High Precision Determination of Vapor Pressures of Metals and Alloys:

I. Cadmium.

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Metallurgy Report No. 14
October 21, 1957.

Princeton University
The James Forrestal Research Center

Under

Office of Naval Research
Contract No. N onr-1858(08)
Project No. NR031-507

Technical Report No. 1.

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ABSTRACT

An apparatus is described for obtaining extremely high precision vapor pressure data based on the Knudsen effusion method. The element Cd has been used to test the apparatus before proceeding with the investigation of certain alloys. The data obtained from this investigation including the heat of vaporization if Cd are reported herein.

This report describes apparatus which has been constructed in order to measure the vapor pressures of metals and alloys by the Knudsen effusion method. The reliability of the apparatus has been established by determining the vapor pressure of solid Cd. These measurements are believed to be the most precise yet made by the Knudsen method.

EXPERIMENTAL

The complete cell is shown in Fig. 1. The body is machined from solid $^1/_2$" tantalum rod. The cap, which contains the effusion orifice, is made by welding a shallow molybdenum cup, drawn from 4 mil molybdenum foil, to a threaded tantalum ring. The center of the cup is dimpled with a sharp punch and this protrusion is ground off leaving an orifice with a knife edge perimeter as may be seen in Fig. 2. which is a photomicrograph of an actual orifice in cross section. The orifice area is determined by projecting its image onto the ground glass screen of a Vickers metallograph and making several tracings at various magnifications. The magnification is determined for each separate setting of the metallograph with a stage micrometer. The area of the tracing is determined either by transfering the outline to graph paper and counting squares or with a planimeter. The precision of this determination is indicated by the sample results given in table 1.

Table 1. Orifice Area Measurements

Area of Tracing (cm^2)	Magnification	Actual Orifice Area (cm^2)	% dev. From Av.	Method
48.10	317.0	4.786×10^{-4}	0.25	Planimeter
48.22	317.0	4.798 "	0.00	Graph
47.93	315.7	4.803 "	0.23	Planimeter
47.80	315.5	4.799 "	0.02	Planimeter
	Av...	4.798×10^{-4}	Av..0.12	

The orifices used in this investigation are believed among the smallest ever to be reported. It is therefore quite certain that

the conditions for effusive flow are obeyed.

The vacuum system consists of an MCF-300 Consolidated Electrodynamics oil diffusion pump backed by a high capacity Welch Duo-Seal mechanical pump. The pressure is measured by a Phillips PSG-06 ionization gauge which had been previously calibrated with a McLeod gauge. At no time during a vapor pressure run does the background pressure exceed 10^{-5}mm and, in fact, it is usually about 5×10^{-6}mm.

The furnace consists of a 4" I.d. x 16" alundum core which is gradient wound with No. 16 Kanthal A-1 wire. Power is supplied to the furnace by the 115 house line and is regulated by a powerstat. The temperature is controlled by a Weston Tag Dalectray controller which receives a signal from a chromel-alumel thermocouple held directly against the furnace windings. A stainless steel vessel containing a rapidly stirred mixture of molten $LiNO_3$ and $Ca(NO_3)_2$ provides a convenient high temperature bath because it has a wide useful temperature range and does not attack pyrex. The temperature differential is less than 0.1°C between the top and bottom of the bath and the average temperature varies by less than 0.1°C during a run. The entire furnace assembly is counterweighted and suspended from pulleys. To the furnace housing are attached eight masonite wheels which ride on 1" x 1" angle iron tracks. The furnace may be rapidly raised or lowered about the vacuum chamber which contains the effusion cell. The temperature is determined by a calibrated Pt-Pt-10% Rh thermocouple in direct contact with the cell. The entire assembly is illustrated in Fig. 3.

RESULTS

The vapor pressure of pure Cd has been determined by the method of weight loss. The equation used for calculating the vapor pressure is

1. $$P_{mm} = \frac{17.14\ G}{A\ t\ C\ I} \left(\frac{T}{M}\right)^{1/2}$$

where A is the area of the orifice in cm^2, T is the temperature in ^oK, and M is the atomic weight of the effusing species. A photomicrograph of an actual orifice, i.e. Fig. 2, permits an estimation of the thickness of the perimeter. For this particular orifice, which is believed to be representative, the edge thickness is estimated to be 0.00016" and consequently the Clausing factor is equated to one. The uncertainty involved in this approximation cannot alter the absolute values of the vapor pressures, subsequently to be given, by more than one percent.

