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DETERMINATION OF THE VAPOR PRESSURE OF
LANTHANUM FLUORIDE
(Information Report)

BY

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ABSTRACT

Preliminary experiments have been made to determine the vapor pressure of lanthanum fluoride between 0.001 and 0.1 millimeter of mercury by means of the Knudsen effusion method. A tantalum cell for this purpose is described. Only preliminary results were obtained and they were all in a relatively high-pressure region. However, a plot of the vapor pressure against the reciprocal of absolute temperature approximates a straight line such as would be predicted from theoretical considerations.

INTRODUCTION

The Knudsen effusion method¹ is probably the most reliable method for determining the vapor pressure of solids or liquids in the pressure range of 10^{-4} to 10^{-1} millimeters of mercury. In this method vapor flows through an orifice into a high vacuum from a space where it is in equilibrium with a solid or liquid at some given temperature. The orifice diameter must be no larger than the mean free path of the molecules of the substance at this pressure and the orifice walls must have no appreciable thickness. Under these conditions the rate of flow depends upon the pressure difference between the inside of the Knudsen cell and the external vacuum chamber, the dimensions of the orifice, and the density of the gas. It can be shown from the kinetic gas theory that the rate of effusion of a gas into a vacuum from an aperture of negligible wall thickness is related to the pressure by the expression:

$$p = W \left(\frac{2\pi RT}{M} \right)^{1/2} \quad (1)$$

where:

p = vapor pressure

W = weight of material effusing per unit orifice area per unit time

T = absolute temperature

M = molecular weight of gas

Thus a determination of the amount of material effusing through an orifice of known area during a given time interval at a given constant temperature will yield all of the necessary data for the calculation of the vapor pressure of the material at that temperature.

EQUIPMENT

The effusion cells used in these experiments were made from tantalum cylinders $\frac{7}{16}$ -inch in diameter and $\frac{1}{2}$ -inch high. A sheet of 0.005-inch tantalum was spot-welded on the top of the cylinder and a hole of the desired size was drilled in the center of this top. The bottom consisted of a tantalum slug designed to have a snug press-fit in the bottom of the cylinder. A salt, the vapor pressure of which was to be measured, was put into the cell and the slug was pressed into place in the bottom of the cell. After initial heating, the slug formed a tight joint with the cylinder walls and no appreciable leakage was observed during the experiments.

The vacuum system was the same as that described in a previous report.² The only modifications were an optically-plane glass at the top of the vacuum chamber to permit observation with the optical pyrometer and a molybdenum wire attached to the bottom cold finger to

hold the cell in the induction coil. The cell was suspended from this molybdenum wire by a wire handle welded onto the cell.

Temperatures were measured by means of a Leeds and Northrup optical pyrometer. It was sighted through the optically-plane glass by reflection from a front-surface mirror. This arrangement resulted in absorption losses caused by only one thickness of glass. The temperature readings were corrected for emissivity according to the equation³

$$\frac{1}{T} = \frac{\lambda}{C_2} \ln \epsilon_\lambda + \frac{1}{T_a} \quad (2)$$

where

T = corrected absolute temperature

λ = average wave length of light used

ϵ_λ = emissivity of tantalum metal

T_a = apparent absolute temperature

C_2 = known constant

Substituting known values, equation (2) becomes

$$\frac{1}{T} = \frac{1}{T_a} + 0.0322 \times 10^{-3} \quad (3)$$

for tantalum. Using equation (3), a graph showing corrected temperature as a function of apparent temperature was constructed and the corrected temperature was read from this graph for each observed temperature.

EXPERIMENTAL

The lanthanum fluoride used in these experiments was prepared by the method of Salutsky and Stites⁴ from lanthanum oxide obtained from the Lindsay Chemical Company. The experimental sequence consisted of filling the cell with 0.6 to 0.8-gram of lanthanum fluoride, pressing in the bottom slug, evacuating in the system to less than 1×10^{-4} millimeters of mercury and heating the sample to about $1,000^\circ\text{C}$. The cell and contents were removed from the system and weighed. The cell was replaced in the vacuum system, the system evacuated and the cell heated to the temperature desired. It was held at this temperature for a measured length of time, allowed to cool in a helium atmosphere, removed, and weighed.

RESULTS

The results of these experiments are tabulated in Table I and are plotted in Figure 1.

The project was suspended after preliminary experiments had been made, consequently these experiments were rough ones designed to determine the optimum size of hole. No correction was made for evaporation during heating and cooling of the cell. These corrections would have been made on more precise data, but it is believed that such errors are small.

TABLE I
 VAPORIZATION OF LANTHANUM FLUORIDE FROM CELLS
 WITH VARIOUS ORIFICE SIZES

T (°K)	ORIFICE AREA (cm ²)	LOSS RATE (g/cm ² /sec)	P (mm)
1678	0.002162	2.0403 x 10 ⁻²	0.1024
1858	0.002162	1.5132 x 10 ⁻²	0.7993
1948	0.002162	9.3494 x 10 ⁻³	50.57
1713	0.007204	1.9626 x 10 ⁻³	0.09954
1833	0.007204	6.1674 x 10 ⁻²	3.236
1933	0.007204	2.0426 x 10 ⁻¹	11.014
1713	0.01538	9.569 x 10 ⁻⁴	0.0485
1823	0.01538	7.9541 x 10 ⁻⁴	0.0416*
1928	0.01538	7.431 x 10 ⁻²	3.998
1623	0.01861	2.902 x 10 ⁻⁴	0.01433
1808	0.01861	3.319 x 10 ⁻³	0.17296*
1908	0.01861	7.242 x 10 ⁻²	3.877
1713	0.03992	1.3268 x 10 ⁻³	0.0653

*KNOWN TO BE IN ERROR DUE TO CLOGGING OF ORIFICE DURING EXPERIMENT AND NOT SHOWN ON FIGURE 1

It is apparent that the vapor pressures are high because the work was done in a high-temperature range. The temperature region was chosen so that a weighable loss would occur in a reasonably short time, for example, in about fifteen minutes. It is now apparent that much longer heating cycles must be used in order to obtain pressures in the range in which this method is valid. It is estimated that a heating cycle of about five hours would be necessary in order to obtain a weighable loss if the vapor pressure were 0.001 millimeter of mercury.

