VAPOR PRESSURES OF ORGANIC CRYSTALS

BY AN EFFUSION METHOD

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By

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## PREFACE

Because of their utility a great deal of research has been devoted to the determination of vapor pressures. Heats of vaporization and sublimation, as well as equilibrium constants and activities are calculated directly from vapor pressures. In addition they enter into many calculations of heats of dissociation and ionization. The vapor pressures of substances are often important in connection with their technical application and with the hazards encountered by industrial workers who breathe their vapors. An outstanding instance of the importance of vapor pressure studies is found in the work of Langmuir on tungsten which revolutionized the incandescent lamp industry.

Several methods are available for measuring ordinary vapor pressures, but most of them fail when applied to the measurement of low vapor pressures such as are exhibited by metals, crystalline salts, many industrial and medicinal products and liquids of high boiling point. Some special studies of methods which are applicable in this field have met with considerable success, but these methods tend to be time consuming and cumbersome. This thesis presents the results of a study of the effusion method originated by Knudsen.

## ACKNOWLEDGMENT

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# INTRODUCTION

Historically, the static method for determining vapor pressures dates from the time of von Babo (1) and Wullner and resulted in the generalizations concerning the relationships between concentration and pressure. As representative of a large class of static methods, may be taken that form in which the substance is introduced into a jacketed Toricellian vacuum and the fall in the column of mercury is measured. Raoult using this method, simple as it is, obtained data which enabled him to enunciate the well-known law which bears his name. This method obviously cannot be used for very small vapor pressures.

Dieterici's differential method as modified by various workers, notably by Frazer and Lovelace (2) is one of great potential accuracy, especially when it employs the Rayleigh manometer. In the hands of the latter workers it has given excellent results with solutions of mannite, potassium chloride and other substances. The chief sources of error are inconstancy of temperature during the experiment and impurities in the experimental material. Very small quantities of certain impurities may give rise to error. The method has not been found applicable below about 0.1 mm. of mercury.

The isotensiscope method of Smith and Menzies (3) is capable of excellent results if care is taken to see to it that all foreign vapors and gases have been removed from

the system.  It has been used in numerous instances.  It is particularly suited to liquids and it may be adapted to any substance by using an inert liquid in the manometer.  The range of pressures to which it is applicable lies somewhat above that for which the differential method may be used.

Dynamic methods have found much wider application than static methods since they are less difficult experimentally, though their intrinsic accuracy seems to be less.  The only one of them which might well be applied to the measurement of small vapor pressures is the gas saturation method originated by Ostwald (4), improved by Walker (5), and probably carried to its highest development by Washburn (6).  It has been applied to the determination of the vapor pressure of mercury at ordinary temperatures by Morley (7) and to the determination of the vapor pressures of iodine by Baxter, Hickey, and Holmes (8), among others.  The important factors are temperature control, the determination of the quantity of air or other gas which is passed and the weighing of the substance carried over by the gas.  Very large volumes of gas must be passed in order to vaporize such a quantity of substance of low volatility as can be determined with reasonable accuracy, and the individual runs commonly require many hours.  While, therefore, the method is an excellent one for the determination of low vapor pressures it is by no means ideal.

Among methods for measurement of very low pressures we have the McLeod Gauge (9) which is really the standard in

the field, the Gaede vacuo-scope (10) which is a refinement of the McLeod gauge, the Knudsen convection gauge (11), and its improved form as developed by DuMonds (12), the quartz fiber vibration gauge suggested and used by Languir (13), and by Coolidge (14), the hot wire manometer of Pirani (15), the ionization gauge (16), and Carver's (17) improved optical manometer which is a refinement of the Rayleigh gauge. These gauges serve very well with the permanent gases, but they are all essentially inaccurate for the determination of the vapor pressures of substances which can condense upon their walls. This difficulty can be avoided in certain cases by maintaining the gauges at constant, high temperatures, or, in the case of the ionization gauge, in a thermostat. This would, in general, involve too great difficulties. The hot wire manometer of Pirani cannot be used for the further reason that many substances are decomposed on coming in contact with the hot wire. These gauges, therefore, can hardly be employed for the purpose which we have in mind.

