

**PROCEDURE FOR DETERMINING VAPOR PRESSURES OF
MATERIALS OF LOW VOLATILITY**

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FOREWORD

This report was prepared by the Lubricants Section, Organic Materials Branch and was initiated under Project No. 7331, "Hydraulic Fluids", Task No. 73310, "Aircraft Lubricating Greases", formerly RDO No. 613-15, "Hydraulic Fluids and Lubricants", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with O. M. Ballentine acting as project engineer.

This report encompasses the work conducted by Captain V. D. Allred under the same project.

WADC TR 54-418

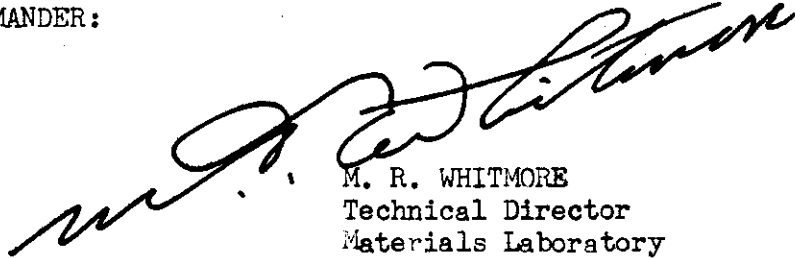
ABSTRACT

An apparatus has been developed for determining absolute vapor pressures of both liquids and solids that exhibit low volatility characteristics. This method has the following advantages: obtaining vapor pressures up to 1000°F, requiring a minimum of operator's time (approximately one (1) hour), relative simplicity and high degree of accuracy in final results. The method employs Knudsen's equation, based on the kinetic theory of gases, in which the weight loss of material per unit time is proportional to the vapor pressure of the material.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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INTRODUCTION

The Air Force has experienced problems in high speed evacuated equipment such as gyro-compasses, in which, under parameters of static evacuation, time, high rotational speed and temperature, oil has been depleted from grease formulations with a resultant loss of lubricating qualities of the grease. To eventually provide greases resistant to such an environment, work was undertaken for the development of a laboratory apparatus suitable for some measurement of the molecular interaction between oils and thickening agents comprising greases. The equipment was therefore designed to permit the obtaining of fundamental knowledge on the ability of constituents to remain in a homogeneous mixture under various parameters by the study of their absolute vapor pressures. The equipment can equally well be utilized as a routine standard tool in measuring vapor pressures of liquids or solids over a wide temperature range.

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SECTION I

General Discussion on the Procedure for Determining Vapor Pressures of Materials of Low Volatility

A. Experimental Equipment Employed in Effusion Method

The experimental equipment used in this investigation consisted of a high vacuum system, a block furnace and effusion chamber, and an effusion cell. A photograph of the actual installation is shown in Figure 2.

Since very high vacuum (e.g. 10^{-4} mm. of mercury) was desirable in these experiments, the construction and maintenance of the vacuum system was a prime consideration. The vacuum system used is shown schematically in Figure 3. This particular system was designed to have a minimum number of joints and stop cocks or other probable sources of leaks and still allow continuous operation independent of the effusion chamber. By proper manipulation it was possible to join or remove the effusion equipment without disturbing the operation of the high vacuum system, a feature which added considerable flexibility to the operation.

Details of construction of the block furnace and effusion chamber are shown in Figures 4 and 5. The block furnace was of brass construction and used a nichrome wire heating element. A constant temperature was maintained by use of a Leeds and Northrop Electromax Controller.

The effusion chamber was designed to allow easy access to the effusion cell. It was made of brass to assure good thermal conductivity between the block furnace and the sample cell. The sample cell was placed or removed by a pair of tongs, which were made from a piece of stiff wire. The tongs engaged the effusion cell in two holes drilled on opposite sides of the bushing.

A cooling coil was necessary to prevent the joint from becoming heated since this would affect the total pressure of the vacuum system by increasing the vapor pressure of the grease used to seal the joint.

*not available
would be
not done
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In order to localize the extreme temperature gradient between the cooling coil and the furnace, a preheat furnace was placed between them. The temperature of the preheat furnace was maintained high enough to prevent any appreciable temperature gradient between the block furnace and the preheat furnace.

