iron alloys is no doubt closely connected with the high kindling temperature of the pure metal. The marked pyrophoric properties of cerium and its alloys is similarly, no doubt, due to the low (130°) kindling temperature of that metal.

Summary

1. Metallic lanthanum was prepared by the electrolysis of the fused chloride with various amounts of potassium fluoride and sodium chloride.

2. The metal prepared by the use of a tungsten cathode did not contain tungsten. Metal prepared in iron cells was always contaminated with iron.

3. The metal is easily corroded in even dry air. Some of its physical constants are as follows: m. p., 826°; d^{15} (absolute alcohol), 6.1598; Brinnell hardness (500 kg. weight), 37; heat of combustion, 1645 cal. per g.; kindling temperature, 445°. The metal is not pyrophoric. Its alloys with iron are harder than the pure metal, and are not pyrophoric.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

VAPOR PRESSURE OF COPPER OXIDE AND OF COPPER

BY EDWARD MACK, GERARD G. OSTERHOF AND HOBART M. KRANER

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In his research on the subject of negative catalysis, Titoff[1] showed that copper in extremely small amounts causes a very great increase in the velocity with which a solution of sodium sulfite is oxidized to sulfate in the presence of dissolved oxygen, the reaction being $2Na_2SO_3 + O_2 = 2Na_2SO_4$. The velocity of this reaction responds in such a sensitive manner to the presence of the merest trace of copper that when a clean strip of copper is dipped into water for about a minute, the copper which is thus dissolved produces a measurable difference in the velocity constant of the reaction. In fact, Titoff found that the addition of enough copper sulfate to the sodium sulfite system to give a 10^{-9} *M* solution of copper ions made a considerable change in the velocity constant.

The present paper is the account of an attempt which we have made to apply this sensitive method of measuring concentrations of copper to the determination of the vapor pressure of copper oxide and also of copper itself, at much lower temperatures than any hitherto reported in the literature. The method is so extremely sensitive that it is easily open to error, and we cannot claim much more for our figures than that they give a qualitative idea of the vapor pressure at the respective temperatures. In view, however, of the scarcity of data in this field, the approximate results which we have obtained are of considerable interest.

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[1] Titoff, *Z. physik. Chem.*, **45**, 641 (1903).

We have first repeated some of Titoff's work with substantially the same results. We have found it almost impossible, as he did, to obtain duplicate values of the velocity constant in experiments run on different days, and at different times of the year, due to the great difficulty of excluding traces of copper, tin, iron and other materials which affect the velocity. A good grade of conductivity water ($0.5-1.1 \times 10^{-6}$ mhos) was always used, and extraordinary precautions were taken in cleaning the reaction vessels.

Experimental

The vapor pressure was determined by the dynamic method.

In the case of copper, a vertical silica tube of 1.2 cm. bore and 30 cm. in length, drawn out at the lower end into a smaller tube with a 0.2 mm. opening, was heated by a Nichrome wire furnace, placed as shown in Fig. 1. A core of copper turnings, free from all small pieces, was packed into the middle of the tube, and supported by a roll of copper gauze which was hung from the top of the silica tube by the wire H. In the case of copper oxide, the silica tube was bent to a right angle at B, so that it could lie horizontally. A core, 2 cm. long, of wire-form copper oxide, such as is used in organic combustion, was packed into the middle of the tube, with a stop made of copper gauze 1.5 cm. long, at each end of the core; the copper stops were later oxidized. The copper oxide was free from dust, and the *horizontal* position insured that none of the scale, which might come off, would fall into the water tube W.

The temperature was measured with a calibrated platinum—platinum-rhodium thermocouple, placed at the side of the silica tube inside of the furnace. We succeeded in heating *copper oxide* at 4 different temperatures and in keeping the temperature very constant for a little more than 3 hours at 600° (±10), 800° (±6), and 900° (±5), and for 1 hour at 1000° (±1), as measured by the thermocouple.

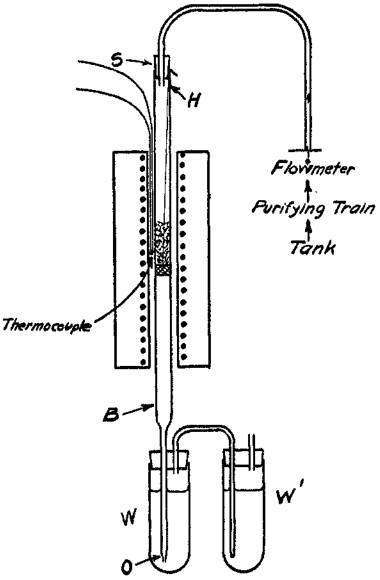

Fig. 1.