The Knudsen method based on the effusion of gases and vapors through an orifice of known area presents an accurate and convenient way of determining vapor pressures of solids, crystals, and liquids of low volatility. It has been used by Knudsen (18), himself, on mercury; by Edgerton (19) on cadmium, zinc, and lead; by Pillings (20) on calcium; and by Mack and Swan (21) on naphthalene, chlor-aniline and certain other substances.

If the pressure upon a crystal at constant temperature
be reduced gradually, a point will be reached eventually at
which it passes to the vapor phase under equilibrium condi-
tions; that is, the crystal begins to evaporate as a liquid
would at its boiling point. Presumably, this is true of any
pure chemical compound regardless of the condition of aggre-
gation of its molecules. It is this equilibrium pressure
which is to be measured.

The principle of the Knudsen method is as follows:
The substance is held in a container at constant tempera-
ture, and its vapor escapes to the surrounding space through
a very small hole. If the orifice is very small, then it
may be assumed that the pressure within is equal to the vapor
pressure of the substance. If the pressure in the effusion
chamber outside the equilibrium box is very low and the ori-
fice is relatively remote from the walls of the chamber and
if, further, the vapor is effectively removed from it by
condensation upon surfaces which are very strongly cooled,
no molecules can return to the effusion chamber. The vapor
then issues from the orifice at its equilibrium pressure.
The weight of material effusing in unit time per unit cross-
sectional area of the orifice is then a measure of the vapor
pressure of the substance. This pressure can be calculated
by using the equation derived from the kinetic gas theory
by Meyers (22) with the modification of Knudsen (18).

$$P_1 - P_0 = \frac{G}{t} \times \frac{W_1 + W_2}{\sqrt{e}}$$

In this equation $P_0$ is the pressure of the system exterior

to the box, G is the weight in grams of the substance effus-
ing in time t, e is the density of the vapor, $W_1$ is the
resistance offered by the hole to the outgoing molecules and
$W_2$ is the resistance of the chamber or, in reality, a mea-
sure of the degree of reflection of the molecules back into
the box. When the chamber is made very large compared to
the cross-sectional area of the effusion orifice, as in these
cases, $W_2$ becomes negligibly small and if $P_0$ is less than
$10^{-5}$ mm. of mercury it can also be neglected. Under low
pressures and ordinary temperatures the vapor obeys the gas
laws and e can be expressed as a function of the molecular
weight. At a pressure of one dyne per square centimeter $W_1$
equals $\sqrt{\frac{2\pi}{A}}$ (23). This reduces the above equation developed
by Knudsen to the familiar equation of Langmuir (23),

$$P = \frac{G}{At} \bigg/ \sqrt{\frac{M}{2\,RT}}$$

P is expressed in dynes per sq. cm., G in grams, R in ergs,
and t in seconds. A is the area in sq. cm. of the effusion
hole and T is the temperature on the Absolute scale. P may
be expressed in millimeters of mercury by dividing the pres-
sure in dynes by 980 which is the acceleration due to grav-
ity times the density of mercury. This factor is 1.333 x $10^4$
at $20°$ C

## EXPERIMENTAL

Our apparatus was essentially the same as that used by
Mack and Swan with an additional modification which would
facilitate removal of the effusion box and make the deter-
minations less time-consuming. Their apparatus consisted
of a large tube of twenty-four sq. cm. cross-sectional
area which led directly into a vapor trap which was cooled
by a mixture of dry ice and acetone. A hollow cylindrical
brass block, which held the effusion box, was sealed with
de Khotinsky cement into the open end of the tube. It had
to be removed each time a weighing of the box containing
the sample was to be made. This end of the apparatus was
immersed in the water of the constant temperature bath
during the runs.

