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CONTENTS

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ON POROUS SOLIDS[*]

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Abstract

A simple steady-state model is used to describe the vapori-
zation, in a Knudsen cell, of a porous solid having a low vapori-
zation coefficient. The description is in terms of the effective
vaporizing area of the solid. The nature of the effective area
and the assumptions in the model are investigated. Procedures
to obtain the equilibrium pressure and vaporization coefficient
from pressures measured by varying the cell and sample geometry
are discussed. A one-parameter, empirical equation is presented
which accurately represents measurements of the vapor pressure of
porous arsenic taken over a large range of Knudsen-cell orifice
areas.

INTRODUCTION

The Knudsen effusion method is widely used to measure low vapor pressures. It is sometimes difficult to relate the pressures obtained from such measurements to the equilibrium vapor pressure. This is particularly true when the substance under investigation has a low vaporization coefficient. Motzfeldt[1] has used a steady state approach to relate the measured and equilibrium pressures for a sample having a low vaporization coefficient. The vaporizing area of the sample was assumed to be equal to the cross-sectional area of the Knudsen cell. Thus the results do not apply to porous solid samples.

In this paper Motzfeldt's equation is generalized to include solid samples with an effective vaporizing area different from the cross-sectional area of the cell, and the nature of the effective vaporizing area is investigated. Although the equations derived from the rough model employed should not be used to calculate the equilibrium pressure and the vaporization coefficient from the measured pressure and other experimentally amenable quantities, they may serve as some guide to proper experimental procedure and will serve to point out the quantities which are sensitive to the particular model chosen. Recognition and inspection of the assumptions in the simple model used also help to interpret experimental results and to determine the type of information which is obtained from non-equilibrium Knudsen measurements.

In addition a simple empirical equation is presented which has been found to represent accurately the measured vapor pressure of porous, solid arsenic as a function of the orifice area of the Knudsen cell.

BACKGROUND AND DEFINITIONS

The pressure measured in a Knudsen effusion experiment is

$$P_m = \frac{q}{W_a a} G \tag{1}$$

where q is the number of moles of vapor which escape through the orifice of area a in unit time, W_a is the fraction of the molecules entering the orifice which exit from it, and $G = (2 \pi RMT)^{1/2}$ where M is the molecular weight of the gaseous species. The fraction W_a was first calculated by Clausing[2] under the assumption that the molecules enter the orifice with a cosine angular distribution. The equilibrium vapor pressure shall be denoted by P_e.

The vaporization coefficient, α_v, may be defined as the ratio of the number of molecules actually leaving unit area of plane surface in unit time to the number of molecules which are calculated to strike that surface in unit time when the surface is in equilibrium with vapor at P_e. The coefficient α_v is closely related to α_c, the condensation coefficient, which is the fraction of molecules striking a plane surface which sticks to the surface. At equilibrium, $\alpha_v = \alpha_c$.

Although most metals have been found to have vaporization and condensation coefficient close to unity, materials which vaporize to polyatomic gaseous species may have very small vaporization coefficients. This appears to be particularly likely when the structure of the gaseous molecule differs appreciably from the structure existing in the solid lattice.[3,4]

Motzfeldt's Equation

Moltzfeldt[1] considered the effect on P_m of a low vaporization

coefficient and of the resistance to flow of the Knudsen cell proper.
It was assumed that the vaporization coefficient is independent of
pressure, i.e., of the extent of saturation of the vapor over the evapora-
ting surface, and, thus, that $\alpha_v = \alpha_c$ at all pressures. Motzfeldt's re-
sult, for a cylindrical cell of cross-sectional area B, cell Clausing
factor W_B, and orifice area a, is

$$\frac{P_e}{P_m} = 1 + \frac{W_a a}{B} \left(\frac{1}{\alpha} - 2 + \frac{1}{W_B} \right) \tag{2}$$

The symbol α without a subscript represents the vaporization and|or
condensation coefficient when these are equivalent and constant, and
distinction is unwarranted. Whitman[5] had obtained the same equation
previously by a more complex derivation. A somewhat simpler equation
has been presented by Speiser and Johnston,[6] and Rossman and Yarwood,[7]
and others. These authors considered the case where the cell resistance
can be neglected ($W_B = 1$) and where the orifice is sufficiently small so
that the pressure throughout the cell is essentially uniform ($W_a a \ll B$).
In that case, only a low vaporization coefficient causes P_m to deviate
from P_e. At these limits, Eq. (2) reduces to their result,

$$\frac{P_e}{P_m} = 1 + \frac{W_a a}{\alpha B} \tag{3}$$

All these authors mention that the effective vaporizing area of a porous
solid with a low vaporization coefficient will be greater than the cross-
sectional area of the cell.

