.580	.199	1161
876	.01634	.0278	759.8	2.200	.343	1141
876	.01626	.0263	759.7	2.095	.322	1141
888	.01530	.0393	762.0	3.330	.523	1126
886	.01616	.0399	760.9	3.231	.509	1126
897	.01740	.0599	761.7	4.470	.651	1114
900	.01537	.0428	759.1	3.600	.557	1110
900	.01507	.0485	759.6	4.155	.619	1110
917	.01580	.0735	758.0	5.980	.777	1090

Part II.   Vapor Pressures of Liquid Sb_2O_3

Method.—The tensimeter method used for liquid oxide is best described by reference to the diagram of Fig. 1. A U-manometer of silica glass, M, has parallel legs five or six inches long, axially separated some four inches. Each leg is provided with a silica glass hook, H, one of which engages the fixed support R, the other being connected

[6] V. Meyer and H. Mensching, *Ber.*, **12**, 1282 (1879).

[7] H. Biltz, *Z. physik. Chem.*, **19**, 385 (1896).

through the quartz glass fiber G with the arm of a good analytical balance, B. The whole manometer is thus freely suspended in the uniform temperature zone of an electric furnace, F. The leg at the fixed support has the side arm S, containing the oxide to be measured. The manometric fluid B is metallic bismuth. Both legs of the manometer are highly evacuated at the beginning of an experiment, and sealed, the temperature of the whole being below that at which vapor pressure is detectable. When the whole manometer is now slowly heated, the displacement of the bismuth column due to vaporization of oxide is determinable from the weight necessary to restore the zero position of the balance.
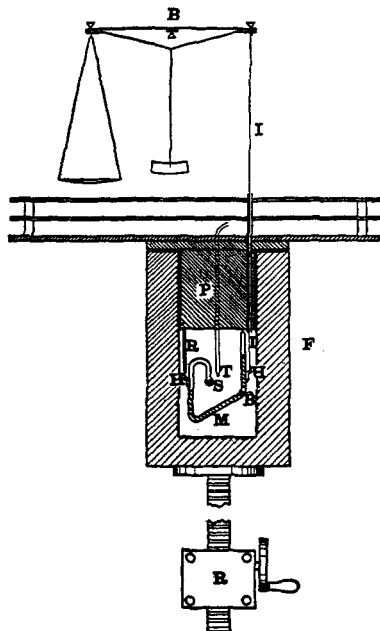
The manometer swings freely between the supports and finds its equilibrium position. It is obvious that the center of gravity must be so adjusted that the two legs of the manometer remain stable in the vertical plane, but the center of gravity must not be too far below the axis of support if good sensitivity is to be obtained.

The balance B is well shielded from the heat of the furnace, the quartz fiber connection being made through a small-bore silica glass tube inserted in the insulating material and plug P. The top of the furnace and the balance are rigidly mounted by suitable supports. The furnace itself is cylindrical in shape with inside dimensions 5×14 inches. It is mounted on a geared rack and may be raised about the manometer and fitted snugly about the top plug P.

It is apparent that this tensimeter must be calibrated before use. The balance weighings give in effect only the displacement of the center of gravity of the instrument as produced by the shift of the manometer liquid. The calibration is accomplished by determining the change in apparent weight produced by known heights of mercury in the cold manometer.

Fig. 1.

The manometer tubes were selected for uniform bore, and so formed that the two arms were parallel and straight over the height of column to be used. For the purpose of calibration the ends were left unsealed and were about half filled with clean mercury. A small Bunsen valve was fitted on the high side of the manometer in order that the mercury might be held at various levels during the calibration. The furnace F was lowered and the manometer with the mercury was suspended so that the high side hung from the quartz fiber. The supports were so adjusted that the center of gravity was well up near the line between the two supports, but low enough so that the manometer was always stable in the vertical plane, when the difference in columns was a maximum. When the manometer is held in the zero position, as indicated by the pointer of the balance, only vertical forces are transmitted by the fiber suspension.

