VAPOR PRESSURE OF METALLIC CALCIUM.

BY NORMAN B. PILLING.

SYNOPSIS.

Vapor Pressure of Calcium, 500–700° C., from Rate of Evaporation in Vacuum.—A drawn wire of calcium was coiled into an open helix and placed in a glass tube which was then evacuated and heated to a definite temperature for a definite time. From the loss of weight due to evaporation the vapor pressure was computed by using a formula derived from the kinetic theory but involving a correction factor for the reflection of molecules by the walls of the hot tube. This factor was assumed to be a constant of the apparatus and was determined by making measurements for zinc and cadmium whose vapor pressures are known. The calcium used had 1.6 per cent. Mg and 1.25 per cent. $CaCl_2$. The values obtained for 500 to 700° C. are well represented by the formula: $\log p = 9.73 - (10{,}170/T)$, the corresponding equations for zinc and cadmium being $9.41 - (7070/T)$ and $9.02 - (5940/T)$ respectively.

Vapor Pressure of Liquid Calcium, Computed using Richards's relation between the vapor pressures of liquid and solid phases, is given by the equation $\log p = 9.27 - 9670/T$. From this equation the *boiling point* comes out 1240° C.

EXPERIMENTAL METHOD.

THE method of measurement involved the determination of the rate of evaporation of a certain weight of metallic calcium of known surface area at constant temperature and in vacuo. From this rate it is possible to compute by means of the kinetic theory of gases the equilibrium vapor pressure. In this way the vapor pressures of tungsten, molybdenum and platinum have been computed.[1]

The following expression has been derived[2] for the vapor pressure of a substance in terms of its rate of evaporation in vacuum:

$$m = \sqrt{\frac{M}{2\pi RT}} \cdot p, \qquad (1)$$

in which

M = molecular weight of vapor (assume metallic vapors to be monatomic).
R = gas constant = 8.32×10^7 ergs/degree.
T = absolute temperature.
p = pressure, dynes/cm.^{2}
m = rate of evaporation, gm./(cm.^{2} sec.).

---

[1] I. Langmuir, Vapor Pressure of Metallic Tungsten, PHYS. REV., II., Vol. 2, p. 329, 1913. I. Langmuir and C. M. J. Mackay, Vapor Pressure of the Metals Platinum and Molybdenum, PHYS. REV., II., vol. 4, p. 377, 1914.

[2] I. Langmuir, Vapor Pressure of Metallic Tungsten, PHYS. REV., II., Vol. 2, p. 329, 1913.

This expression is valid when the following postulates hold

1. That at low vapor pressures (few millimeters) the mutual interference between vapor molecules is so slight as to make the rate of evaporation a function of temperature only and independent of the external pressure.

2. That the rate of condensation is proportional to the vapor pressure.

3. That the coefficient of reflection with respect to both metal surface and enveloping walls is zero.

The above equation then will give the rate of evaporation in a vacuous space whose enveloping walls are cold or remotely distant. As will be shown later, in the experimental arrangement adopted the enveloping walls have been made neither remote nor cold, and hence another factor, the reflection of calcium molecules from this enveloping surface back to the metallic surface with consequent condensation has to be taken into account.

Let s = coefficient of reflection from the enveloping walls. Then

$$m = \sqrt{\frac{M}{2\pi RT}}\cdot p(1 - s). \qquad (2)$$

Solving for p, and changing p from dynes/cm.^{2} to millimeters of mercury (1 mm. Hg = 1333 dynes/cm.^{2})

$$\log p = \log m + \tfrac{1}{2}\log T + \tfrac{1}{2}\log\frac{2\pi R}{M} - \log(1 - s) - 3.125. \qquad (3)$$

Details of the experimental method used are shown in the apparatus diagram (Fig. 1). A 19/32″ bore pyrex glass tube closed at the bottom extended to the middle of a vertical electrically heated tube resistance furnace. This ignition tube was connected to a standard set of mercury diffusion pumps through a greased stopcock; a liquid air trap was placed between the stopcock and the furnace to prevent vapors from the lubricant of the cock and mercury from the pumps diffusing back into the ignition tube. The calcium in the form of a drawn wire helix was cleaned, weighed and immediately dropped into the ignition tube through a suitable opening at the top. In its initial position (Fig. 1) the helix

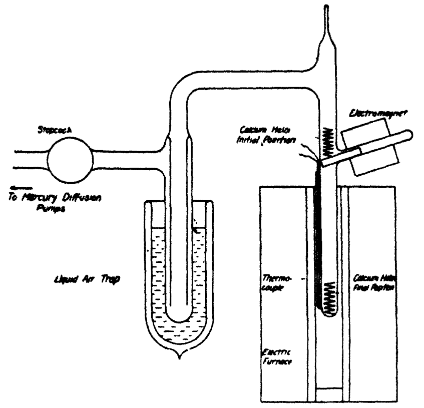

Fig. 1.

rested on a steel pin which projected across the heating tube from an inclined lateral tube above the top of the furnace. As soon as the specimen was in place the top of the heating tube was sealed off and the entire system was evacuated. A platinum-platinrhodium thermocouple within a slender quartz protection tube was lashed to the outside of the glass tube with asbestos tape. When the furnace had reached a steady temperature and time had been given for the removal of absorbed moisture, etc., from the inside of the tube, the steel pin was withdrawn with an external electromagnet and the calcium helix dropped into the furnace. At the end of the run, the furnace was lowered away from the ignition tube, and the calcium cooled in vacuo. When cold, the tube was cracked open and the loss in weight of the calcium helix determined.