Assumptions

The derivation of Eq. (2) involves assumptions additional to those

of a plane, vaporizing surface and $\alpha_v = \alpha_c$ independent of pressure. Some
of these are the assumptions usually made in calculating the properties
of dilute gas systems, such as: the vapor is an ideal gas, collisions
between molecules can be neglected, and molecules are reflected from a
surface with a cosine angular distribution independent of the incident
directions. These conditions can be closely realized at low pressures
where the mean free path of the vapor is greater than the dimensions of
the cell.

The derivations cited above invoke further assumptions. The molecu-
lar flow across a horizontal plane of the cell is considered uniform over
the plane. Carlson[8] has demonstrated that rigorous application of the
cosine reflection law in a calculation of the type carried out by Clausing[1]
leads to a radial dependence of the mass flow across a plane perpendicular
to the axis of a cylindrical Knudsen cell. The derivation of Eq. (2)
which makes use of the Clausing factor for the cell, W_B, also requires
that the Clausing factor for the molecules rebounding off the top of the
cell after a certain fraction have been lost through the orifice be the
same as if the rebounding molecules had vaporized uniformly from the
whole cell cross-sectional area. The magnitude of the error due to these
last two assumptions has been discussed by Whitman,[5] Carlson,[8] and Balson.[9]
Balson presents numerical calculations of the fraction escaping through
the orifice which should be more accurate than the use of the cell Clausing
factor, W_B.

MODEL APPLICABLE TO SOLID SAMPLES

In this section the steady-state approach used by Motzfeldt is
extended to cover the general case in which the sample has an effective
vaporizing area different from the cross-sectional area of the cell. The
assumptions made in deriving Eq. (2) are also made here. The effect of
these assumptions will be discussed further below. It is assumed that
$\alpha_V = \alpha_c$ = constant α at all pressures, not because the steady-state
model requires such an assumption, but because the functional form of
the possible variation of α_c and α_V with pressure is unknown. The model
presented here can be solved readily with $\alpha_V \neq \alpha_c$. In that case α_V and
α_c can be interpreted as functions of the extent of saturation in the
cell, which have different values for every steady-state attained. As
the functional form of this variation is unknown, however, such an
approach lacks concrete meaning and introduces conceptual difficulties.
These difficulties might lead to inconsistencies in the solution or in
the definition of auxiliary quantities such as the effective area.

Consider a Knudsen cell, shown in Fig. 1, of cross-sectional area
B, which contains a sample which has an effective vaporizing area A'.
Note that A' can be vastly different from B. The Clausing factor of the
orifice of area $\underline{a}$ is W_a and the Clausing factor of the cell is W_B. Con-
sider the two planes represented by dotted lines in Fig. 1. Plane 1 is
just below the orifice and plane 2 is just above the sample surface.
Let u_1 be the number of moles of vapor which pass upwards through unit
area of plane 1 in unit time. The total mass flux upwards through plane
1 is then $u_1 B$. It is assumed that the vapor density across planes

a

B

1

2

A'
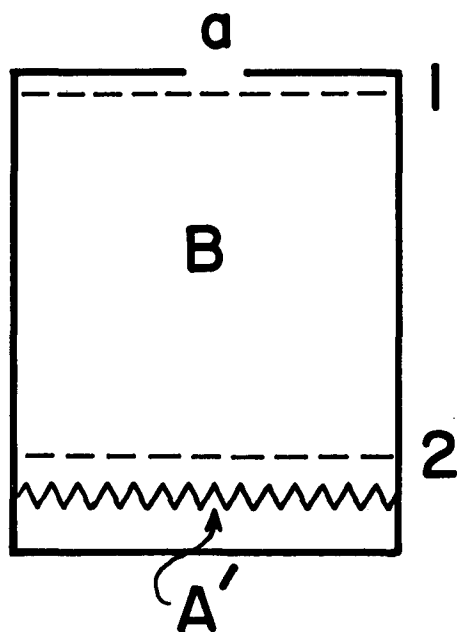
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Fig. 1. Diagram of effusion cell.