For the actual calibration a cathetometer was used to make readings of the heights of the various displacements of the mercury column corresponding to the weights balancing the downward force on the quartz fiber. Figure 3 shows a graph of such weighings in grams and corresponding heights in centimeters of mercury, and constitutes a calibration for one of the manometers used. If the manometer were perfectly con-

structed and the suspension were frictionless and unaltered during the calibration, the points would fall on a straight line.   Each manometer had its own characteristic curve, but the slope of the line depends only upon the bore of the tube and the distance between the two supports.   The nearly precisely constant ratio between increases in weight
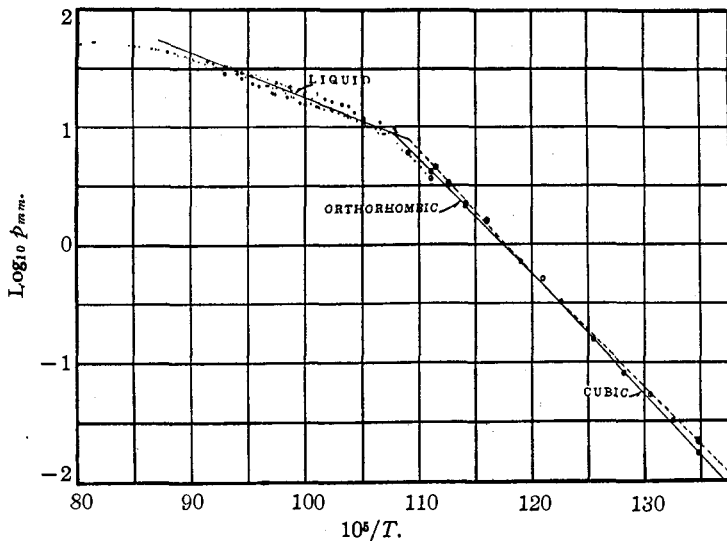

Fig. 2.

and increases in pressure over the whole range of the manometer is shown in Fig. 3, by the close approximation to a straight line.   The chart shows that an increase in 1 g. weight of the downward force on the quartz fiber support corresponds to an increase
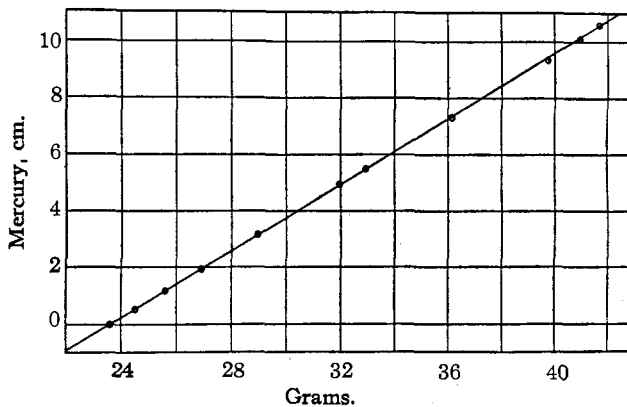

Fig. 3.

of 0.5823 mm. of mercury pressure in the manometer.   Since silica glass has little thermal expansion, the calibration of the apparatus remains practically unaltered over wide temperature ranges.   Moreover, it is obvious that for any other manometer fluid of different density ranging over the same heights of column for which the calibration

was made, the increment of weight above that corresponding to zero pressure will always be proportional to the pressure (measured in mm. of mercury) as determined from the calibration chart with mercury, provided that the bore of the manometer is true to within the accuracy of weighing. This avoidance of density corrections for the manometer fluid at high temperatures is one of the chief advantages of the tensimeter.

Bismuth was chosen as the manometric fluid for making the vapor pressure determinations. It is liquid and has a negligible vapor pressure over the range of temperatures required, and has no stable oxide with a lower dissociation pressure than antimony trioxide. If this latter were not the case bismuth trioxide would be formed in the sample side of the manometer by reaction with the antimony trioxide vapor. The work of Simon and Thaler[8] has shown the dissociation pressure of $(Sb_2O_3)_2$ to be of the order of magnitude of 10^{-8} mm. at $656°$, the melting point. It may also be noted that the free energy of formation of Sb_2O_3 at room temperature as given by Schuhmann[9] is -148.6 Cal., which is considerably greater than the free energy of formation of Bi_2O_3, -119.2 Cal., as calculated from Ditte and Metzner's[10] value of ΔH and the known entropies of Bi,[11] O_2[12] and Bi_2O_3.[11] The observed fact that no bismuth oxide was formed confirms the initial choice of bismuth.

After the manometers were calibrated, the two open ends were sealed onto two silica glass tubes through which pure bismuth and the solid sample of antimony trioxide were introduced into the apparatus. It was found to be very important that both sample and bismuth be completely outgassed before sealing the manometer and again pulling off the evacuating tubes. This was practically accomplished by heating the bismuth to a red heat for a considerable time while maintaining a good vacuum on both sides of the manometer. Finally the sample of antimony trioxide was fused in the small bulb S and the manometer sealed off and disconnected from the evacuating apparatus.