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The effusion cell temperature was determined by an iron-constantan thermocouple placed in a brass ring which fits snugly around the upper portion of the effusion cell receiver. This couple was connected to a continuously recording potentiometer so that the temperature was known during each experimental run.

Figures 6 and 7 are photographs of the effusion cell. This cell consisted of an aluminum cup, a glass interliner, a lead gasket, a thin (e.g. 0.09 mm) copper disk which had a 1.7955 mm² hole carefully drilled in it, and a brass bushing which held the disk tightly in place. Advantages of this type of cell were: the sample would be easily placed in or removed from the cell, and a variety of easily interchanged orifices could be used. The area of the orifice was calculated from the diameter which was accurately determined by measuring it with a micrometer type microscope.

B. Experimental Procedure for Determining Vapor Pressures

The high vacuum side of the vacuum system was evacuated with a three stage oil diffusion pump to less than 10⁻⁴ mm of Hg pressure. The effusion cell chamber was heated to constant temperature by a combination block and preheating furnace.

A suitably prepared sample was introduced into the effusion cell. The cell was weighed to the nearest tenth of a milligram and then placed in the effusion chamber by lowering the cell into position with a pair of tongs.

The effusion cell chamber and block furnace was then attached to the glass tapered joint, 6 in Figure 3, by raising the assembly with a modified automobile bumper jack. This permitted relative ease in moving the heavy effusion cell assembly especially when the assembly was heated. It was necessary to heat the assembly to constant temperature prior to being charged with a test sample to prevent loss of sample due to evaporation. The chamber was partially evacuated by opening it to the low vacuum side of the equipment (stop cock 7 open and stop cocks 4 and 8 closed, Figure 3). This measure was considered necessary to prevent oxidation and possible flash vaporization of the sample.

The effusion chamber was then opened to the high vacuum side of the system (close stop cock 7 and open stop cocks 4 and 8, Figure 3) and an accurately timed run commenced. The length of time for a run depended upon the expected rate of effusion and varied from one to eight hours in

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these particular determinations. Since a larger weight loss added considerable accuracy to a determination, each run was allowed to proceed for a maximum practical time.

At the conclusion of a run, the effusion unit was isolated from the vacuum system (close stop cocks 4 and 8 and open stop cocks 7 and 9, Figure 3), the effusion cell removed and weighed, and the weight loss per unit time computed.

In these experiments, it may be necessary to determine the molecular weight of the effusing vapor by removing a sample from the effusion chamber cold trap, 5 in Figure 3, and analyzing it.

For some applications, it may not be necessary to calculate absolute pressures of a material for an indication of that material's volatility since the experimentally obtained weight effusion rate is proportional to this property. This would especially be more practical in the case of blended samples in which it would be difficult to ascertain the molecular weight.

C. Derivation of Equation Used in Effusion Method

The Knudsen or effusion method (2,3,5 and 8) of determining vapor pressure is based upon the rate of molecular transfer thru an orifice, of known area, from a region of equilibrium vapor pressure to a region of essentially no pressure (10^{-5} mm of Hg).

The effusion equation may be written as follows:

$$p_0 - p_s = \left(\frac{w}{t}\right) \left(\frac{r_1 + r_2}{\rho^{1/2}}\right) \quad I$$

Where

p_0 is the equilibrium vapor pressure of the test material at a given temperature

p_s is the total pressure in the system in which the material is effusing.

w is the weight of the material which has effused in time t

ρ is the density of the effusing test material vapor at a pressure of one dyne per square centimeter.

r_1 is the specific resistance of the orifice to effusion and is a function of the cross sectional area of the orifice.

r_2 is the specific resistance of the orifice to effusion and is a function of the thickness of the orifice plate.

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When the thickness of the orifice plate is less than one-tenth the orifice diameter then r_2 may be neglected compared to r_1 . The specific resistance η , may then be expressed by the following relationship: $r_1 = \sqrt{\frac{2}{A}}$. This is an empirical relationship where A is the cross sectional area of the orifice. The density may be expressed by its equivalent in the ideal gas law as follows: $\rho = \frac{pM}{RT}$ or when the density equals one dyne/cm² as specified, $\rho = \frac{M}{RT}$. Substituting these expressions in equation I and neglecting p_0 for system pressures less than (10^{-4} to 10^{-5} mm of Hg) $p_0 = \left(\frac{w}{x}\right)\left(\frac{1}{A}\right)\sqrt{\frac{2\pi RT}{M}}$ where p_0 is in dynes per square centimeter, R, the gas constant in ergs is 8.314×10^9 x 10 ergs deg⁻¹ mole⁻¹, T, the absolute temperature in degrees Kelvin, M is the molecular weight of the effusing vapor, A is the area of the orifice in square centimeters and w/t is the rate of effusion in grams per second.