The experimental procedure is as follows: The Ta cell and cap are first cleaned and ignited to a dull red heat in vacuo for several minutes. After cooling the cell is loaded with two pieces of Bakers reagent grade Cd weighing about ten grams. The cell is weighed, inserted into the vacuum chamber and immediately connected to the vacuum system. The system is then outgassed for sixteen hours with the cell held at a temperature of 80^oC. The effusion run commences with the furnace being quickly raised to a position which immerses the cell to a depth of ten inches. Vacuum and temperature readings are taken a four minute intervals until the equilibrium pressure and temperature are achieved. After which the Philips gauge is excluded from the system and temperature readings are continued at thirty minute intervals. The experiment is concluded by dropping the furnace and rapidly cooling the cell by immersing the vacuum chamber in cold water. The temperature falls 100^oC within a minute after the furnace is lowered and there is, therefore, essentially no error arising from the termination of the run.

There is considerable error introduced by thermal lag during the initial period of the run. The lag varies with the temperature of the furnace and the heat capacity of the cell contents. However, as the temperature of the cell is known of each instant an empirical formula may be applied to correct for the initial departure from thermal equilibrium. A schematic ver-

sion of a typical time-temperature curve is shown in Fig. 4. Corrections are obtained in the following manner: The vapor pressure is calculated using the final equilibrium temperature Te, (See Fig. 4), in conjunction with the total weight effused and the time interval $t_t - t_e$. This yields a somewhat high value because the time interval is too small. Vapor pressures are calculated in this manner for each measurement and these results are plotted against T^{-1} on semi-log paper. The resulting straight line has very nearly the correct slope as the percentage error is very nearly the same for each measurement. Using this graph the weight loss during $t_e - t_o$ may be obtained and subtracted from the total weight loss. The arithmetic of these various steps may be outlined thus:

2. $$\Delta W = \frac{\lambda.P.\Delta t}{17.14}\left(\frac{M}{T}\right)^{\frac{1}{2}} z$$

$$= C.P.\Delta t.T^{-\frac{1}{2}} z$$

3. $$\Delta W_{t_f - t_e} = \Delta W - \sum_{i=1}^{n} \Delta W_i$$

where the last term represents the weight loss during the interval $t_e - t_o$.

4. $$\sum_{i=1}^{n} \Delta W_i = C \sum_{i=1}^{n} P_i . \Delta t_i . T_i^{-\frac{1}{2}} z$$

where P_i and $T_i^{-\frac{1}{2}} z$ are the pressure and temperature corresponding to the midpoint of Δt. The value for $T^{-\frac{1}{2}} z$ is obtained from the experimental time-temperature graph and P_i from the initial log P versus T^{-1} graph. These corrective calculations may be iterated to get increased accuracy. For the present work only one such correction was warranted in view of the other sources of error.

The data including the corrected pressures are given in Table 2. These data represent all the measurements made but one, which was clearly in error.

Table 2. Cd Vapor Pressure

T^oK	Orifice Area ($cm^2 \times 10^{-3}$)	Total Weight Loss(mg)	Corr. Weight Loss(mg)	$t_f - t_e$ Sec.x10^4	Pressure (mm x 10^{-3})	ΔH_0^o(K.C.)
497.1	2.483	2.34	2.26	2.736	1.254	26.82
508.1	2.483	2.93	2.77	1.920	2.242	26.82
519.7	0.4799	5.35	4.73	1.950	4.028	26.82
527.6	2.483	1.38	1.22	1.812	5.913	26.82
537.4	2.483	18.95	17.54	2.820	9.348	26.81
550.9	0.4799	3.24	3.02	1.644	17.02	26.83

The enthalpy of vaporization at 0^oK, ΔH_0^o is determined by solving eq. 5

5. $$\Delta H_0^o = -2.303\ RT\ [\log P - {}^3/_2 \log T + B - 4.369]$$

where $$B = \int_0^T \frac{dT}{RT^2} \int_0^T C_p(T)dT$$

Although values are to be found elsewhere in the literature[1], the present authors recalculated B making use of the more recent heat capacity data of Smith and Walcott[2] and Craig and Co-workers.[3] Above 300^oC the equation given for the heat capacity by Kubaschewski and Evans[4] was used. The results of these calculations at the pertinent temperatures are given in Table 3.