A complete drawing of our entire apparatus, including
the McLeod gauge and diffusion pump, is given in Fig. 1.
The equilibrium boxes were made of brass. They weighed
about thirty grams each. In the top of the lid, which
screwed on hermetically, was a hole of about one centimeter
diameter. Over this hole was soldered a thin copper disk
in which a tiny hole was made by piercing with a needle.
The disk was then polished with emery paper to remove any
rough edges from the hole. The diameter of the hole was
determined by two methods; first, by means of a Gaertner
comparator, and second, by means of an eye-piece micro-
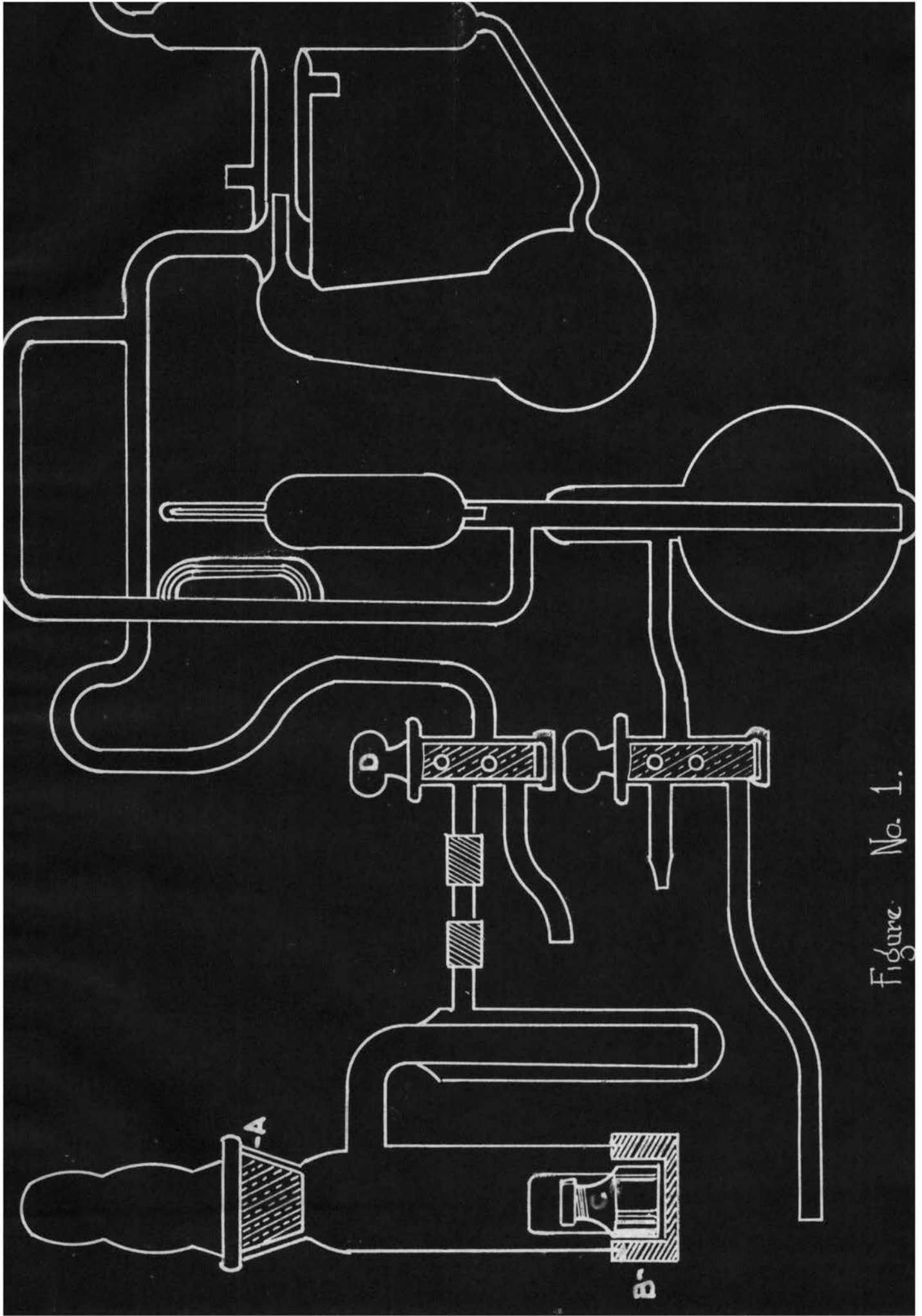meter. Measurements made with the two instruments on five

Figure. No. 1.