1 and 2 is uniform. Let d_1 be the number of moles of vapor which pass downwards through unit area of plane 1 in unit time. Similarly define u_2 and d_2 for plane 2.

The number of moles of vapor which escape through the orifice in unit time, q, will be equal to the number that enter the orifice, $u_1 a$, times the fraction which get through the orifice, W_a. Thus $q = u_1 W_a a$ and the measured pressure, $P_m = u_1 G$ (cf. Eq. (1)). The equilibrium pressure is related to the number of moles of gas, r, which evaporate from area A' in unit time by the Langmuir equation,

$$P_e = \frac{r}{\alpha_v A'} G \tag{4}$$

The number of moles which vaporize from unit area in unit time is thus given by $\alpha_v P_e / G$.

Now apply a mass balance to the flow of vapor through the cell after a steady-state has been attained. The number of moles of vapor which escape from the cell in unit time equals the net number crossing planes 1 and 2 and equals the number vaporizing minus the number condensing.

$$u_1 W_a a = (u_1 - d_1) B \tag{5}$$

$$= (u_2 - d_2) B \tag{6}$$

$$= \alpha_v P_e A'/G - \alpha_c d_2 A' \tag{7}$$

The total number of moles which pass downwards through plane 2 is equal to the number from plane 1 which reach plane 2 plus the number passing upwards through plane 2 which do not reach plane 1.

$$d_2 B = d_1 W_B B + u_2 (1 - W_B) B \tag{8}$$

This equation assumes the applicability of Clausing factors to the

situation inside a Knudsen cell.

Equating u_1 with P_m/G and α_c with α_v these four equations can be solved to yield

$$\frac{P_e}{P_m} = 1 + W_a a \left(\frac{1}{\alpha A'} - \frac{2}{B} + \frac{1}{W_B B} \right) \tag{9}$$

This equation reduces to Motzfeldt's result, Eq. (2), as expected, when the effective vaporizing area is equal to the cell area, that is when $A' = B$. Equation (9) reduces to the simple form used by Speiser and Johnston, Eq. (3), when $\alpha A' \ll W_B B$, showing that the area appropriate to that equation is the same effective area used here. This last limit is the most important result of equations of this type because of the ambiguities involved in the estimation of the resistance to flow of the cell proper. This may be more true for a porous solid than for the plane vaporizing surface considered by Motzfeldt because, with a porous solid having a low vaporization coefficient, the vaporizing molecules might not cross plane 2 with a cosine angular distribution.

THE EFFECTIVE VAPORIZING AREA

The effective vaporizing area of a porous solid is defined to be the area of plane sample surface which would give rise to the observed rate of vaporization. The pressure above, and temperature of, the porous solid and the plane surface being compared should be equal. The rate of vaporization of the plane surface is taken to include only those molecules vaporizing from the surface and does not include molecules in the ambient vapor which strike the surface and are reflected without condensation.

If the observed rate of evaporation is r moles/sec, the evaporation coefficient has been determined by vaporization from a plane surface, and the equilibrium vapor pressure is known, the effective area can be evaluated from the Langmuir equation (4), $A' = rG/\alpha_v P_e$. Usually, the evaporation coefficient is not known from other experiments and the product $\alpha_v A'$ is determined. This definition of the effective vaporizing area implies that the rate of vaporization is always given by $P_e \alpha_v A'/G$.

The magnitude of the effective vaporizing area is a function of the condensation coefficient, the total vaporizing area of the sample, and the geometry of the sample as will be seen in the simple calculations below. It is, however, independent of the pressure in the Knudsen cell -- as long as α_c is independent of pressure. The effective area has a minimum value equal to the area of the plane immediately above the sample when $\alpha_c = 1$. This minimum value is equal to the cross-sectional area of the cell, $A' = B$, when the sample completely covers the cell bottom.

The effective vaporizing area approaches a maximum value equal to the total vaporizing area of the sample, A, as the condensation coefficient approaches zero. This limit means that almost every molecule which

vaporizes escapes because the molecule will not recondense until it has made a very large number of collisions with the surface. In practice this means that increasing the total vaporizing area of a substance with a very low condensation coefficient (on the order of 10^{-6} for example) increases the effective area proportionately. If the sample were a porous solid a Langmuir evaporation rate which increased directly with the depth of sample in the crucible would be observed.