Table 3.

T^oK	B
497.1	2.222
508.1	2.249
519.7	2.277
527.6	2.295
537.4	2.319
550.9	2.350

The enthalpy of vaporization is 10cal. less at 298.2^oK than at 0^oK thus a value of 26.81 ± 0.01 K.Cal is obtained for ΔH^o_{298}. This figure is compared with other critically selected values in Table 4.

Table 4. Enthalpy of Vaporization of Cd

ΔH°_{298}	Reference
26.81 ± 0.01	this work
26.78 ± 0.05	"Selected Values etc."[5]
26.75 ± 0.05	Kubaschewski and Evans[4]
27.01	Kelley[6]

There is no available method for checking the accuracy of the absolute magnitude of the vapor pressure. However, in the case of Cd the experimental results for the liquid phase are in good agreement. The value of the vapor pressure at the melting point given by the most recent compilation, 'Selected Values etc.'[5], is 1.38×10^{-4} atm. and 1.29×10^{-4} atm is the value obtained by extrapolating the data reported here.

As the results of this investigation are in good agreement with other previously reported values no effort was made to tabulate free energy functions which would only duplicate those already in existence.

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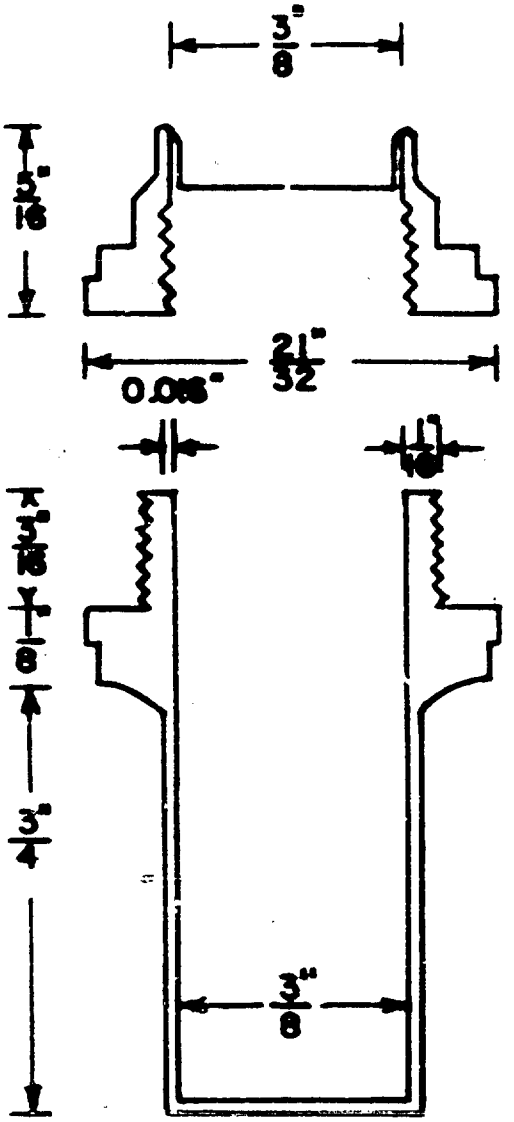