Insertion of the combined constant values given in equation II provides a direct means of calculating the vapor pressure, p_0 in microns, from the experimental data w/t and T.

$$p_0 \text{ (microns)} = 17047.5 \left(\frac{w}{x}\right) \left(\frac{1}{A}\right) \sqrt{\frac{T}{M}} \quad \text{II}$$

D. Standardization of Effusion Cell

Standardization of the effusion cell was accomplished by determining, experimentally, the vapor pressure of triple distilled di-(2-ethylhexyl) sebacate and comparing these values to a vapor pressure-temperature curve obtained from the equation $\log_{10} p = -\frac{A}{T} + B$, Figure I, where the constants A and B for di-(2-ethylhexyl) sebacate are 5934 and 12.25, respectively. The plot of $\log_{10} p.v.s. \frac{1}{T}$ was a straight line curve over the limited range of temperature employed. The experimentally obtained vapor pressure data of di-(2-ethylhexyl) sebacate are given in Table I.

Literature source for p.v.s.

SECTION II

Conclusions

The effusion equipment and method described in this report can be considered standard for satisfactory determination of absolute vapor pressures of low volatile materials such as aircraft lubricating greases.

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This equipment can also be employed for fundamental research studies where accurate and reproducible vapor pressure data are required.

Bob! Nothing new developed here. This method used for last 30 years in chemistry & physics. See Dr. Madam's work at Argonne on vapor pressure measurements of plutonium compounds.

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VAPOR PRESSURE OF DI-(2-ETHYLHEXYL) SEBACATE

- VAPOR PRESSURE DETERMINED BY EQUATION:

