

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE DECOMPOSITION OF THALLIC OXIDE¹

By A. B. F. DUNCAN

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In studies of the thermal decomposition of metallic oxides, relatively little attention has been paid to the influence of particle size on the equilibrium oxygen pressures. L. Wöhler,² in a study of the decomposition of several oxides, observed that the equilibrium pressure of a sample at a fixed temperature was not constant but gradually fell. A. J. Allmand³ attributed this to changes in particle size during heating, while Wöhler claimed that solid solutions of the products with the original oxide were formed. The influence of particle size on the decomposition of carbonates and mercuric oxide has been studied by Centnerszwer and co-workers.⁴

If a sample of oxide is prepared by precipitation in cold solution, or from a hydroxide by dehydration at low temperatures, the sample would usually contain a large proportion of very small particles. If the oxide loses oxygen at low temperatures, at which there is a slow rate of growth of the particles to larger ones, we may obtain apparent equilibrium values which are in error due to the fact that the original solid was not in a thermodynamic steady state. By varying the conditions of precipitation and dehydration we get samples which give different equilibrium pressures at the same temperature. If a quantity of oxygen is withdrawn after the equilibrium pressure is reached and a lower equilibrium pressure is obtained at the same temperature, it cannot be decided whether a solution has been formed or whether a change in the degree of dispersion of the solid has taken place.

Matters are somewhat simplified when we can work with oxides above their melting points. The size of the particles no longer enters the question and any lowering of the decomposition pressure must show solution. Milan has recently studied⁵ the decomposition of vanadium pentoxide above its melting point and found that small quantities of the lower oxide, V_2O_4 , lowered the decomposition pressure of pure V_2O_5 by large amounts.

Experiments on the loss of oxygen by thallic oxide have been made by Lamy,⁶ T. Carnelley and J. Walker,⁷ and O. Rabe.⁸ The behavior of this

¹ From the dissertation submitted by A. B. F. Duncan in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Wöhler, *Z. Elektrochem.*, **17**, 98 (1911).

³ Allmand, *J. Chem. Soc.*, **97**, 618 (1910).

⁴ Centnerszwer and co-workers, *Z. physik. Chem.*, **124**, 225 (1926); **130**, 189 (1927); **132**, 185 (1928).

⁵ Milan, *J. Phys. Chem.*, **33**, 498 (1929).

⁶ Lamy, *Ann. Chem. Phys.*, [3] **67**, 400 (1863).

⁷ Carnelley and Walker, *J. Chem. Soc.*, **53**, (1888).

⁸ Rabe, *Z. anorg. Chem.*, **55**, 136 (1907).

oxide on being heated seems to depend on its method of preparation. If the oxide is prepared from the hydrate, $Tl_2O_3 \cdot H_2O$, it loses oxygen below 100° , before all the water is removed. The brown crystalline modification loses oxygen below 500° , but according to Rabe⁹ the black crystalline modification may be heated for hours at 500° without change. The behavior of Tl_2O_3 heated in a vacuum has not been studied. The decomposition of the oxide is thus seen to depend on the method of preparation, but the brown forms change over to the black by melting under a pressure of oxygen sufficient to prevent decomposition.

Two experimental difficulties are met in the study of the decomposition of thallic oxide. The oxides are chemically active and attack fused quartz, forming silicates, and dissolve platinum and silver. In addition, thallic oxide is somewhat volatile at the temperatures used and would distil into cooler parts of the apparatus, changing the composition of the residue, or react with the fused quartz, leaving an excess of oxygen. In this work a vessel of pure fused magnesium oxide¹⁰ was found to be satisfactory since it was not attacked chemically and apparently not dissolved by the oxides. The pure oxide was molded, sintered at a high temperature and finally heated at 2500° in the induction furnace. The surface was well glazed. The second difficulty was avoided by enclosing the crucible and oxide in a vacuum-tight vessel of pure silver. At high temperatures oxygen quickly diffused through the walls but the thallic oxide could not, so it was all kept at constant temperature. Details in regard to the construction of this vessel are given in the following section.