Figure 1
EFFUSION CELL

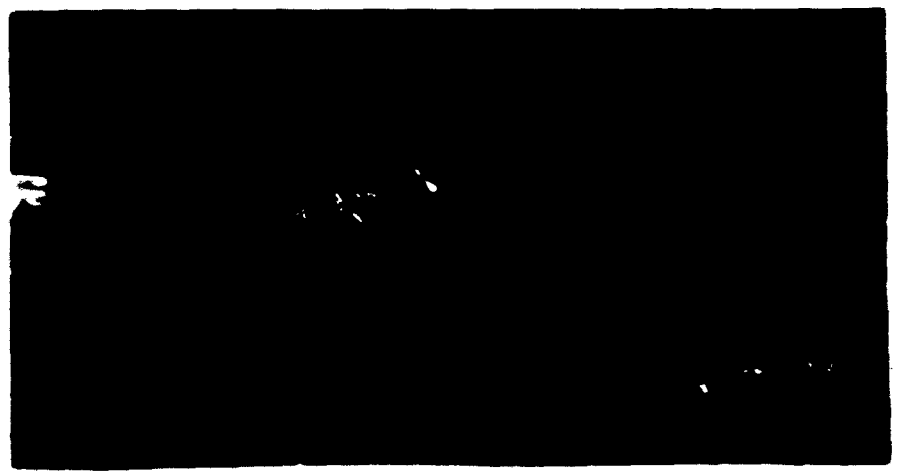
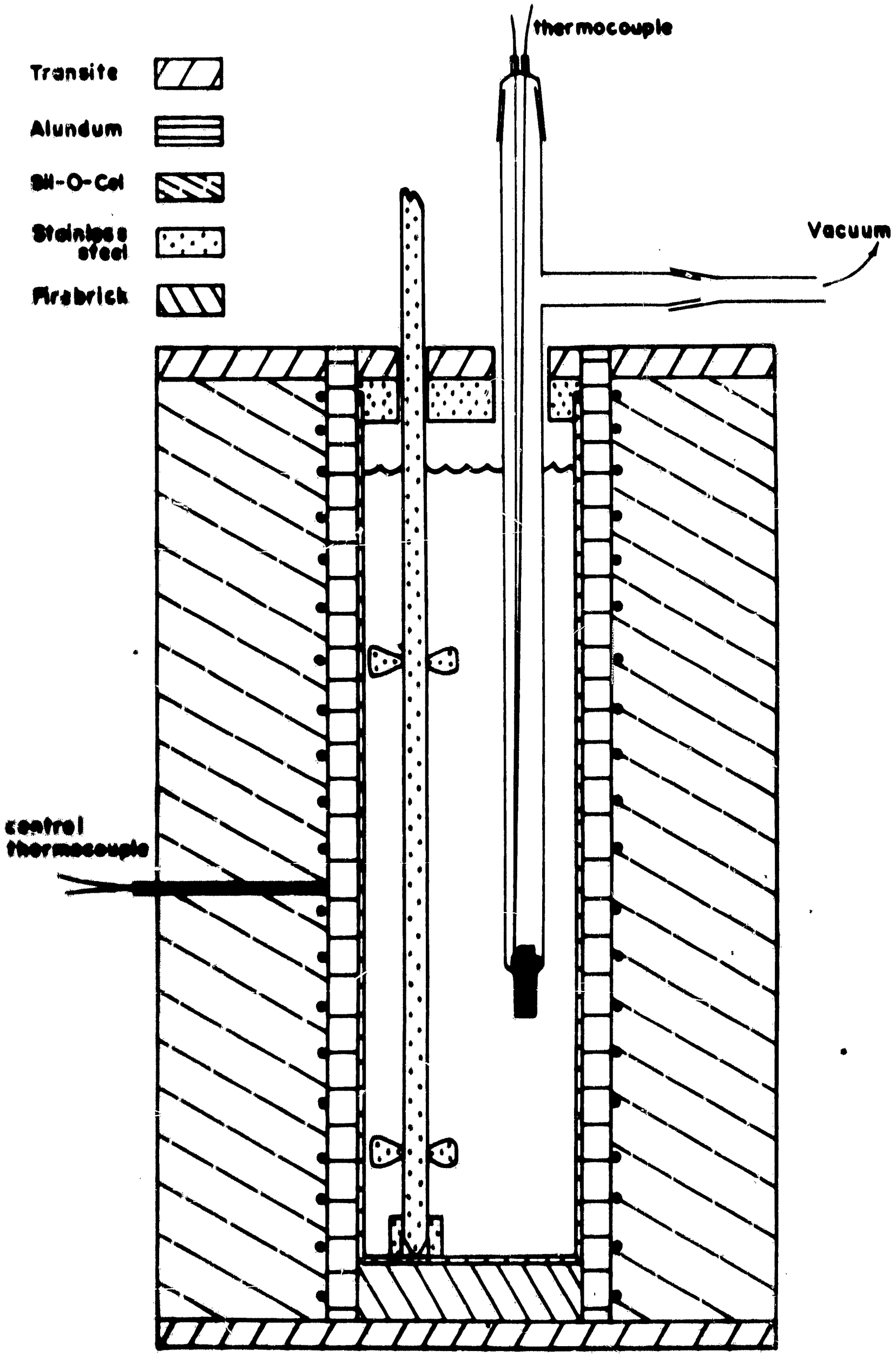