different diameters of the hole, which checked very well,
gave the average value for the first box .1981 $\pm$ .0003 mm.
Its area was 3.03 x $10^{-4}$ sq. cm. Two other similar boxes
were also used. The diameters of their holes were .2056
and .323 mm. respectively. All three proved equally good.
The block, which held the effusion box snugly, was also
made of brass and was machined to fit the tube of 50 mm.
bore that was used for the chamber. It was sealed in place
with softened picein which was allowed to set until firm.
The effusion box could be removed without disturbing this
block through a large ground-glass joint sealed into the
top as shown at A of Fig. 1. The female part of the joint,
which was sealed on, had an inside diameter just large
enough to permit removal of the box. A special stop-cock
grease (Cenco No. 15520) designed for high vacuum work was
used on the ground glass connections. It effectively pre-
vented leaking and had no detectible vapor pressure. The
tube leading from the chamber into the trap was of 12 mm.
bore in order to be sure of very little vapor resistance
at this point. The vapor trap was cooled by a mixture of
dry ice and acetone in order to remove any mercury vapors
diffusing back into the chamber from the pump or gauge, and
also to prevent contamination of the pumps by the organic
vapor. The evacuation system consisted of a mercury dif-
fusion pump backed by a Cenco Hyvac pump. A mercury sealed
stop-cock connected the effusion chamber and trap to the
evacuating system. If the system had been previously out-

gassed by pumping for several hours the pressure in the effusion chamber was reduced to $1 \times 10^{-5}$ mm. of mercury in four minutes after opening the stop-cock leading into it. The McLeod gauge was used in testing the pressure on the system from time to time to make sure that it was low enough to be negligible. The effusion chamber, excluding the trap, was immersed in a constant temperature bath that was controlled by a mercury thermo-regulator. The temperature could easily be maintained to .03 degree and usually to .01 of a degree. The bath was stirred vigorously, in order to insure constant temperature throughout. The thermometer was calibrated by comparison with a thermometer calibrated by the Bureau of Standards.

## PROCEDURE

The material whose vapor pressure was to be determined was placed in a thin layer on the bottom of the box, usually about enough being taken to cover the surface. The box was first weighed then lowered by a hook through the opening at A into the brass block B. The male element of the ground-glass joint was then covered with the special high vacuum lubricant and put in place. The box was allowed to remain in the effusion chamber approximately one hour before starting the experiment to be sure that the crystals had come to temperature. Good heat transfer was obtained through the brass block from the bath into the effusion box.

During this time the stop-cock K was closed and the other part of the system was evacuated. When the system had come to temperature the stop-cock was opened and the run started. The time, during which the experiment ran, was measured in seconds by means of a Cenco timer. The pressure was checked from time to time during the experiment to make sure that it remained negligible. Mack (24) has stated that the molecules evaporating from a newly formed surface come off in aggregates of molecules and not as single molecules, at first. We believe this to be true since our first determinations were usually too high. For this reason the first runs were discarded. The average length of the runs was about four hours, never less than three, and some of about eight hours duration. The long runs were necessary in order that accurately weighable amounts might be lost by effusion.

The accuracy of the apparatus was checked by determining the vapor pressure of naphthalene at 30 degrees Centigrade. Two samples, purified by two different methods, were used. In the first, C.P. naphthalene was recrystallized from ethyl alcohol four times, then dried and put in a vacuum desiccator and evacuated for several hours. The results are given in the following table with the results of Mack and Swan and Barker (21) on the samples which they purified in the same manner.

Vapor Pressure in Millimeters of Mercury of Naphthalene at 30°C.

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Mack and Swan------------- .163   (3 determinations)
Barker-------------------- .163
Barker-------------------- .164   (Dynamic Method)
Trimble and Smith-------- .165   (3 determinations)
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The data agree within the experimental error. We believe with Mack and Swan that "the differences among the various results are due as much to different degrees of purity of the samples with which the determinations were made, as to the methods of determination themselves." The second sample of naphthalene was a portion of the first which had been recrystallized from alcohol and then sublimed three times. The increase in purity of the sample was made evident by the rise of the vapor pressure to .172 then to .176, which was found, also, by Mack and Swan, after this further purification. We feel this is ample proof of the correctness of the calibration of the apparatus. A sample calculation is given below employing Langmuir's equation. At 30 degrees Centigrade .0525 grams of naphthalene effused in 8001 seconds through an orifice of $3.03 \times 10^{-4}$ sq. cm. cross-section area.