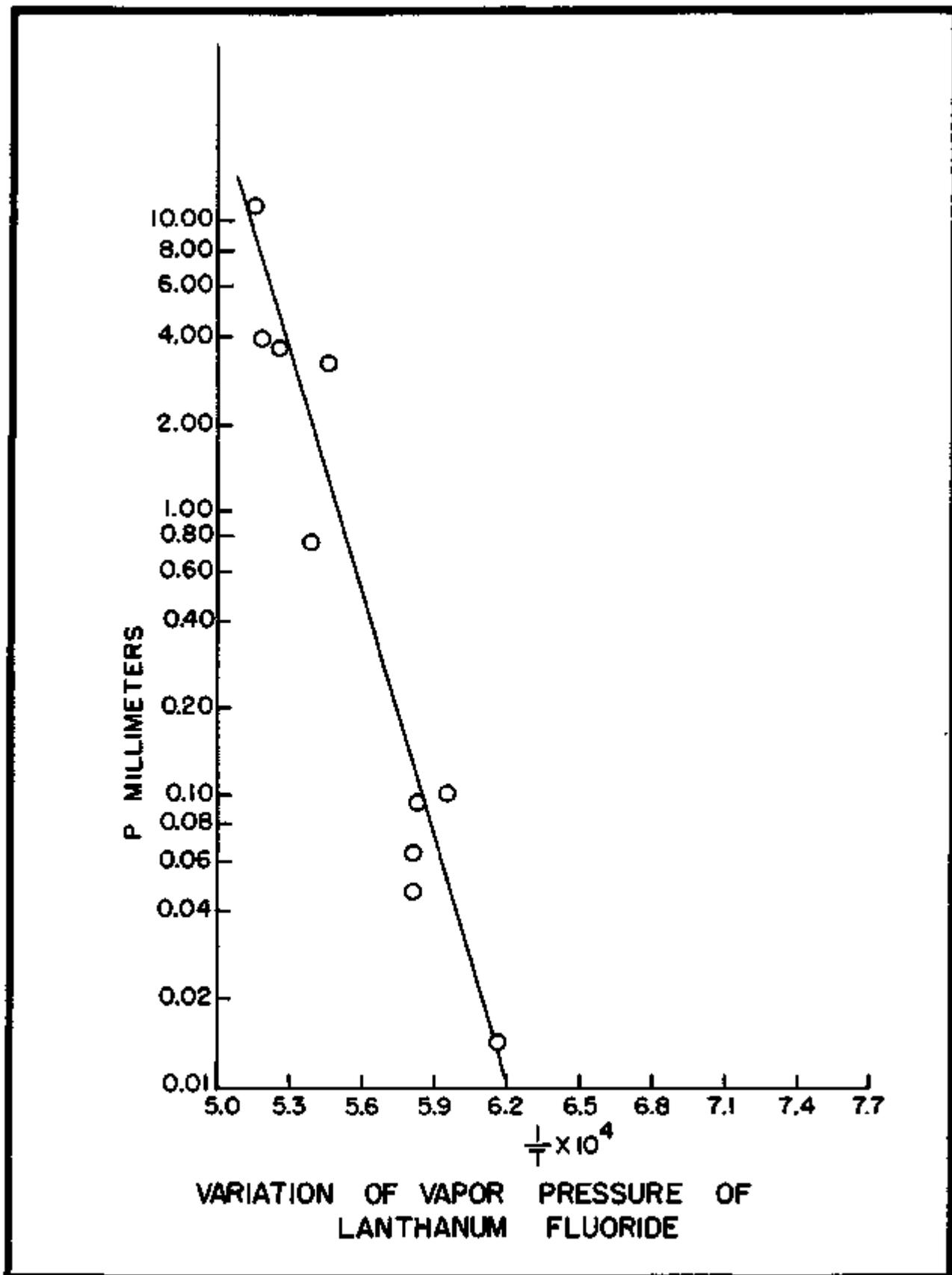
A simplified expression for the expected vapor pressure-temperature variation may be derived from theoretical considerations.⁵ The Clausius-Clapeyron equation is

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2} \quad (4)$$

where the assumptions have been made that the gas is a perfect gas and that the specific volume of the gas is large compared with that of the condensed phase. Equation (4) can be integrated to yield

$$\ln p = \frac{-\Delta H}{RT} + \text{Constant} \quad (5)$$

if the assumptions are made that ΔC_p , the difference between the heat capacities of the gas and the condensed phase, is very small and that ΔH , the latent heat of evaporation or



5660

FIGURE 1

sublimation, is constant over the temperature range being investigated. This latter assumption is valid only for fairly narrow temperature ranges, but the error is sufficiently small so that it has been considered negligible by other workers.* Equation (5) is of the form

$$\log p = \frac{-A}{T} + B \quad (6)$$

and is the theoretical justification for the empirical equation (6) which has been found to hold for most vapor pressure temperature relationships. It may be seen from equation (6) that a plot of $\log p$ vs $\frac{1}{T}$ should yield a straight line. Even though the data are rough and, in general, are not in the valid pressure range, it may be seen from Figure 1 that they roughly plot a straight line.

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