$$\log_{10} P = -\frac{5934}{T} + 12.25$$

(REF: TRANS FAR SOC, 44, 816, (1948) ✓

O EXPERIMENTAL POINT DETERMINED BY EFFUSION METHOD

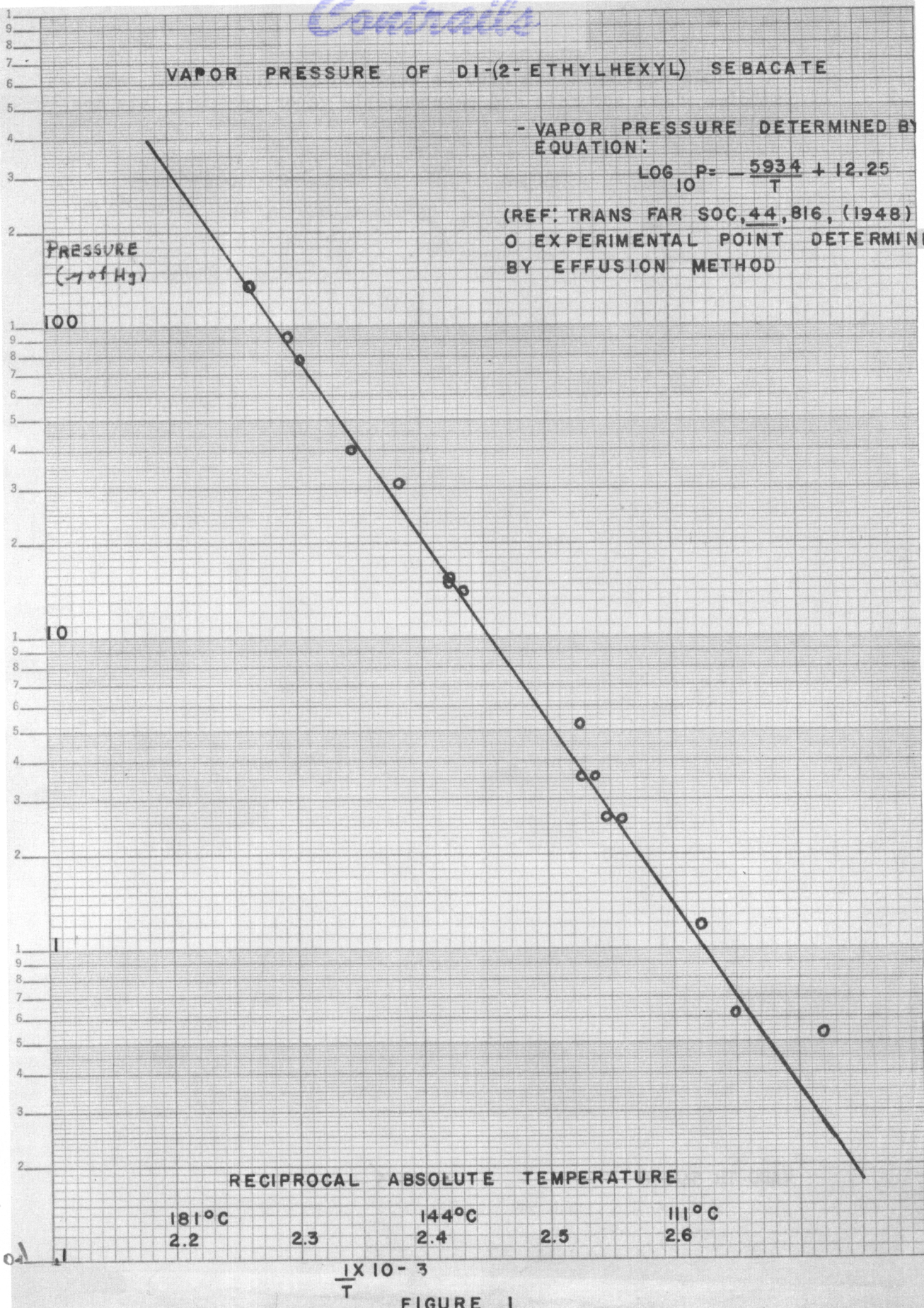


FIGURE 1

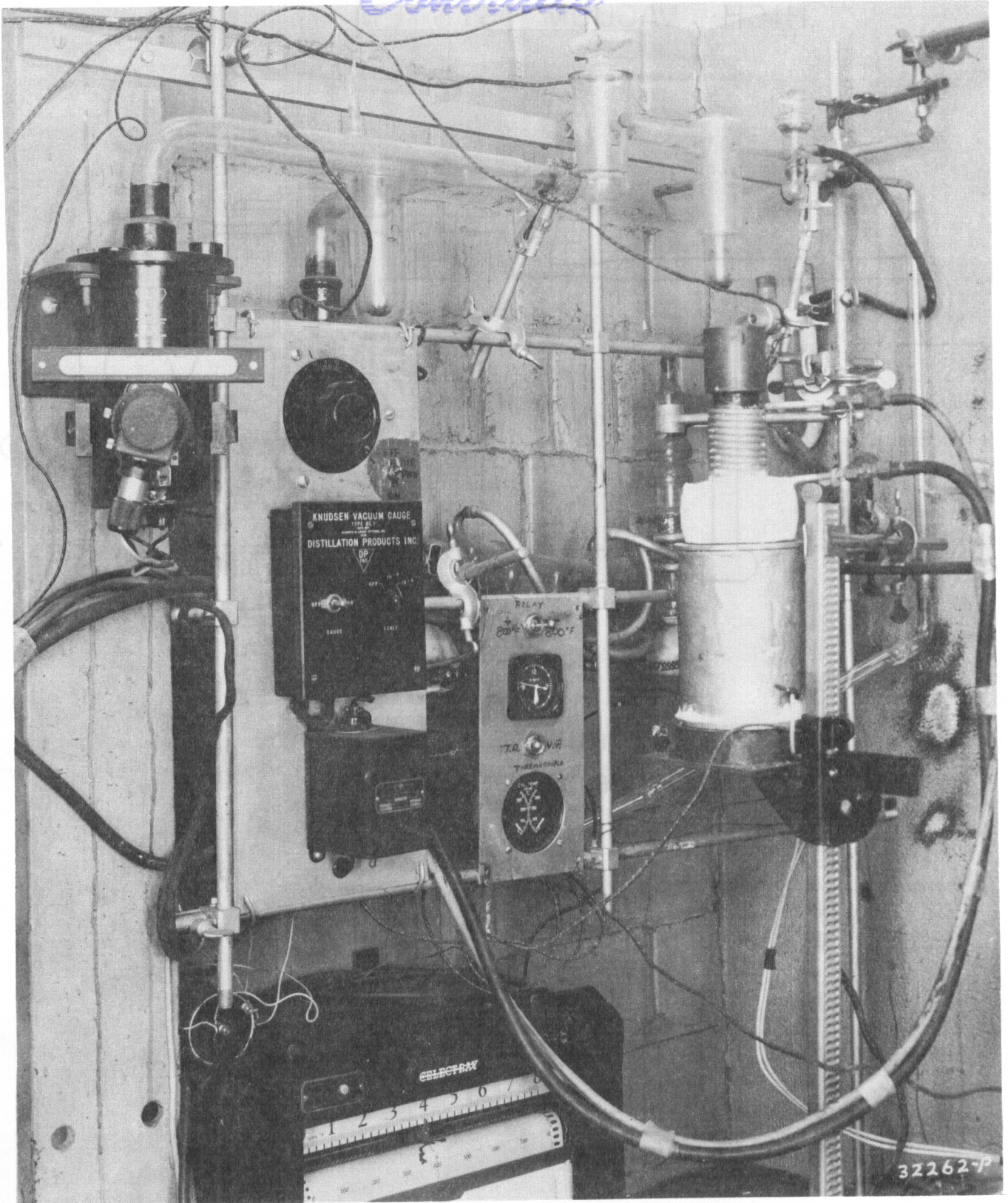
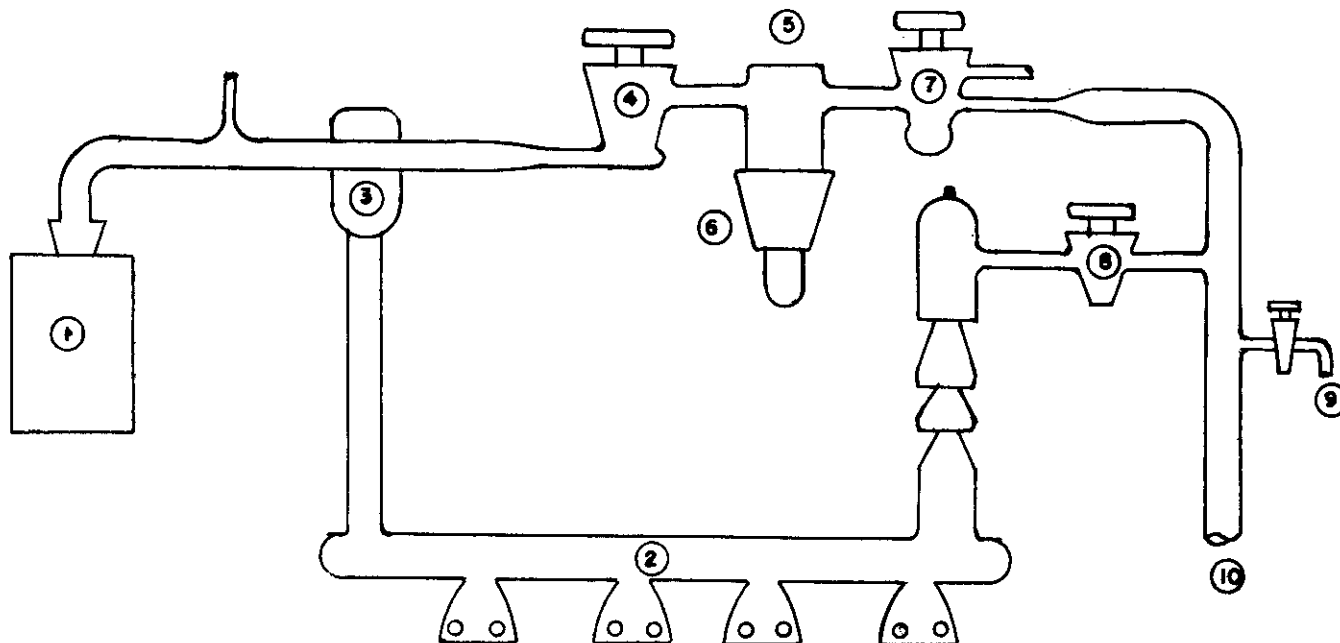


FIGURE 2

EFFUSION APPARATUS

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HIGH VACUUM SYSTEM



1. KNUDSEN HIGH VACUUM GAGE.
2. THREE STAGE OIL DIFFUSION PUMP.
3. COLD TRAP.
4. HIGH VACUUM STOPCOCK.
5. COLD TRAP.
6. EFFUSION CHAMBER JOINT.
7. THREE WAY HIGH VACUUM STOPCOCK.
8. LARGE BORE STOPCOCK.
9. FOREPUMP VENT.
10. FOREPUMP CONNECTION.