The *copper* was heated to an average temperature of 810° for 4 hours, and the temperature did not vary more than 20°, except at the beginning when it rose to 850° for 10 minutes, and once near the middle of the experiment when it rose again to 850° for 5 minutes.

A stream of nitrogen from a tank was purified by passage through a train of bottles (sulfuric acid, alkaline pyrogallol, sticks of potassium hydroxide in 2 towers and a trap), and then made to flow over the copper core at a rate of 50 cc. per minute, measured by a calibrated flow-meter. With copper oxide, oxygen from a tank was used. In both cases the inert gas, carrying the vapor from the copper or from the copper oxide, bubbled out of the small orifice O through the water columns W and W′. The rubber stopper S was kept cool by a jet of cold air directed against the silica tube just below S. We suspected at first, from the work of S. W. Young[2] with another catalytic oxidation reaction, that the presence of rubber stoppers or of rubber tubing in the system might make a disturbance in the catalytic effect of the copper solutions, but our tests showed that this was not the case.

Knowing the rate of flow of the inert gas, the temperature of the core, and the amount of material evaporated from the core and absorbed by the water columns W and W′, the vapor pressure of the material in the core may be calculated, provided the following three assumptions hold: (1) the inert gas passing through the core becomes *saturated* with the vapor from the core; (2) the vapor actually *reaches* the water columns without condensing on the walls of the silica tube; (3) the water columns absorb *all* of the vapor.

(1) Von Wartenberg[3] has employed the dynamic method to measure the vapor pressures of such metals as silver, lead and thallium at temperatures above their melting points. The loss in weight suffered by the molten metal in a small boat placed in a heating tube, when a known volume of inert gas had passed over the surface of the metal, was determined. Von Wartenberg found that the vapor was *not saturated* unless the rate of flow of the gas was quite small. For example, in the case of lead at 808°, a rate of flow of 83.4 cc. per minute gave only 72% saturation; 55.7 cc. per minute, 79%; 41.7 cc. per minute, 85%; 27.8 cc. per minute, 90%; all on the basis of an extrapolated vapor 100% saturated at zero rate of flow. In our own experiments the area of the surface exposed by both the copper and the copper oxide was very much larger (90 sq. cm. for copper, 50 sq. cm. for the oxide) than that of the metal in von Wartenberg's boat. It seems reasonably certain that at the rate of 50 cc. per minute the inert gas was saturated with the vapor from the core. (2) The difference in temperature between the core and the water columns, which were kept at about 0° by an ice pack, was great and it is possible that some of the vapor may have condensed on the cooler portions of the silica tube. (3) In the case of copper oxide, more than 99 times as much copper oxide was absorbed in Column W than in W′, and it is then fair to assume that practically all of the oxide vapor was caught. With copper, however, the result was not so good. Only 1.3 times as much was caught by W as by W′; consequently, some unabsorbed copper vapor may have passed through the second tube.

All three of the above possible errors would tend to give low values for the vapor pressure, so that the vapor pressures of copper oxide and of copper are at least as great as the values we have found, and may be greater.

To determine the amounts of copper and copper oxide absorbed in solution in W and W′, several reaction flasks of about 500 cc. capacity made of either Jena or Pyrex glass, were washed with boiling hot conc. hydrochloric acid, sodium hydroxide and sulfuric

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[2] Young, THIS JOURNAL, **23**, 119 (1901).

[3] Von Wartenberg, *Z. Elektrochem.*, **19**, 482 (1913).

acid solutions, rinsed with distilled water and finally steamed for several hours. Into each one of these flasks was put 198 cc. of conductivity water, which had first been boiled and then saturated with pure oxygen at 0°. To this was then added 25 cc. of the solution containing the dissolved copper to be tested, together with 25 cc. of conductivity water, making a total volume of 248 cc. in the reaction vessel. When cooled to 0°, 2 cc. of 0.5 *N* sodium sulfite solution was added, and after the mixture had been thoroughly shaken, 25 cc. was removed with a pipette and added to 25 cc. of 0.01 *N* iodine solution. By titration of the excess iodine with 0.01 *N* sodium thiosulfate solution, the concentration of the unchanged sodium sulfite was calculated. Tests were taken at various intervals of time and the velocity constant of the reaction determined from the equation, $K = 1000 \times \frac{\log A - \log B}{t}$, where A is the initial concentration of sodium sulfite, B is the concentration at the time of test, and t is the time in hours from the beginning.