Figure 2
PHOTOMICROGRAPHS OF ORIFICE IN CROSS-SECTION



FURNACE ASSEMBLY AND VACUUM CHAMBER

Figure [redacted]

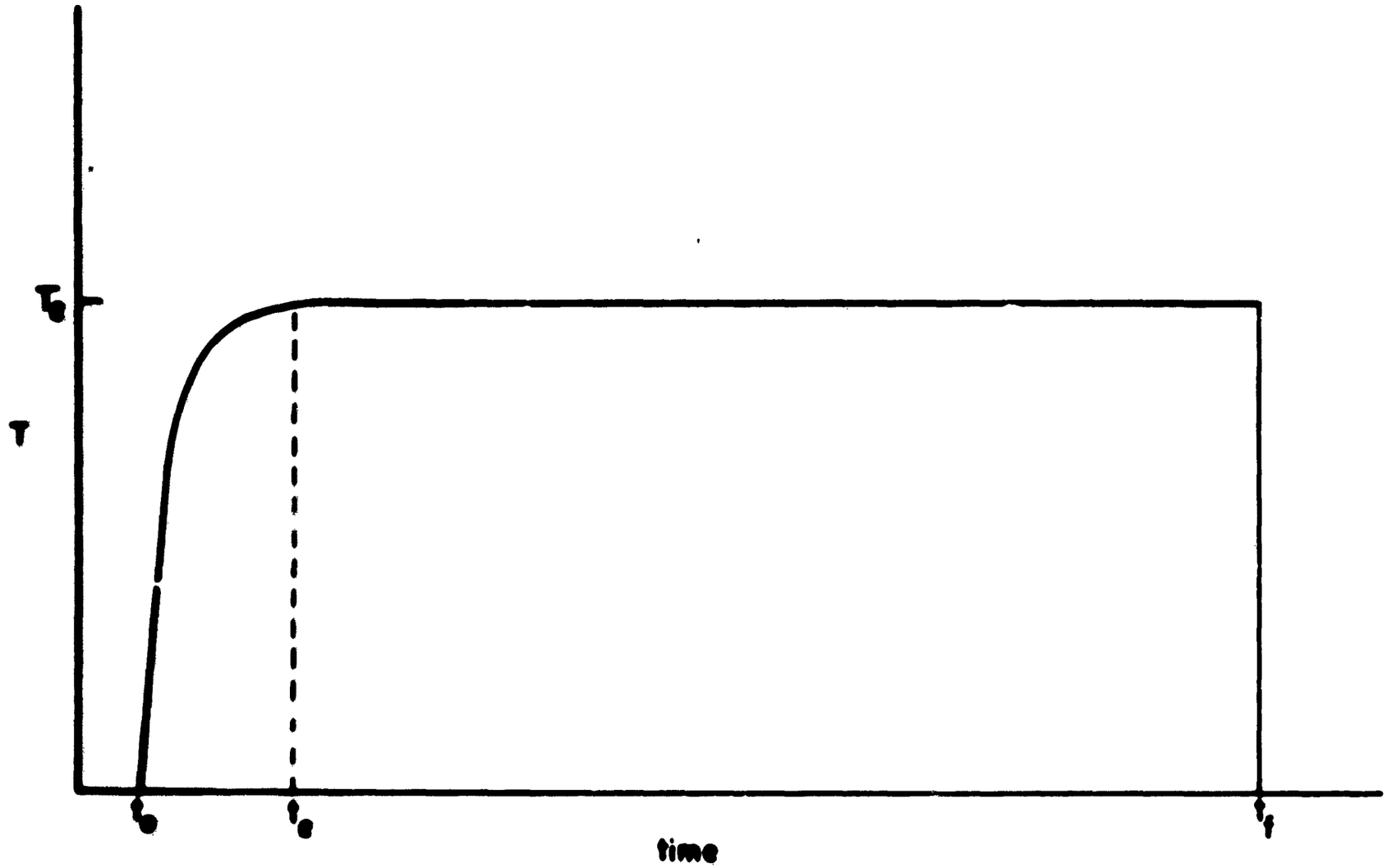