FIGURE 3

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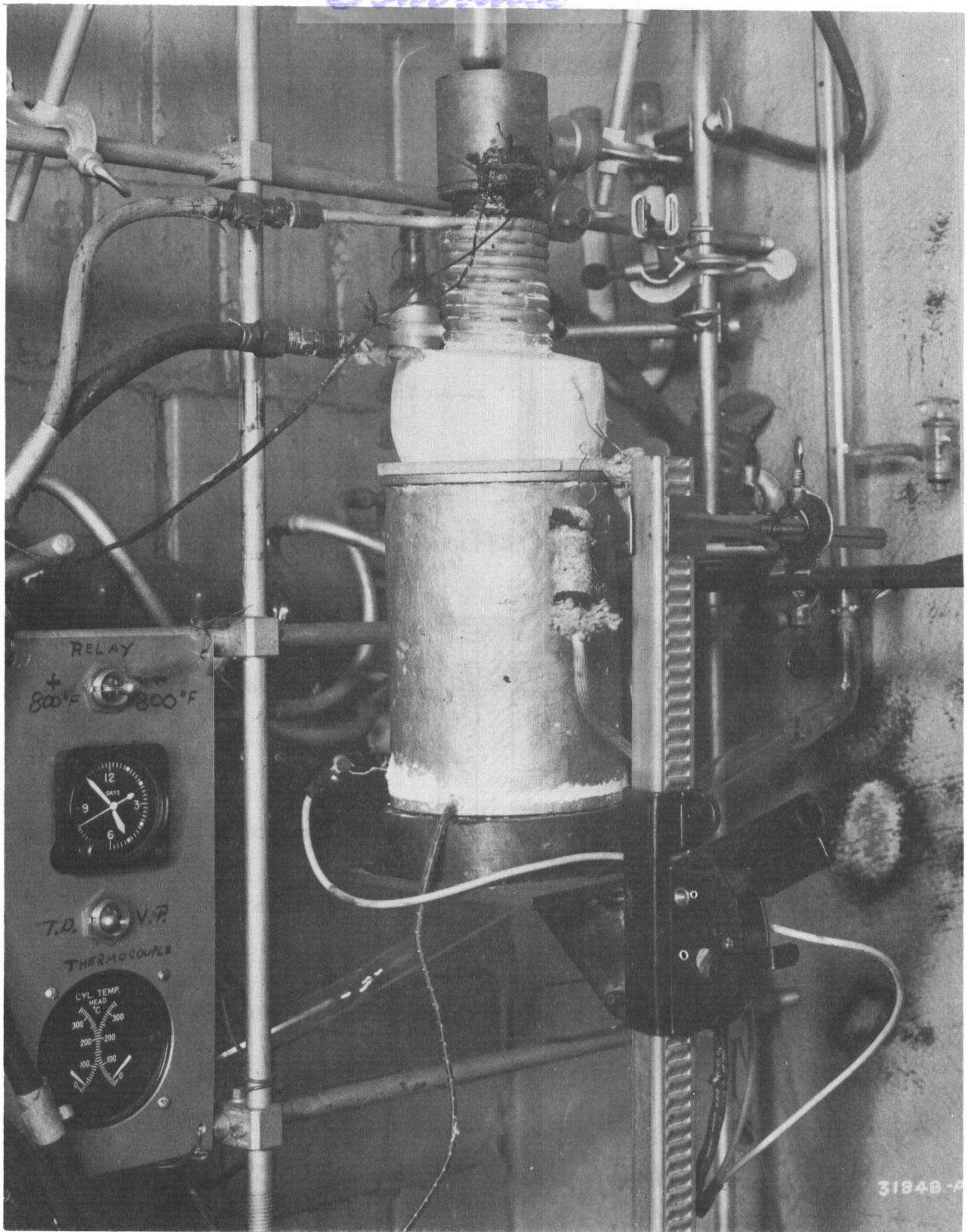
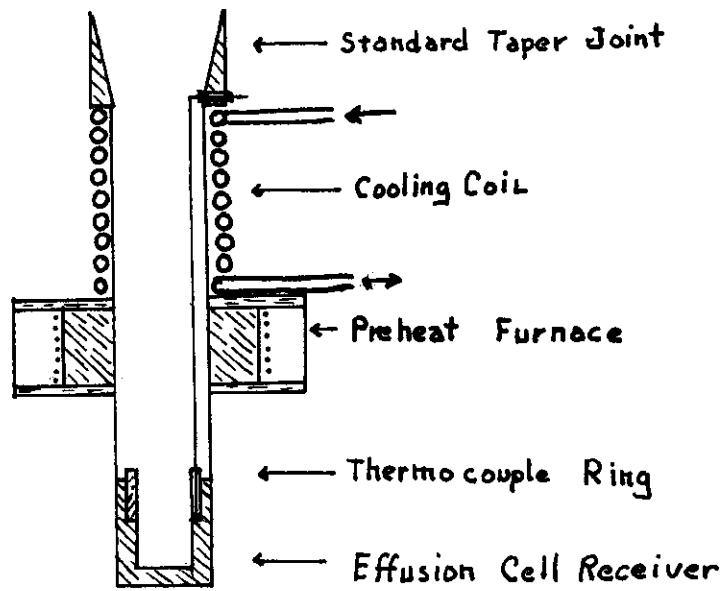