TABLE I

OXIDATION OF SODIUM SULFITE SOLUTION BY CONDUCTIVITY WATER WITHOUT THE ADDITION OF COPPER

Time hours	$Na_2S_2O_3$ 1 cc. = 0.9861 cc. 0.01 N I	Na_2SO_3 concn. in g.-equiv.	Velocity constant K
0.000	1.100	0.005673	..
0.180	1.21	0.005590	(35.6)
0.682	11.62	0.005429	28.0
1.182	12.04	0.005268	27.2
2.192	12.86	0.004940	27.4
3.697	14.04	0.004472	27.9
5.195	15.22	0.004009	29.0
6.618	16.43	0.003491	31.9
		Av.	28.6
		Maximum deviation	3.3

We have found values for K_{H_2O}, using conductivity water, varying from 6 to 81, and Titoff gives a list of 17 values from 10.4 to 71.

Enough copper sulfate was added to the reaction flask in different runs to make the solution 10^{-9} N, 2×10^{-8} N, 10^{-7} N and 10^{-6} N, and the value of K determined for each solution. The velocity constants for the copper K_{Cu} were obtained by subtracting K_{H_2O}, the velocity constant when no copper is added, from each $K_{solution}$.

TABLE II

EFFECT OF VERY DILUTE COPPER SOLUTIONS

$CuSO_4$ soln. N	Av. $K_{solution}$	Av. K_{H_2O}	Av. K_{Cu}	Max. deviation[a]
10^{-9}	71.4	11.6	59.8	2.4
2×10^{-8}	220	81	139	6.6
10^{-7}	230	81	149	5.6
10^{-6}	362	43	319	(only one value)

[a] This number is the sum of the maximum deviation for $K_{solution}$ and K_{H_2O}.

Titoff showed that K_{Cu} was a linear function of the concentration of the copper up to 5×10^{-8} N, and that above this point while it still gave a linear relation, the slope of the line was less than before (plotting K_{Cu}

as ordinates and concentration as abscissas). We have obtained a curve which at first rises sharply, flattens at about $10^{-8}\,N$ copper concentration, and from that point to $10^{-6}\,N$ gives a linear relation. This divergence from Titoff's results is probably due to the presence of a small amount of tin, as the conductivity water used was taken from a block tin condenser, but this should not interfere with our calculations.

Calculations

The vapor pressure of the copper oxide was calculated with the equation: $p = \frac{\text{moles CuO}}{\text{moles CuO} + \text{moles } O_2} \times 760$ mm. The number of moles of copper oxide collected in the solution in tube W was determined by finding the velocity constant K_{Cu}, and comparing this with the values of K_{Cu} found for known concentrations of copper. The comparison gave an interpolated value for the concentration of copper in the tube W. The number of moles of oxygen was computed from the total volume of gas (reduced to standard conditions) which passed over the heated copper oxide core. The calculations for copper were made in the same way.

Table III

Vapor Pressure of Copper Oxide

		Av. K_{Cu}	Max. deviation	Interp. value for quant. of Cu in tube W Moles	Inert gas passed through core Moles	Vapor press. Mm.
CuO at	600°	30.3	0.4	7.6×10^{-11}	0.432	1.34×10^{-7}
	800°	171	1	6.5×10^{-8}	0.429	1.15×10^{-4}
	950°	362	(only one value)	3.7×10^{-7}	0.412	6.8×10^{-4}
	1000°	149	2.6	1.5×10^{-8}	0.133	0.86×10^{-4}
Cu at	810°	40.6	3.1	3.4×10^{-10}	0.477	5.4×10^{-7}

Discussion of Results

Von Wartenberg attempted the determination of the vapor pressure of copper by the dynamic method, but even at a temperature as high as 1360° the loss of weight from molten copper in a boat was too small to be measured with a balance. Apparently, the only available data are those of Greenwood,[4] who determined the vapor pressure of copper by a boiling-point method and gives the values 98.8 mm. at 1980°, 258.4 mm. at 2180°, and 760 mm. at 2310°. In Fig. 2, Greenwood's values have been expressed graphically according to the scheme used by Johnston,[5] in which the logarithms of p in mm. are plotted as abscissas against $1000/T$ as ordinates, where T is the absolute temperature. Our own figure for the vapor pressure of copper at 810° (plotted as a small square), *almost 1200° lower than the lowest temperature at which Greenwood worked,* is in quite good

[4] Greenwood, *Proc. Roy. Soc. London,* **83A,** 486 (1910).