Figure [redacted] HYPOTHETICAL THERMAL LAG CURVE

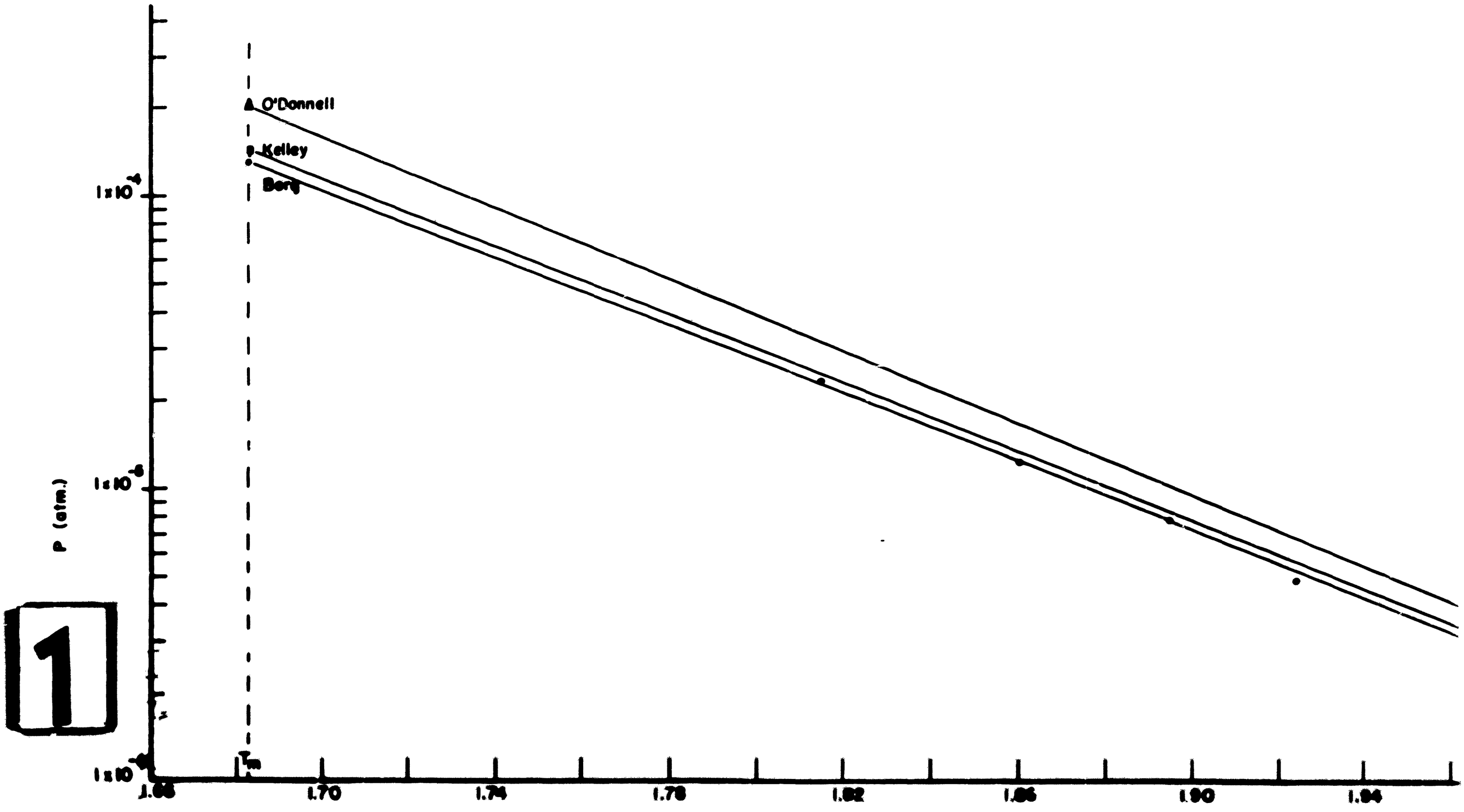


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Figure 9 VAPOR PRESSURE OF CADMIUM