Substituting these values in the Langmuir equation with R expressed in ergs, and then converting to mm. of mercury by dividing by the acceleration due to gravity in dynes and the density of mercury, the vapor pressure of naphthalene is calculated to be .176. A general equation derived from the above to facilitate calculation is as follows:

$$P_{mm} = \frac{G \sqrt{T} (5.463)}{At \sqrt{M}}$$

The vapor pressures of three compounds were determined using the apparatus just described. The first of these compounds was picric acid. C.P. picric acid, containing ten percent water was used as starting material. It was purified by distilling twice with toluene, then precipitating from hot ether and drying in an oven. It was then kept in a highly evacuated desiccator over sulphuric acid for several hours. Also to test for complete freedom from water, it was put under high vacuum in the effusion chamber of the apparatus for two or three hours, meanwhile the chamber being cut off from the vacuum pumps. The trap was checked carefully to see if any water or other very volatile material had come over. None had as far as it was possible to determine. We feel certain, therefore, that the sample was pure, being particularly free from water.

In experiments using thymol, the Eastman C.P. reagent material was recrystallized three times each from benzene, alcohol, and ether; dried in an oven and then put under vacuum for some time. When we were sure that no volatile impurities

remained, the thymol was then doubly sublimed. It melted
sharply at 51 degrees Centigrade.

The vapor pressure of naphthalene picrate was next deter-
mined. Dr. O. C. Dermer was kind enough to prepare this for
us. This was done by dissolving mole for mole of naphthalene
and picric acid, with a slight excess of picric acid, in
alcohol. This was then crystallized from hot alcohol and
dried.

The data of the various experiments, together with the
pressures calculated from them, are given in Table 1. Each
set of data represents an average of two or more determina-
tions that did not differ by more than two percent.

## Table 1

| Compound | Box No. | Grams Lost | Time Seconds | Press. mm. Calc. | Temp. C. |
|---|---|---|---|---|---|
| Naphthalene (First method of purification) | 1 | .0870 | 14543 | .165 | 30 |
| Naphthalene (Second method of purification) | 1 | .0525 | 8001 | .176 | 30 |
| Thymol | 1 | .0148 | 15167 | .0240 | 25 |
| Thymol | 3 | .0103 | 4056 | .0238 | 25 |
| Thymol | 1 | .0108 | 6429 | .0417 | 30 |
| Thymol | 1 | .0301 | 9914 | .0759 | 35 |
| Thymol | 1 | .0640 | 13071 | .124 | 40 |
| Picric Acid | 2 | .0004 | 12800 | .000602 | 25 |
| Picric Acid | 3 | .0013 | 11604 | .000850 | 30 |
| Picric Acid | 2 | .0006 | 10189 | .00119 | 35 |
| Picric Acid | 2 | .0011 | 12272 | .00172 | 40 |
| Naphthalene Picrate | 2 | .0035 | 23607 | .00219 | 25 |
| " " | 1 | .0028 | 15901 | .00287 | 30 |
| " " | 1 | .0059 | 23044 | .00414 | 35 |
| " " | 2 | .0045 | 13114 | .00519 | 40 |

## Data on Holes in Effusion Boxes

| No. | Diameter mm. | Area Sq. Cm. |
|---|---|---|
| 1 | .1981 | $3.03 \times 10^{-4}$ |
| 2 | .2056 | $3.08 \times 10^{-4}$ |
| 3 | .3230 | $8.19 \times 10^{-4}$ |

## RESULTS

When the logarithm of vapor pressure to the base ten is plotted against the reciprocal of temperature, good straight lines are found for thymol and picric acid as shown in Graph 1. By a well-known application of the Clausius-Clapeyron equation the heat of vaporization may be found by multiplying the slope of the line by -2.303 R where R is the gas constant in calories. The empirical equations and the molar heats of vaporization for these substances are given in Table 2. The accuracy of the data does not justify an attempt to employ the more accurate equation of Kirchoff.

### Table 2

#### Heats of Vaporization

| | | Molar heat |
|---|---|---|
| Thymol | $\log p(\text{mm.}) = -4,435/T + 13.26$ | 20,295 |
| Picric Acid | $\log p(\text{mm.}) = -2,705/T + 5.858$ | 12,381 |