[5] Johnston, *J. Ind. Eng. Chem.,* **9,** 876 (1917).

agreement with the extrapolated value. The values for the vapor pressure of cupric oxide are plotted with circles. Substitution of the values at 600° and 800° in the integrated Clapeyron-Clausius equation, $\log p_2 - \log p_1 = \frac{H}{R} \cdot \frac{T_2 - T_1}{T_1\ T_2}$, integrated on the assumption that H, the heat of vaporization, does not vary with change of temperature, gives about 63,000 calories for heat of vaporization of copper oxide. The assumption is made in this calculation that there is no dissociation of copper oxide at 800°. This is supported by the recent data of Smyth and Roberts,[6]

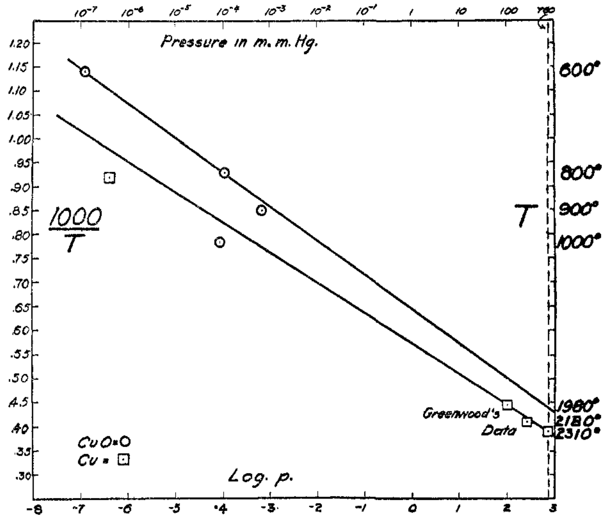

Fig. 2.

who give the dissociation pressure of oxygen in the system 4 CuO (s) $\rightleftarrows$ $2Cu_2O(s) + O_2$, as 12.5 mm. at 900°, about 3 mm. at 838°, and about 1 mm. at 800°. This is also in agreement with the work of Foote and Smith.[7]

For copper, the heat of vaporization has been calculated by Johnston[5] to be 75,000 calories. The line drawn through the points at 600° and 800°, and extrapolated to atmospheric pressure, gives a (hypothetical) boiling point of 2000° for copper oxide as compared with 2310° for copper. Of course, cupric oxide decomposes completely into cuprous oxide far below its boiling point, in fact, much below its melting point, even when the oxygen pressure is atmospheric (750 mm. in our silica tube).

It will be seen from Fig. 2, that the values which we have obtained for the vapor pressure of copper oxide at 900° and 1000°, do not fall on the extrapolated line, but considerably to the left of the line. An interpreta-

[6] Smyth and Roberts, THIS JOURNAL, 42, 2603 (1920).

[7] Foote and Smith, *ibid.*, 30, 1344 (1908).

tion which might be put upon this divergence is that the cupric oxide begins to dissociate at about 900°. In the neighborhood of 1000° we are no longer measuring the vapor pressure of cupric oxide, but of cuprous oxide, or of a solution of cuprous and cupric oxides. Unfortunately for this interpretation, however, Smyth and Roberts have shown that solid solution of cuprous oxide in cupric oxide does not take place in the temperature range where both oxides remain solid. Furthermore, the same authors have shown that the dissociation temperature of cupric oxide in equilibrium with oxygen gas at a pressure of 750 mm. is about 1100°, instead of 900°.

It is hardly to be expected, however, that the method which we have described is reliable enough, especially at the higher temperatures, to justify conclusions of more than a qualitative nature.

Summary

1. Using a catalytic method of determining copper in extremely small concentrations, the vapor pressure of copper oxide has been determined by the dynamic method at four temperatures, and found to be about 1×10^{-7} mm. at 600°, 1×10^{-4} mm. at 800°, 7×10^{-4} mm. at 900°, and 1×10^{-4} mm. at 1000°.

2. The calculated heat of vaporization for copper oxide in the range 600–800° is 63,000 calories.

3. The vapor pressure of copper at 810°, almost 1200° lower than for any previously recorded data, is at least 5×10^{-7} mm.

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[Contribution from the Chemical Laboratory of the University of Michigan]

THE ELECTROMETRIC TITRATION OF THE HALIDES IN THE PRESENCE OF ONE ANOTHER

By H. H. Willard and Florence Fenwick

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I. The Determination of Total Halide by Titration with Silver Nitrate

The usual silver titration of the halides and thiocyanate can be made more accurate and simple by using the electrometric indicator.[1] The break at the end-point with the bimetallic electrode system previously described[2] decreases in magnitude as the solubility of the silver salt increases and is, therefore, poorest in the titration of chloride. The end-

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[1] Behrend, *Z. physik. Chem.*, **11**, 485, 466 (1893). Dutoit and v. Weisse, *J. chim. phys.*, **9**, 578 (1911). Treadwell and Weiss, *Helvetica Chim. Acta*, **2**, 672, 680 (1919). Pinkhof, "Over de toepassing der elektrometrische titraties," *Dissertation*, Amsterdam, **1919**. Liebich, "Die potentiometrische Bestimmung von Chlor, Brom und Jod," *Dissertation*, Dresden, **1920**.

[2] This Journal, **44**, 2516 (1922).