There is another limit upon the effective area which is imposed by the thermodynamic condition that the mass flow in any plane in any direction cannot be greater than the mass flow corresponding to the equilibrium pressure.

$$u_2 \leq P_e / G \tag{10}$$

$$u_2 B \leq B \, P_e / G \tag{11}$$

The rate of evaporation from the sample is $P_e \alpha_v A'/G$. As some of the molecules traveling downwards through plane 2 are reflected when $\alpha_c < 1$,

$$u_2 B \geq P_e \, \alpha_v \, A'/G \tag{12}$$

Combining (11) and (12) yields the condition

$$\alpha_v A' \leq B \tag{13}$$

the equal sign holding only when $\alpha_v = \alpha_c = 1$.

In summary, the following limits exist for the effective area, A', of a homogenous solid sample with total vaporizing area, A, which completely covers the bottom of a cell of cross-sectional area, B:

$$B \leq A' \leq \begin{cases} B/\alpha_v \\ \text{or} \\ A \end{cases} \text{whichever is less} \tag{14}$$

Some Calculations of the Effective Area

Vidale[10] has presented an interesting approximation to the effective

area of a uniform, porous, powder sample by considering the problem to be

one of diffusion through the powder. It was assumed that $\alpha_v = \alpha_c = $ constant.

The powder sample can be considered to be infinitely deep when α_v is large

enough and the sample is deep enough for the equilibrium pressure to be

maintained at the bottom of the porous sample. Vidale's analysis for

this case yields

$$A' = 1.55\sqrt{\frac{\epsilon}{\alpha_c}} \quad B \tag{15}$$

where ϵ is the ratio of pore volume to total volume of the powder and

the other symbols have the same meaning as before. When α_c becomes very

small ($< 10^{-10}$) Vidale's equations give

$$A' = \frac{6(1-\epsilon)\ell}{d} B \tag{16}$$

where d is the average diameter of a powder particle and ℓ is the depth

of powder in the crucible. Thus when α_c is very small the effective area

is directly proportional to the depth of sample, or total vaporizing area,

and independent of the value of α_c, as expected.

An attempt to treat the effective area problem has been made by

Melville[11] who derived an equation for the rate of vaporization from a

wedge-shaped crack. Unfortunately, in addition to mathematical errors,

Melville incorrectly assumes that the fraction of molecules escaping on

each rebound is the same as the fraction which escaped upon the initial

vaporization. The problem of the effective vaporizing area of a pore in

a substance with a low condensation coefficient is in many ways equivalent

to the problem of the deviation from black-body radiation of the radiation

emerging from various parts of cylindrical cavity. This latter problem
has been discussed by a number of authors,[12-17] who used a variety of
mathematical approximation to obtain numerical results.

Vaporization in a Spherical Cavity

This section is concerned with the rate of molecular flow through
an opening of plane area A_0 when the total vaporizing area is A and no
molecules return to the cavity through the opening A_0. The crucial
assumption is that the number of molecules striking any elemental area
of surface is the same as that striking any other elemental area, both
initially and on all rebounds. This assumption is true for a spherical
cavity containing a homogenous vaporizing surface as a consequence of the
cosine spatial distribution of the vaporizing and reflected molecules.
The model serves also as an approximation to other geometries where the
area of the opening, A_0, is considerably smaller than the area of the
wall containing the opening.

Consider the spherical cavity shown in Fig. 2. The opening has
plane area, A_0, and area on the sphere, S_0. For the sake of generality
only a portion of the spherical surface, A, is considered to consist of
vaporizing sample. The remainder of the spherical surface is S. This
could correspond, for example, to a different crystal face of the vapori-
zing material. Now follow a particular group of molecules which evapor-
ate from A in unit time.

(1) Of those that vaporize initially a fraction $S_0/(S_0+S+A)$ escape.
$S/(S_0+S+A)$ hit the wall while $A/(S_0+S+A)$ hit the vaporizing surface again.
Of those that strike the vaporizing surface a fraction α_c condense, so
$(1-\alpha_c) A/(S_0+S+A)$ make first rebound. As all molecules hitting the wall