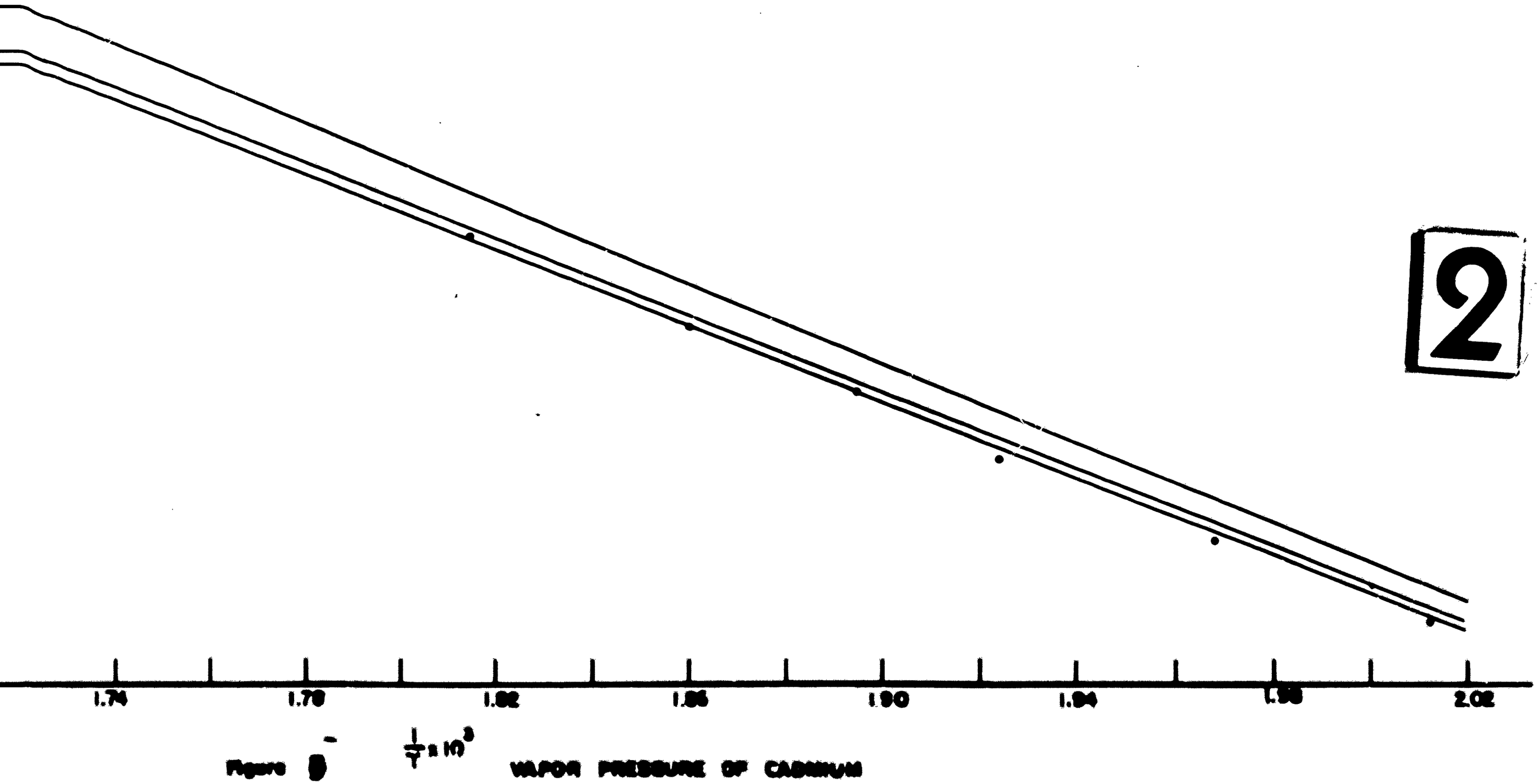

Figure 8 — $\frac{1}{T} \times 10^3$ VAPOR PRESSURE OF CADMIUM

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