At temperatures above 600° C. the pyrex glass collapsed. A somewhat larger tube was then used, into which an unglazed usalite porcelain liner, 19/32″ bore, was slipped, which acted as a support for the softened glass.

In all cases except cadmium the evaporated metal condensed as a mirror at the mouth of the furnace. The cadmium condensed just below the furnace mouth.

Determination of Coefficient of Reflection.

In evaluating the coefficient of reflection, the rates of evaporation of several metals with known vapor pressures were measured under various conditions, from which the coefficient was computed by substitution in equation (2). A search of the vapor pressure literature showed the data to be very incomplete and unsatisfactory regarding values of the vapor pressures of the solid metals. Almost all of the data are based on extrapolated curves from the liquid state, oftentimes with the weight of very few measurements.

The vapor pressure of solid zinc and solid cadmium has been measured over a considerable temperature range by a dynamic method by Egerton.[1] Accordingly equations were deduced from his data which were used as standards of reference in measuring the reflection coefficient with zinc and cadmium. These equations follow.

$$\text{Zinc:} \qquad \log p = -\frac{7070}{T} + 9.41,$$

$$\text{Cadmium:} \quad \log p = -\frac{5940}{T} + 9.02.$$

The zinc which was used in this determination was 0.124 cm. diameter Horse Head brand zinc wire furnished drawn to size by the New Jersey

---

[1] A. C. Egerton, Vapor Pressure of Zinc, Cadmium and Mercury, Phil. Mag., Vol. 33, p. 33, 1917.

Composition of Zinc and Cadmium Wire.

	Zn	Cd	Fe	Pb	As
Zinc (no. 077).....	99.94(*d*)	nil	.01	.05	——
Cadmium (no. 075)	nil	99.99(*d*)	——	nil	.006

d = by difference.

TABLE I.

Coefficient of Reflection, Zinc and Cadmium Vapor.

Metal.	No.	Temperature, ° C.	Ignition Tube Reflect. Surf.	Vapor Pressure, mm.	s	log $(1 - s)$
Zinc........	3558	301	Pyrex glass.........	.00133	.99369	−2.200
	3556	404	Pyrex glass.........	.0813	.99230	−2.113
	3557	405	Pyrex glass.........	.0840	.99236	−2.117
	3582	402	Usalite porcelain	.0759	.99198	−2.096
Cadmium...	3559	302	Pyrex glass.........	.0488	.99213	−2.104

Zinc Company. The cadmium was a rod rolled and drawn to wire 0.103 cm. diameter in the laboratory.

Upon examination of this table it will be seen that within the limits of experimental error the coefficient of reflection is a very large but constant quantity, practically independent of temperature, nature of reflecting surface (glass or porcelain) and vapor (metal). The experimental error was largest with no. 3558; the mean value of the four other measurements of log $(1 - s)$ is − 2.107, which was taken as a characteristic constant of the apparatus and used in the reduction of data on calcium.

VAPOR PRESSURE OF CALCIUM.

The calcium metal with which the following determinations were made was a laboratory product prepared electrolytically by Mr. P. H. Brace.[1] This was forged, rolled and drawn cold to wire 0.106 cm. diameter, and stored for use in Lectroseal oil. Analysis of a large piece of the undrawn material follows.

Analysis of Calcium. No. 092.

Ca..	97.16
Mg..	1.62
Fe..	0.009
$CaCl_2$..	1.25
	100.04

---

[1] See P. H. Brace, Transactions, American Electro-chemical Society, 1920, p. 69.

In preparing the wire for use, a measured length was coiled into an open helix 8 mm. diameter. The oil was removed by soaking in xylene, and the crust of calcium salt on the surface removed by pickling in dilute hydrochloric acid in alcohol. When the surface was bright, the acid was rinsed off in alcohol, the alcohol removed by momentary immersion in ether, which attacked the metal vigorously, and then dried quickly in air. The wire diameter was then measured, the helix weighed, placed in the apparatus and sealed off as soon as possible.

TABLE II.

Rate of Evaporation of Calcium.