Apparatus

The apparatus consisted of the fused quartz reaction tube, a water jacketed gas buret, a manometer, a McLeod gage and a mercury vapor pump backed by an oil pump. The pumps could be cut off from the apparatus by a mercury trap.

The manometer was a U-tube, both arms being one meter long. The top of one arm was connected to the reaction tube and gas buret and the other arm led to the McLeod gage and pumps. At the bottom of the U was sealed a tube 80 cm. long, carrying rubber hose and leveling bulb. With the mercury bulb lowered the manometer, reaction vessel and gas buret could be put in connection with the pumps and McLeod gage. By raising the mercury the manometer gave direct pressure readings provided a high vacuum was maintained over the arm connected to the pumps. The manometer and scale to which it was fixed was calibrated. The fused quartz reaction tube is shown in Fig. 1. The platinum-platinum-10% rhodium thermocouple was in the inner fused quartz tube and the hot junction about three millimeters from the silver cup, well in the zone of constant temperature of the furnace. Temperatures were measured on a Leeds and Northrup portable potentiometer, and are considered accurate to 3° . The platinum furnace has been described.¹¹ The gas buret and fused quartz tube were connected to

⁹ Rabe, *Z. anorg. Chem.*, **48**, 431 (1906).

¹⁰ We are indebted to the Bureau of Standards, Pyrometer Division, for their cooperation in making this vessel.

¹¹ Morse and Frazer, *Am. Chem. J.*, **32**, 93 (1904).

the manometer by graded seals. The volume was made as small as possible by the use of capillary pyrex tubing. The space within the quartz-pyrex graded seal was taken by a closely fitting glass tube sealed at both ends.

The silver cup was designed so that it could be filled with oxygen at atmospheric pressure and sealed in that condition. The silver was specially purified in this Laboratory. The bottom cylindrical cup was 5 cm. high, 2.5 cm. in diameter, 0.17 mm. thick and was spun in one piece. The top, also spun in one piece, had a rim projecting upward 1.5 cm., and fitted closely in the cup. In the center of the top was a cone which had a small hole in the tip.

Sealing the Silver Cup.—A weighed sample of thallic oxide was placed in the magnesia crucible which was placed in the silver cup. The top was put in place and fused to the cup with a small oxygen-gas flame, without the use of solder. During this operation, the cup was partly immersed in water.

After sealing, the cup was placed in the pyrex tube shown in Fig. 2, which was sealed to the manometer and gas buret. Then with the lower stopcock closed and the upper opened the apparatus, including the interior of the silver cup, was thoroughly pumped out. Then the volume of the apparatus was found by admitting a known quantity of air and measuring the pressure. The air was pumped out and oxygen (99.8%) was admitted to atmospheric pressure. Then a rapid stream of oxygen was started from a tank through a rubber tube. The upper stopcock was closed. The rubber tube was fitted on the lower stopcock, which was quickly opened and the ground joint disconnected. With oxygen rapidly passing upward around the cup the hole was closed as tightly as possible by pressing the tip of the cone with pliers. Then the cup was taken out and the tip sealed by melting in the oxygen-gas flame. The cup was replaced in the pyrex tube, the apparatus pumped out and the volume of the apparatus again determined. The volume was shown to be much less and the decrease in volume minus the volumes of silver, magnesia and thallic oxide gave the oxygen inclosed.

Preparation of Thallic Oxide.—The method of preparing black crystalline thallic oxide given by Rabe⁹ was used with slight modification. The product was washed with 5 *N* nitric acid, then with hot water until free from acid and dried at 120°. It was later fused under an oxygen pressure greater than the decomposition pressure. The product used consisted of well-defined black needles.

Experimental Procedure

The silver cup after sealing was sealed inside the fused quartz container shown in Fig. 1. This was packed in the furnace and then sealed to the apparatus. The total volume of the reaction system was found by admitting a known quantity of air and reading pressure after the mercury had been raised above the gas buret to a mark on the capillary tubing.