It is apparent that the curve for naphthalene picrate is not a straight line as it should be if it behaves as do the other two substances. It has been found by various workers that compounds of this type commonly dissociate in the neighborhood of room temperature, and this may account for the abnormality. Our calculations were made using the theoretical molecular weight of naphthalene picrate 357.2. If, however dissociation occurs the statistical mean molecular weight, which is lower, should have been used. Moreover, since
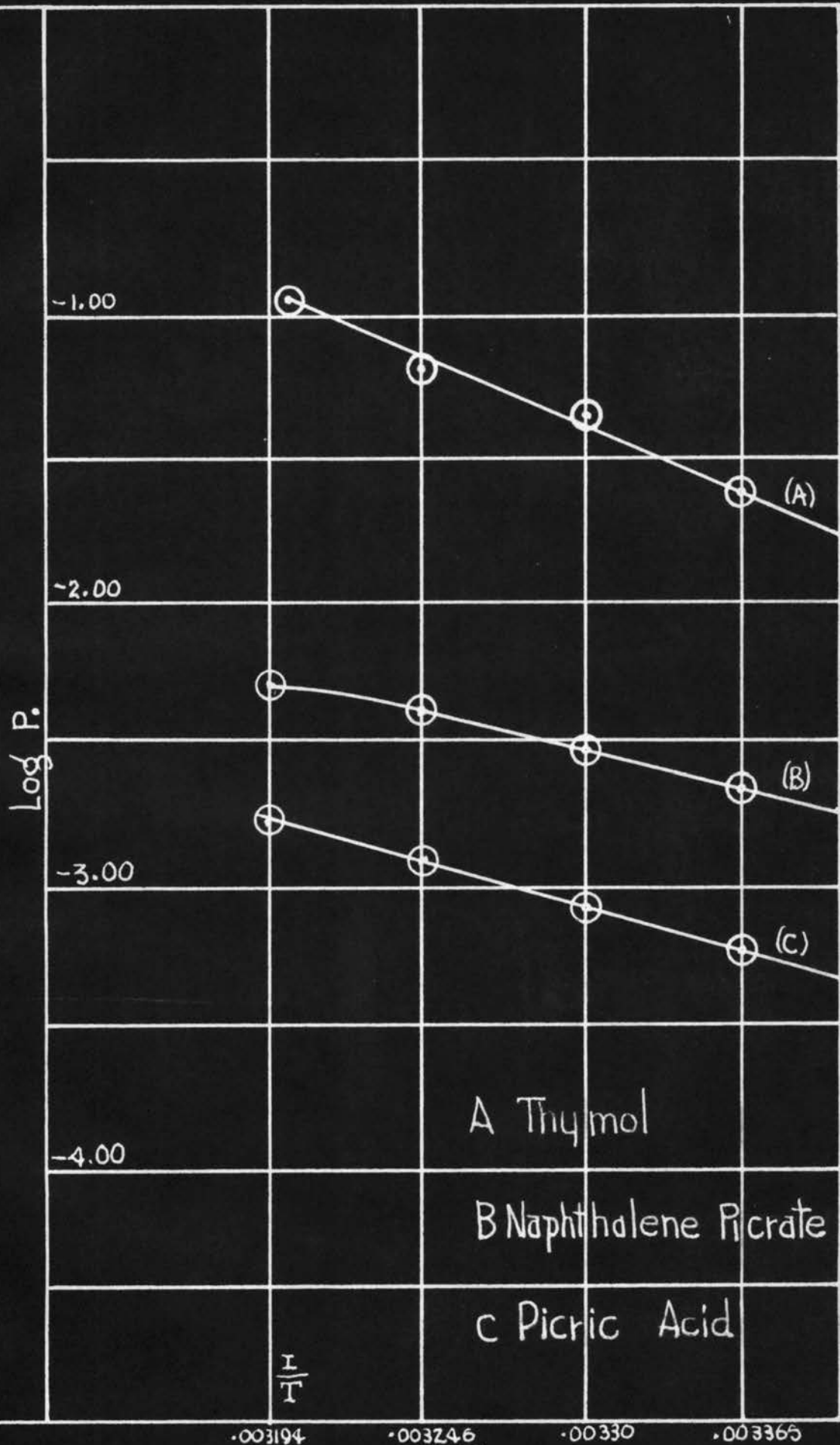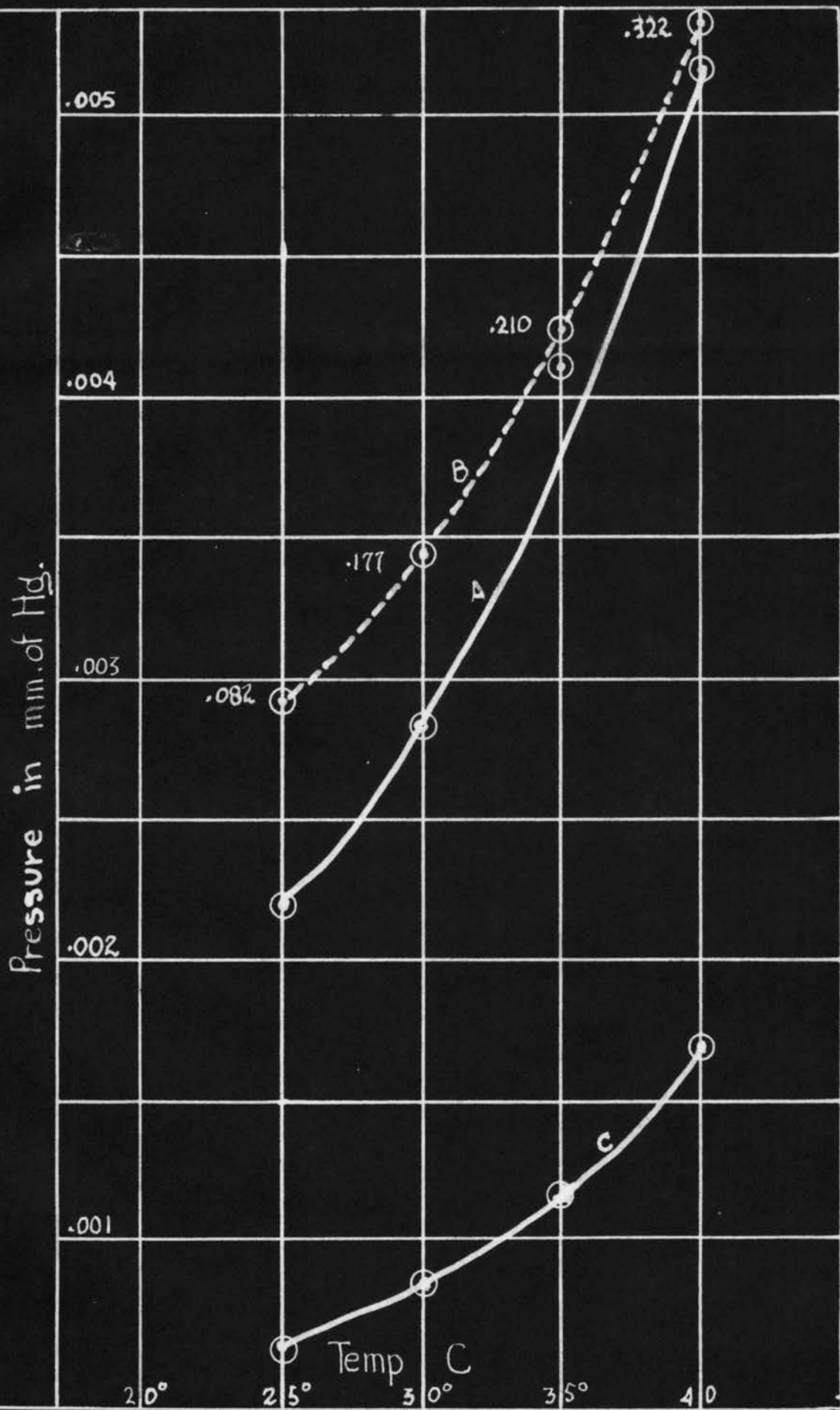
Graph I