No.	Temperature ° C.	Specimen.		Weight of Calcium Evaporated, gm.	Time, min.	Rate of Evaporation, gm./(cm². sec).
		Weight, gm.	Surface Area, cm².			
3448	503	0.3694	10.8	0.0024	64	0.058×10^{-6}
3452	553	0.9312	25.8	0.0267	76	0.227
3451	605	0.4414	11.7	0.0366	58	0.900
3449	608	0.4460	12.7	0.0413	50	1.08
3456	652	0.5696	13.5	0.0843	18	5.78
3457	700	0.5689	13.1	0.1621	12.5	15.9

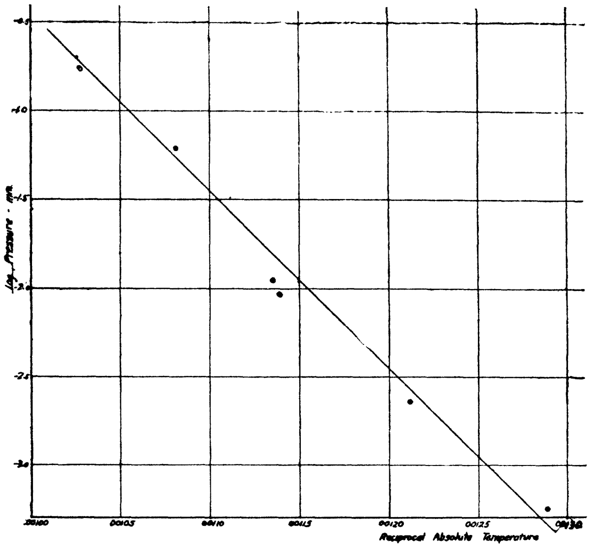

Fig. 2.

Experimental data have been obtained for the temperature range 500–700° C.

Table III.

Vapor Pressure of Calcium.

No.	Temperature, °C.	Pressure, mm. Hg.
3448	503	.000561
3452	553	.00227
3451	605	.00931
3449	608	.0112
3456	652	.0614
3457	700	.173

The experimentally determined values of vapor pressure are plotted in Fig. 2, the coördinates being log pressure and reciprocal absolute temperature. The relation is linear, and the best straight line is

$$\log p = -\frac{10{,}170}{T} + 9.73, \tag{4}$$

representing the vapor pressure of solid calcium. Richards[1] making use of the Clausius-Clapeyron equation and Richards's rule, has derived a relation between the vapor pressure of the solid and liquid phases which has experimental verification for several substances. If the vapor pressure curves are expressed

$$\log p = -\frac{A}{T} + B \text{ (solid)}$$

and

$$\log p = -\frac{A'}{T} + B' \text{ (liquid)},$$

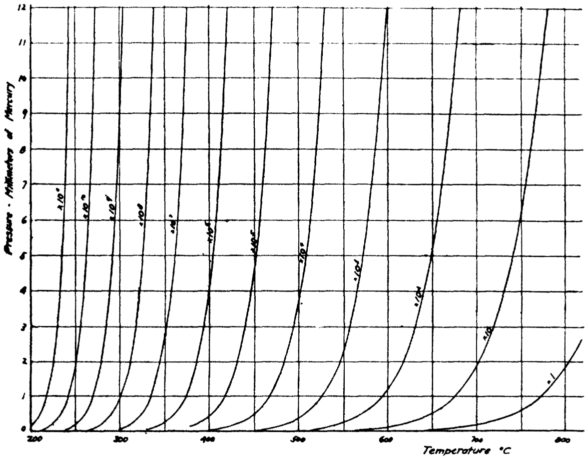

Fig. 3.
Vapor Pressure of Solid Calcium.

---

[1] J. W. Richards, The Vapor Tensions of the Metals, Journal Franklin Institute, Vol. 187, p. 581, 1919.

the relation between the four constants is as follows:

$$A' = A - 0.46\ Tm.p.$$
$$B' = B - 0.46.$$

Taking the melting point of calcium to be 805° C.[1]

$$\log p = -\frac{9670}{T} + 9.27, \qquad (5)$$

the vapor pressure curve for liquid calcium.

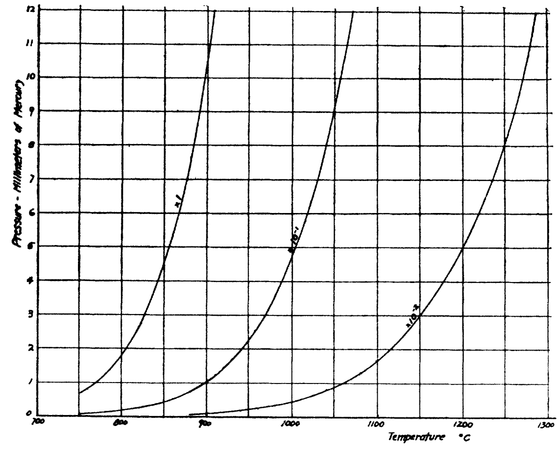

Fig. 4.

Vapor Pressure of Liquid Calcium.

Charts representing equations (4) and (5), the vapor pressures of solid and liquid calcium respectively, are given in Figs. 3 and 4.

From the vapor pressure curves the following constants may be computed.

Normal boiling point, 760 mm.	1240° C
Vapor pressure at melting point, 805° C.	2.0 mm.
Heat of vaporization	
Trouton's rule $\frac{23T}{\text{At.Wt.}}$	867 cal./gm
Clapeyron eq. $\frac{4.57A'}{\text{At.Wt.}}$	1100 cal./gm

WESTINGHOUSE RESEARCH LABORATORY,
EAST PITTSBURGH, PA.,
May 24, 1921.

---

[1] Soc. Franc. de Physique, p. 258.