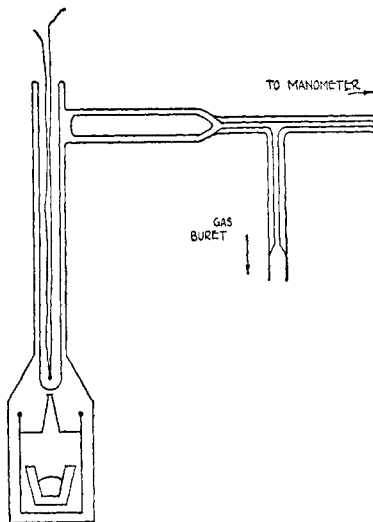


Fig. 1.

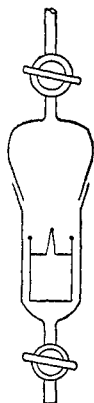


Fig. 2.

The reaction tube was evacuated for several days with the furnace heated to 450°. The furnace was brought to 750° and oxygen admitted from the gas buret to 760 millimeters' pressure. After heating at this temperature and pressure for several hours, the furnace was slowly cooled, the oxygen pressure being kept constant at 760 millimeters. The system was pumped out. The mercury was raised above the stopcock of the gas buret and the manometer set; then the following experiments were made.

The oxygen pressures at five different temperatures were measured. To insure equilibrium the temperature was kept constant until there was no further change in pressure. The temperature was increased for a time and then changed to its former value, at which the pressure also assumed its former value. Pressures were measured to the nearest millimeter. After cooling very slowly to room temperature the pressure remaining was less than one millimeter.

The furnace was heated and the mercury drawn back into the gas buret. When a sufficient quantity of oxygen had collected, a definite volume at known temperature and pressure was withdrawn from the system by closing the stopcock of the buret. The mercury was raised above the stopcock and the furnace slowly cooled. The melt contained a mixture of thallic and thalious oxides and the composition was fixed by the oxygen removed.

The oxide mixture was heated at the same temperatures that were used previously and measurements of the equilibrium pressures were obtained. At the conclusion another definite quantity of oxygen was removed. Four series of pressure measurements were made, representing the decomposition of the pure oxide and three different mixtures of the two oxides.

During the fifth series of measurements erratic results were obtained and after a short time the reaction tube broke. It was found that the melted oxides had crept over the sides of the magnesia crucible, made a hole in the bottom of the silver cup and then a hole in the quartz glass. Thalious oxide vapor does not attack silver, for the upper part of the cup was quite clean.

The total volume of the apparatus from the zero mark of the manometer was known to be 57.94 cc. The volume outside the furnace was measured by filling with mercury and weighing. It was found to be 8 cc. The volume in the hot portion was then 49.94 or 50 cc. One centimeter of the manometer contained 0.135 cc. The total volume at room temperature was then $8 + 0.135$ times the pressure reading.

Results

In Table I are recorded the oxygen pressures at different temperatures. From the temperatures and volumes of the different parts of the apparatus the number of moles of oxygen at the equilibrium pressures may be calculated. The moles of oxygen will give directly the Tl_2O present, and since the original weight of Tl_2O_3 is known, the mole fraction of Tl_2O may be calculated.

As an example is shown the calculation of the moles of oxygen in equilibrium with a mixture of thallic and thalious oxides at 676°, after the first quantity of oxygen had been withdrawn.

At the beginning of the work, the cup was full of oxygen at atmospheric pressure, which was 0.000692 mole. The first oxygen withdrawn from the system totaled 0.00175 mole. Then actually the difference, 0.001058 mole, was removed from the Tl_2O_3 . There was originally 0.01567 mole of Tl_2O_3 present. Then the composition of the mixture before heating

to 676° was Tl_2O_3 , 0.014612 mole; Tl_2O , 0.001058 mole. At the temperature under consideration the oxygen present was given by the expression

$$N_{O_2} = \frac{p_{O_2}}{R} \left(\frac{V_h}{T_h} + \frac{V_c + V_m}{T_r} \right)$$

where v_h is the volume in the furnace, v_c that outside the furnace up to the zero mark of the manometer, v_m the volume in the manometer, T_h the furnace temperature, T_r the prevailing room temperature and p_{O_2} the oxygen pressure in atmospheres.