dissociation is commonly more extensive the higher the temperature, this mean molecular weight would decrease progressively as the temperature rises. If this correction could be made, the calculations would lead to higher vapor pressures than those which we found and the discrepancies would be greater the higher the temperature; that is, the lower 1/T. It seems reasonable to assume that, if correct mean molecular weights were used, a straight line would be found for this substance as for the others. The course of our curve, then, is just what would be expected if dissociation does occur. No data are to be found in the literature upon the degree of dissociation of naphthalene picrate within the temperature range here covered, neither is there any method known by means of which it can be calculated using data such as ours, so far as we have been able to discover.

In Graph 2 we give, for comparison, the curves as calculated by us for naphthalene picrate (A), and for picric acid (C), as well as the vapor pressure for naphthalene using the data from Lange's Handbook (25). If dissociation were complete the ordinates (A) should be about one-half the sum of those of (B) and (C). In other words, the vapor pressures of naphthalene picrate should be about one-half the sum of the vapor pressures of the decomposition products if pure. Calculation shows that they are actually not more than about five percent of that sum. From this it may be concluded that this substance is only slightly dissociated between 25 and 40 degrees.

Graph II.

## DISCUSSION AND CONCLUSIONS

The time spent in developing the method, and in constructing and calibrating the apparatus prevented us from studying as many compounds as we desired.

We feel that our modification of the apparatus is equally as good as that used by Mack and Swan and that it offers a further advantage in that it facilitates the removal of the effusion box without disturbing the block which closes the apparatus. No reason was found to suspect that any material condensed at any point in the effusion chamber.

Within reasonable limits, the vapor pressure of the substance effusing under the conditions as outlined in the experiment is independent of the area of the effusion hole. This was demonstrated by using three boxes with effusion holes varying from 3.03 to 8.19 x $10^{-4}$ sq. cm. in area. As shown in Table 1, the vapor pressure of thymol, calculated from data obtained using box two differed by .0002 mm. of mercury from that calculated from data using box one. The area of the hole in the second box was 2.7 times as great as that in the first box.

Several sources of error are apparent in our experiments. The chief one probably was in weighing the effusion box by which the amount of material lost by effusion was determined. When only a few milligrams of material was lost in three hours out of a box weighing thirty grams a large relative error would be expected. This error may be

estimated from the experiments with naphthalene. The results of the literature, using the first method of purification, as estimated by Mack and Swan, agree within two percent. Our value easily falls within this limit. Equally good agreement is found using naphthalene purified by the second method. We believe then, that our results can be considered accurate within two percent.

Since organic crystals possess a low heat conductivity the temperature of the crystals, particularly at their surfaces, might be in question but since one hour was allowed for the crystals to come to temperature we feel this is of little consequence. The external pressures were kept very low so that the P in the Knudsen equation is a negligible factor. Since the actual time of each determination was usually a few thousand seconds, the error introduced at the beginning of the experiment by the time required to attain a good vacuum was considerably less than one percent.

The Knudsen method which we have just given in detail is applicable in many fields where vapor pressure data on solids and liquids of low volatility is needed. Since there is nothing particularly critical in the design of the apparatus it presents no difficulty in its construction.

Perhaps the greatest criticism of the apparatus and method is that the effusion box must be removed from the effusion chamber each time a weighing is to be made. This takes time and introduces a chance for error. A great improvement in the apparatus would be some type of balance

which would enable one to measure the loss in weight directly at any time interval. Plotting the loss in weight against the time in seconds, would give a straight line, the slope of which would be the G/t of Langmuir's equation. One run of six or seven hours would give results more accurate than four or five individual runs as carried out at present. The construction of a very light effusion box which could be sealed hermetically presented one of our most difficult problems. Aluminum was found unsatisfactory because of its porosity. Glass was out of the question since the box needed to be opened and closed without changing the size of the effusion hole. Other factors, particularly capillarity, would make glass undesirable.

We feel that with more refinement of the apparatus much can be done in vapor pressure studies of substances of low volatility.

# SUMMARY

The Knudsen method as used by Mack and Swan, for measuring very small vapor pressures, has been further modified to facilitate such determinations.

Using our apparatus, the vapor pressures of naphthalene, as found by us, agreed closely with the values given in the literature.

Vapor pressure studies were made on thymol and picric acid. The empirical equations for the relationship between vapor pressure and temperature are given as well as the molar heats of vaporization calculated from the slope of their curves.

A study on the vapor pressure of naphthalene picrate was made at four different temperatures. An attempt was made to establish the fact that the degree of dissociation of the compound in the temperature range studied is small. The exact degree of dissociation could not be calculated from our data.

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# AUTOBIOGRAPHY

I, Ishmael Leon Smith, was born at Tulsa, Oklahoma, July 22, 1915. I attended public school in Oklahoma City and Britton, Oklahoma and was graduated from Britton High School in May, 1933.

In September, 1933, I enrolled in Central State Teachers College at Edmond, Oklahoma and received the Bachelor of Science degree in May, 1937.

After teaching mathematics and science for one year in the public school at Putnam, Oklahoma, I entered the Graduate School at the Oklahoma Agricultural and Mechanical College in September, 1938, where I have been employed as a graduate assistant until the present time.