The outgassed and sealed tensimeter was now ready to suspend in the furnace. The furnace was brought up to temperature beforehand so that the danger of the bismuth freezing and breaking the manometer was avoided. At the outset the temperature was such that a weighing corresponding to a negligible pressure of $(Sb_2O_3)_2$ could be determined. The temperature of the furnace was then gradually increased and at regular intervals weighings were taken from which the increase in weight and the corresponding vapor pressures could be obtained. In the course of two or three hours a temperature range from a few degrees below the melting point up to temperatures of about $800°$ was covered. Rapid slagging of the silica glass manometer commenced at this point.

To check the results of the balanced manometer, measurements were also made with a stationary tensimeter in which the height of the manometer columns was read directly. This manometer was similar to the balanced form, but was fixed in a special furnace made of two large electric muffle heaters placed about 2.5 cm. apart in a well-insulated box. The silica glass manometer was in the middle uniform temperature region between the two plates. Bismuth was again used as manometer liquid. Narrow slits covered with clear mica were left open in the two opposite ends of the furnace in order to observe the meniscus of the bismuth in the two arms of the manometer. The lighting of the inside of the furnace was through the slot in the furnace opposite to that through which the cathetometer was sighted. The side of the manometer containing the sample of antimony trioxide was evacuated and sealed. The arm into which the

[8] Simon and Thaler, *Z. anorg. Chem.*, **162**, 253 (1927).

[9] Schuhmann, THIS JOURNAL, **46**, 59 (1924).

[10] Ditte and Metzner, *Compt. rend.*, **115**, 1303 (1892).

[11] Anderson, THIS JOURNAL, **52**, 2720 (1930).

[12] Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

liquid bismuth was displaced was kept connected to an evacuating system during the measurements. The pressures were determined by reading the height of the bismuth column directly with a cathetometer.

In using the stationary tensimeter, corrections for the density of the liquid bismuth at various temperatures are necessary. The data for this were taken from the work of Yoscharu and Maleyama.[13]

Results of Measurements on Liquid Oxide

The method of the balanced manometer furnishes a large number of experimental observations at temperatures differing by small intervals, and it would seem unnecessary to present data for all individual points. Figure 2 shows the individual points obtained. The results of the balanced manometer method are shown as dots and the direct readings as crosses.

The determinations by the balanced manometer method were made on a single sample of oxide with the manometer for which the calibration curve is shown in Fig. 3. Two complete series of determinations were made over the temperature range from 600 to 800°. In a third final series the temperatures were carried to the slagging point of the sample, evidenced by a noticeable vapor-pressure lowering. This occurred at about 800°, as is clearly shown by the falling off of the plotted values at the high temperature end of the liquid-phase curve of Fig. 2. The last series was stopped at 975°, and at this temperature the contamination of the sample with slagged silica was such that there was no further vapor-pressure increase with temperature rise. There exists a range of about 150° over which the vapor pressures of the liquid phase were satisfactorily measurable. Because of the extremely corrosive nature of liquid antimony trioxide and its power to react with materials suitable for apparatus construction, it is doubtful whether the range could be lengthened.

The results obtained with the stationary manometer, shown as crosses in Fig. 2, are in fair agreement with those obtained by the balanced manometer method. Two series of determinations on a single sample were made over a temperature range from 650 to 800°. The first series was made on slowly ascending and the second on a descending temperature–pressure scale. At the completion of the measurements the sample of antimony trioxide solidified crystalline, but analysis showed a molal content of 10% of silica. This large content of silica in the sample may have been partly due to a thin shell of quartz glazed with antimony trioxide which scaled off the inside of the manometer on removing the mass of solidified sample.

Derived Vapor Pressure Data.—Assuming that the data obtained may be expressed by a straight line upon a log p–$1/T$ chart, analytic expressions may be obtained for the various forms of oxide. The vapor pressure of

[13] Yoscharu and Maleyama, *Sci. Repts. Tôhoku, Imp. Univ. 1st series,* **18,** 19–46 (1929).

cubic antimony trioxide as shown in the corresponding curve of Fig. 2 is

$$\log_{10} p_{mm.} = 12.195 - \frac{10,357}{T}$$

that for orthorhombic,

$$\log_{10} p_{mm.} = 11.318 - \frac{9625}{T}$$

and for the liquid

$$\log_{10} p_{mm.} = 5.137 - \frac{3900}{T}$$

where log p is the common logarithm of vapor pressure expressed in millimeters and T is the absolute temperature.