$$N_{O_2} = \frac{3.9}{76 \times 82.07} \left(\frac{50}{949} + \frac{8 + 0.527}{295.5} \right) = 0.000051$$

$$\text{Moles of } Tl_2O = 0.000051 + 0.001058 = 0.001109$$

$$\text{Mole fraction of } Tl_2O = \frac{0.001109}{0.01567} = 0.0708$$

Thus a solution 7.08 mole per cent. of Tl_2O is in equilibrium with oxygen at a pressure of 3.9 cm. at 676°.

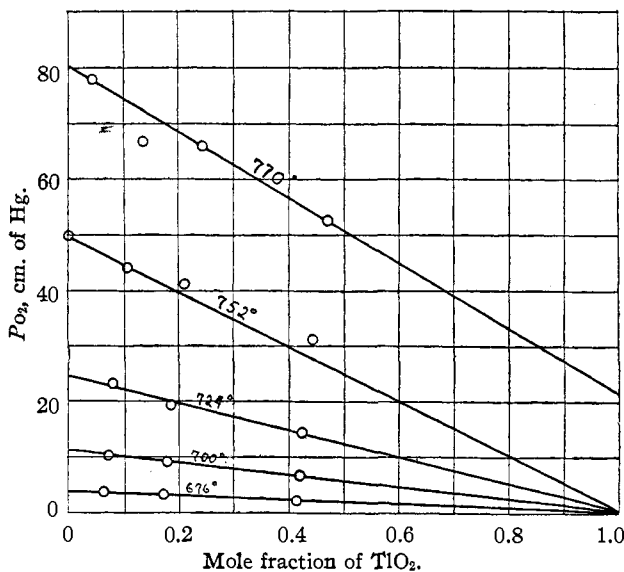


Fig. 3.

From the calculated values of the mole fraction of Tl_2O a pressure-composition diagram was plotted, which is shown in Fig. 3. The isotherms are apparently straight lines over a long pressure range. By extrapolating these lines to zero mole fraction of Tl_2O , the decomposition pressures of pure Tl_2O_3 are obtained. These values are given in Table II.

The equilibrium constant for the reaction $Tl_2O_3 = Tl_2O + O_2$ may be calculated from these pressures at different temperatures since K_p under

these conditions is equal to the oxygen pressure over pure Tl_2O_3 . Values of K_p are given. Pressure-temperature curves for any mixture of the two oxides could be constructed from values read from the pressure-composition curves.

TABLE I
OBSERVED DATA

Temp., °C.	Press., cm.	Moles of O_2	Mole fraction of Tl_2O
Moles of Tl_2O_3 originally present, 0.01567; Moles of O_2 originally present, 0.000692			
676	19.5	0.000277	...
700	25.6	.000370	...
724	31.7	.000465	...
752	48.8	.000767	0.00479
770	77.8	.00138	.0440
Oxygen removed = $0.00175 - 0.000692 = 0.001058$; composition of residue (mole fraction of Tl_2O) = 0.0675			
676	3.9	0.0000510	0.0708
700	10.1	.0001345	.0762
724	23.4	.000330	.0886
752	43.9	.000676	.1109
770	66.4	.001124	.1395
Oxygen removed = 0.00173 mole; composition of residue = 0.178			
676	3.3	0.0000429	0.181
700	8.5	.000112	.185
724	18.8	.000258	.1945
752	41.0	.000622	.218
770	66.0	.00111	.249
Oxygen removed = 0.00382 mole; composition of residue = 0.422			
676	1.8	0.0000233	0.4232
700	6.4	.0000837	.4270
724	14.2	.000191	.4339
752	20.7	.000443	.4500
770	52.4	.000830	.4760

TABLE II
DECOMPOSITION PRESSURES OF PURE Tl_2O_3

Temperature, °K.	949	973	997	1025	1043
Pressure, cm. of Hg	4.2	11.5	25.5	50.0	80.0
K_p , atm.	0.0552	0.1515	0.338	0.656	1.052