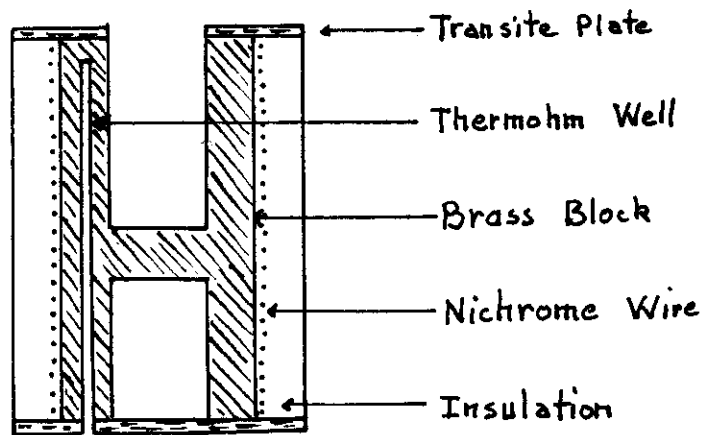
FIGURE 4
FURNACE AND EFFUSION CHAMBER

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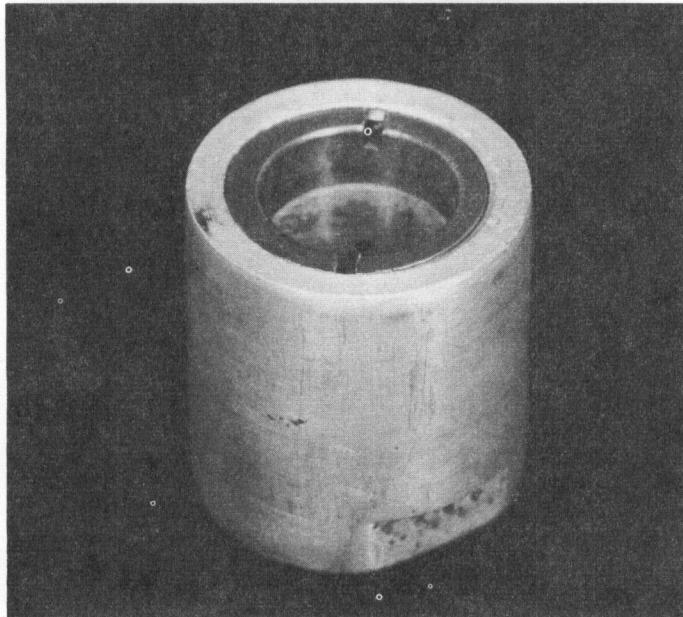
Detail of Effusion Chamber



