JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 55 MAY, 1933 NUMBER 5

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, AT THE UNIVERSITY OF CALIFORNIA]

The Vapor Pressure of Cadmium Oxide[1]

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The determinations of cadmium oxide vapor pressure described in this article were carried out as a part of the general program of the Pacific Experiment Station of the U. S. Bureau of Mines, in its study of the thermodynamic properties of metallurgically important materials, particularly oxides and sulfides. Aside from possible theoretical interest, the vapor pressure of cadmium oxide is of considerable importance in connection with the metallurgical treatment of cadmium-containing fumes and dusts produced as by-products in the metallurgy of lead and zinc. The technical use of cadmium metal has had substantial growth in the last decade, and may be expected to continue under future normal conditions. Concentrated deposits of cadmium ores are not known in nature, and commercial metal is recovered from a small percentage (0.2 to 0.4) contained in most zinc and many lead ores.

Previous Work.—Older references in the literature on the volatility of cadmium oxide are in considerable disagreement. More recently Feiser[3] has determined several points on a vapor pressure curve for CdO at temperatures from 1000 to 1200°. These points are in fair agreement with the present work, considering that a loss in weight method was used by Feiser to determine vapor pressures, and that the work consequently was subject to considerable error and difficulty in manipulation.

Preparation of CdO.—About 20 g. of C. P. cadmium oxide was placed in a large platinum crucible and heated for several hours in air in an electric pot furnace at 1200° to cause crystal growth and to remove water and volatile impurities, the previously yellow powder becoming a dark bluish-brown, fine crystalline mass. On crushing it appeared completely homogeneous under a microscope, but the crystals were so small that no determination of their form could be made. After the vapor pressure measurements a portion of the material used was reëxamined and shown to be physically and chemically unchanged.

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(3) Feiser, *Metall u. Erz*, **26**, 280 (1929).

Method.—The inert gas saturation method was used to determine the vapor pressure of CdO. The same method was used successfully in determining the vapor pressures of two solid modifications of Sb_2O_3[4] and was practically identical with that used by Eastman and Duschak,[5] so that it need not be described again. One essential modification which was made, however, consisted in fitting the apparatus with a condenser tube of very light mass (about 1-mm. bore), which could be weighed on a button balance, sensitive to 0.01 mg. Experiments of long duration were unsatisfactory because of the slight corrosive action of cadmium oxide vapor on the silica weighing tube, even at partial pressures of the oxide of the order of magnitude of one millimeter.

Vapor Pressure Measurements.—The vapor pressure determinations were carried out over a range of temperature from 860 to 1040°. The upper limit was determined by the temperature at which the silica glass apparatus began to show a slight devitrification. The lower limit was determined by the accuracy with which small amounts of sublimed cadmium oxide could be weighed in the condensing tube. Weighings were made on deposited samples as little as 0.00008 g., which at 867° and for the volume of nitrogen saturated corresponded to a vapor pressure of 0.08 mm. A number of experiments were made at each temperature, decreasing the rate of flow of the nitrogen through the saturator, ensuring conditions for complete saturation of the inert gas by the cadmium oxide. The weight of condensed cadmium oxide varied between 0.00008 and 0.00378 g., and the nitrogen saturated between 0.0043 and 0.011. The total pressure was always within the limit 752–759 mm.

The vapor pressures thus derived for solid cadmium oxide are shown in Table I. In the calculation of vapor pressure the molecule of cadmium oxide in the gas phase was

TABLE I

VAPOR PRESSURE DETERMINATIONS OF CADMIUM OXIDE

Temp., °K.	Millimoles of N_2 saturated	CdO condensed, mg.	V. p. calcd. from exp. data, mm.	V. p. from "smoothed" curve
1140	5.86	0.08	0.080	0.093
1163	7.16	.16	.131	.139
1163	6.95	.16	.135	
1190	9.36	.26	.163	.240
1190	9.19	.28	.179	
1190	9.23	.25	.162	
1190	11.0	.29	.155	
1190	5.19	.22	.248	
1190	4.81	.20	.243	
1216	7.02	.29	.322	.397
1216	8.63	.48	.327	
1216	4.31	.27	.368	
1242	6.03	.41	.398	.634
1242	5.39	.44	.479	
1242	6.74	.58	.504	
1242	8.95	.96	.628	
1266	5.22	.74	.823	.984
1266	5.84	.92	.926	
1305	9.12	2.68	1.716	1.91
1311	10.5	3.78	2.003	2.10

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(4) Hincke, THIS JOURNAL, **52**, 3869 (1930).

(5) Eastman and Duschak, Tech. Paper No. 225, Bureau of Mines (1919).

assumed to be CdO. No vapor density measurements are available, but this assumption is in many ways very reasonable, because of the simplicity of the unimolecular CdO from the valence point of view and because of the fact that vapor density experiments show cadmium vapor to be practically unimolecular. The pressures are reduced to millimeters of mercury at 0°.

Reference to the data of Table I shows that in most cases a decrease in the nitrogen used corresponding to a slower rate of passage of nitrogen through the apparatus increased the vapor pressure determined therefrom. Ordinarily under such circumstances one might plot the apparent vapor pressure against the rate and extrapolate to zero rate, but such a procedure in this case would not be justifiable, since the differences involved are of the same order of magnitude as the experimental error. In determining the vapor pressures from the smooth curve, the results were plotted upon a large scale (curve not shown), using the conventional log P *vs.* $1/T$ chart, and a straight line was drawn in such a manner as to most nearly approach all of the highest values of vapor pressure determined. This straight line had the analytical form

$$\log_{10} p_{\text{mm.}} = 9.59 - \frac{12{,}150}{T}$$

From the slope of the line of the chart the molal heat of vaporization (ΔH) over the temperature range of the experiment may be calculated to be 55,600 cal., and the extrapolated normal sublimation point is 1813°.

Summary

The vapor pressure of CdO has been determined by the inert gas saturation method over a temperature range from 860 to 1050°. The molal heat of sublimation over this range has been calculated to be 55,600 cal.

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RECEIVED AUGUST 15, 1932
PUBLISHED MAY 6, 1933