TABLE III
VALUES

T , °K.	$-R \ln K$	$1/T$	ΔH	ΔF
949	5.7736	0.001055	77,000	5479
973	3.77436	.001028	71,400	3672
997	2.16942	.001002	77,000	2163
1025	0.3432	.000977	77,000	352
1043	-0.10138	.000958	-106

The heat of the reaction within the temperature range studied may be found by plotting $-R \ln K$ against $1/T$, shown in Fig. 4. Four of the five points fall on a straight line. The slope of the line at any point gives the heat of the reaction at that temperature. From the equilibrium constants the free energy of the reaction at certain temperatures was calculated. Values of the heat of the reaction and the free energy are given in Table III.

The Melting Point of Thallous Oxide

Reference to the composition-pressure diagram shows that unless Tl_2O_3 melts below $715-710^\circ$, the melting point cannot be determined in air, since the decomposition pressure at 720° is 25.5 cm., while the partial pressure of oxygen in air is about 16 cm. This shows that former determinations must be in error due to the presence of Tl_2O . In addition, former determinations were made in glass, and the silicates formed must have contaminated the oxide.

The determination was carried out in the apparatus illustrated in Fig. 5. This was joined to the system used in the study of the decomposition pressures in the place formerly occupied by the reaction vessel. About 6 g. of black crystalline thallic oxide was placed in a fused magnesia crucible, which had been sealed previously inside a fused quartz bulb. The bulb was joined to the rest of the apparatus by a graded seal. The hot junction of the platinum-platinum-rhodium thermocouple was immersed in the oxide. The wires were insulated by fused quartz beads and led out of the apparatus through seals of de Khotinsky wax.

An oxygen pressure of one atmosphere was maintained over the oxide during the measurements. Readings of temperature and time were taken and cooling curves plotted. Five determinations were made. The first curve, because of too rapid cooling, showed no break. The next three showed breaks at 715 , 717 and 717° . The last showed two breaks, one at 718° , and an indefinite break at about 730° . The melting point is considered to be $717 \pm 5^\circ$.

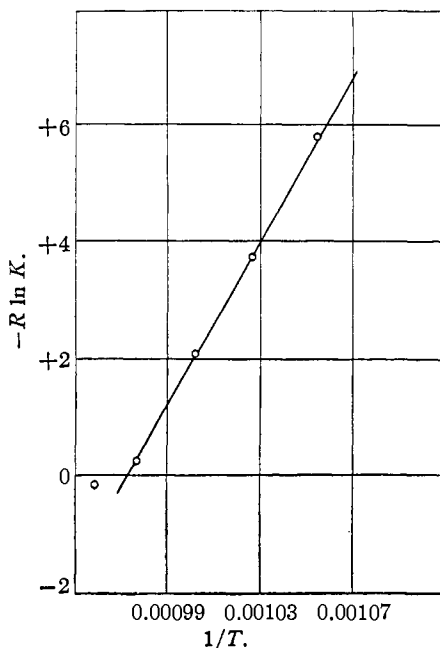


Fig. 4.

At the end of the fifth determination the fused quartz tube cracked and the thermocouple wires were found to be badly attacked. This probably accounts for the irregularity observed in the fifth determination.

Discussion

From the results obtained it is evident that the oxygen pressures are dependent not only on the temperature but also on the composition of the mixed oxides in equilibrium with the oxygen. If this were not the case the isotherms would have all been parallel to the composition axis. In this respect the decomposition of thallic oxide differs from the decomposition of silver oxide, mercuric oxide and cupric oxide, in which two condensed phases are present. The decomposition of ferric oxide, barium peroxide and vanadium pentoxide^{12,5} gives only one condensed phase, a solid or liquid solution, depending on the temperature. Thallic oxide is to be classed with these latter oxides.