Detail of Brass Block Furnace

Figure 5

Schematic Diagram of Block Furnace and Effusion Cell Chamber



REPRODUCED FROM THE NATIONAL ARCHIVES
AT COLLEGE PARK, MARYLAND

FIGURE 6

EFFUSION CELL (APPROXIMATELY 1 1/4 ACTUAL SIZE)

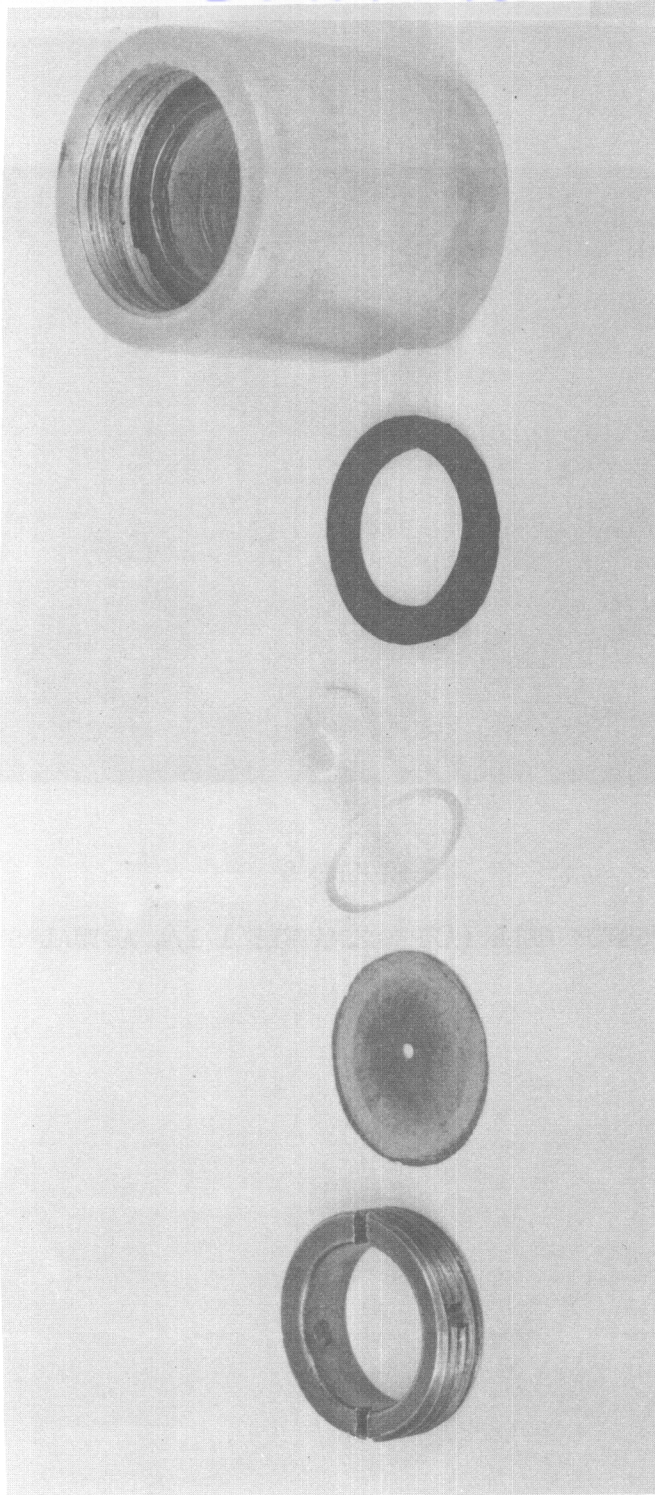


FIGURE 7
EXPANDED VIEW OF EFFUSION CELL

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Table I

Temperature-Pressure Data for Di-(2-Ethylhexyl) Sebacate
Obtained by the Effusion Method

Temperature (t°C)	Absolute Temperature (°K ⁻¹)	Vapor Pressure (Micron)
101	2.674	0.52
112	2.597	0.59
116	2.570	1.15
126	2.506	2.51
128	2.494	2.53
129	2.486	3.45
131	2.475	3.47
131	2.475	5.12
144	2.398	14.93
147	2.381	13.45
147	2.381	13.49
148	2.370	14.45
148	2.370	14.72
149	2.368	12.90
156	2.330	30.70
163	2.294	39.06
171	2.252	76.70
173	2.242	90.30
179	2.212	131.50

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