The molal (Sb_4O_6) heats of vaporization at the temperatures of the experiment, calculated from the slopes of the lines of Fig. 2 are as follows: for the cubic modification, $\Delta H = +47,320$ cal.; for the orthorhombic, $\Delta H = +44,080$ cal.; and for the liquid antimony trioxide, $\Delta H = +17,830$

TABLE III

VAPOR PRESSURE OF ANTIMONY TRIOXIDE

Form of Sb_2O_3	Temp., °C.	Pressure in mm. of mercury	$\log_{10} p_{mm.}$
Orthorhombic (metastable)	450	0.010	−2.00
Cubic (stable)	450	.0075	−2.125
Cubic (stable)	475	.0224	−1.650
Cubic (stable)	500	.0625	−1.204
Cubic (stable)	525	.1645	−0.783
Cubic (stable)	550	.406	− .391
Computed Transition Temperature			
Cubic and orthorhombic (stable)	557	0.525	−0.280
Orthorhombic (stable)	575	0.908	− .042
Orthorhombic (stable)	600	2.42	.384
Orthorhombic (stable)	625	3.91	.592
Orthorhombic (stable)	650	7.60	.881
Computed Melting Point			
Orthorhombic (stable)	655	8.50	0.930
Cubic (metastable)	642	(7.43)[a]	.872
Liquid (stable)	675	10.42	1.018
Liquid (stable)	700	13.32	1.125
Liquid (stable)	725	16.90	1.228
Liquid (stable)	750	20.78	1.318
Liquid (stable)	775	25.93	1.414
Liquid (stable)	800	31.76	1.502
Liquid (stable)	825	(38.36)	1.584
Liquid (stable)	850	(45.9)	1.662
Liquid (stable)	875	(54.8)	1.739
Liquid (stable)	900	(64.6)	1.810
Normal boiling point	1456	(760)	2.881

[a] Values in parentheses are extrapolated from curve.

cal. From these data the molal heat of transition of cubic into orthorhombic oxide is $\Delta H_{830} = +3240$ cal., and the molal heats of fusion are 26,250 cal. for the orthorhombic and 29,490 cal. for the cubic. For convenience of reference, vapor pressures as read from the chart of Fig. 2 are shown tabularly in Table III, which shows the vapor and sublimation pressures of the stable modification at 25°-temperature intervals over the determined range.

Summary

1. The vapor pressures of cubic and orthorhombic solid antimony trioxide have been measured between the temperatures 470 and 650° by the gas saturation method.

2. The vapor pressure of liquid antimony trioxide has been determined over the temperature range from 656 to 800°, using a new type of static balanced tensimeter. These values were checked by direct tensimeter measurement.

3. Heats of vaporization and transformation have been calculated from the vapor pressure data.

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THE IONIZATION CONSTANT OF WATER AT 25° FROM THE ELECTROMOTIVE FORCE OF CELLS WITHOUT LIQUID JUNCTION

BY ELLIOTT J. ROBERTS

In view of the fact that all previous determinations of the ionization constant of water by the electromotive force method have involved cells containing liquid junctions, it appeared to be worth while to make a determination involving no liquid junctions. This has been accomplished by a new method, the basis of which consists of the measurement of two electrodes of the second kind, directly against each other in a common solution containing ions requisite to the reversibility of both electrodes.

In the present case, the two electrodes of the second kind were Pt,H_2,-H_2O,OH^- and Ag,AgCl,Cl^-, and the solution in which they were measured was a mixture of sodium hydroxide and sodium chloride. Thus the complete cell was

$$Pt,H_2,NaOH\ (m_1) + NaCl\ (m_2),AgCl,Ag$$
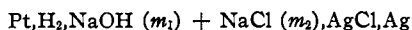
The electromotive force of this cell at 25° may be represented by the equation

$$E = E_a^\circ - E_b^\circ - 0.05915 \log m_{Cl^-}/m_{OH^-} - 0.05915 \log \frac{\gamma_{Cl^-}\alpha_{H_2O}}{\gamma_{OH^-}} \qquad (1)$$