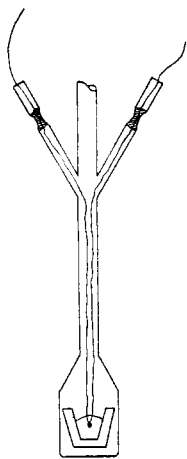


Fig. 5.

It is interesting to note that the isotherms on the pressure-composition diagram are straight lines over large variations in composition. If we apply Raoult's law to this system we find that the ratio of p_{O_2} (which is directly related to the vapor pressure of Tl_2O_3) to the mole fraction Tl_2O_3 is almost constant at constant temperature. Raoult's law seems to be obeyed in this case. This may be due to chemical similarity of the two oxides. Both are basic and show no acidic properties. Although both are polar compounds, the fields of force about the two kinds of molecules may not be different enough to cause wide departures from Raoult's law. In contrast, V_2O_5 is more acidic than basic and V_2O_4 , the lower oxide formed by its decomposition, is basic. In the study of the decomposition of V_2O_5 wide variations from Raoult's law were found. We have no evidence that these oxides are associated or dissociated in solution. We have calculated the composition curve assuming that for every mole of oxygen in the gas phase there dissolves one mole of Tl_2O in Tl_2O_3 . If either oxide were polymerized, the oxygen pressures would be the same but the mole fractions of Tl_2O differ, giving a different pressure-composition diagram. There seems to be no special reason why this should be the case, but it must be admitted as a possibility.

An examination of the 770° isotherm shows that the best straight line does not cut the 100 mole per cent. Tl_2O line at $p = 0$, as do the other

¹² Lewis, *THIS JOURNAL*, **28**, 139 (1906); Keyes and Hara, *ibid.*, **44**, 479 (1922); Hulett and G. B. Taylor, *J. Phys. Chem.*, **17**, 567 (1913); Smyth and Roberts, *THIS JOURNAL*, **42**, 2582 (1920); Sosman and Hostetter, *ibid.*, **38**, 807 (1916); Hildebrand, *ibid.*, **34**, 246 (1912).

isotherms. The line may be correct as drawn, indicating dissociation of the lower oxide. There are no data on the dissociation of Tl_2O at these temperatures. Or the line may cut the composition axis at mole fraction $Tl_2O = 1$, and the observed equilibrium values displaced from the true ones because of volatilization of the lower oxide from the solution at this high temperature, which would make the solution less concentrated in Tl_2O than is determined from the oxygen pressures. In general, the 770° isotherm does not seem to be as dependable as the other four. Furthermore, the value of the equilibrium constant obtained from the extrapolation of this curve does not fall on the straight line with the other four as shown in Fig. 4.

It is unfortunate that the heat of reaction and free energy values cannot be extrapolated to low temperatures with any degree of accuracy, but these quantities change very rapidly with temperature and an accurate knowledge of the specific heats and their variation with temperature is needed. Values for Tl_2O_3 could perhaps be determined using a sufficient pressure of oxygen to prevent decomposition, but the determination of the values for Tl_2O at these high temperatures does not seem practicable.

One of the handicaps to this work has been the lack of information about the physical and chemical properties of pure Tl_2O . Indeed, it is doubtful whether pure dry Tl_2O has ever been prepared. Its preparation, purification and any subsequent transference must be carried out in the absence of oxygen and carbon dioxide. This, coupled with its volatile nature at high temperatures, makes a study of the pure oxide very difficult.

In conclusion, the author wishes to express appreciation to Dr. J. C. W. Frazer and to Dr. W. A. Patrick, who suggested this study and under whose direction it was done.

Summary

The equilibrium pressures of oxygen over thallic oxide and mixtures of thallic and thallic oxide have been determined, from which a pressure-composition diagram has been constructed.

The equilibrium pressures of oxygen depend both on the temperature and the composition of the mixture of oxides.

Thallic oxide dissolves in thallic oxide, forming solid and liquid solutions.

The solutions of the oxides appear to obey Raoult's law over the concentration range investigated.

The melting point of thallic oxide has been redetermined, and found to be $717 \pm 5^\circ$.

Values for the heat of the reaction and the free energy change are calculated for several temperatures.