S₀

A₀

S

A
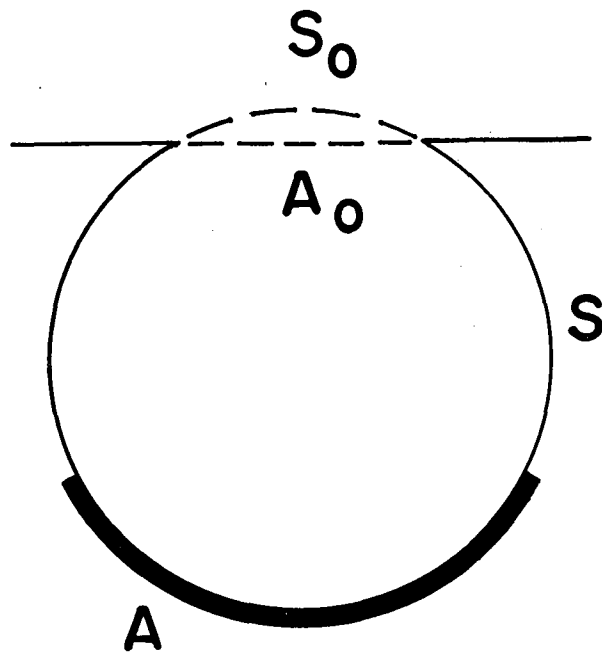
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Fig. 2. Diagram of spherical vaporizing cavity.

rebound the total fraction of the initially vaporizing molecules which make the first rebound is $[S+(1-\alpha_c)A]/(S_0+S+A)$.

(2) Of those that make the first rebound a fraction $S_0/(S_0+S+A)$ escape, that is, the fraction $S_0[S+(1-\alpha_c)A]/(S_0+S+A)^2$ of the initially vaporizing molecules escape after the first rebound. The fraction $S[S+(1-\alpha_c)A]/(S_0+S+A)^2$ rebound from the walls and $(1-\alpha_c)A[S+(1-\alpha_c)A]/(S_0+S+A)^2$ rebound from the sample surface. Thus the total fraction of the initially vaporizing molecules making the second rebound is $[S+(1-\alpha_c)A]^2/(S_0+S+A)^2$.

(3) The fraction which escape after the second rebound is then $S_0[S+(1-\alpha_c)A]^2/(S_0+S+A)^3$.

(4) The fraction of the initially vaporizing molecules which escape through the opening after the nth rebound is

$$\left[\frac{S+(1-\alpha_c)A}{S_0+S+A}\right]^n \cdot \frac{S}{S_0+S+A}$$

Summing the fractions which escape on each of an infinite number of rebounds gives

$$\text{Total fraction escaping} = \frac{S_0}{S_0+\alpha_c A}$$

The rate of vaporization inside the cavity is $\alpha_v AP_e/G$. The rate of escape of molecules through the opening, which is the rate which is measured, is then

$$r = \frac{\alpha_v AP_e}{G} \cdot \frac{S_0}{S_0+\alpha_c A} \tag{17}$$

The effective area, which has been defined by the equation $A' = rG/\alpha_v P_e$, is simply

$$A' = \frac{S_0 A}{S_0+\alpha_c A} \tag{18}$$

It can be shown that the plane area, A_o, is related to the spherical area, S_o, by $A_o = S_o(S+A)/(S_o+S+A)$. The effective vaporizing area of the cavity can then be expressed as

$$A' = \frac{1}{\alpha_c(\frac{1}{\alpha_c A} + \frac{1}{A_o} - \frac{1}{S+A})} \qquad (19)$$

If the cavity were a spherical cavity in a homogenous sample S would be zero.

$$A' = \frac{1}{\alpha_c(\frac{1}{\alpha_c A} + \frac{1}{A_o} - \frac{1}{A})} \qquad (20)$$

Examination of this result shows the effective area to behave as expected. When the condensation coefficient, α_c, is very small the effective area, A', is equal to the total vaporizing area, A. When $\alpha_c = 1$, $A' = A_o$, the area of the opening.

It is interesting to consider this cavity as a Knudsen cell. If r in Eq. (17) is equated with q in Eq. (1) and the area A_o is designated as the orifice area, a, (with $W_a = 1$, $\alpha_v = \alpha_c = \alpha$, and S = 0) one obtains

$$\frac{P_e}{P_m} = 1 + \frac{a}{A}(\frac{1}{\alpha} - 1) \qquad (21)$$

which is identical with Motzfeldt's result, Eq. (2), when the resistance of the cell to flow is negligible ($W_B = 1$). The derivation of Eq. (21) shows that Motzfeldt's equation would be expected to be a good approximation to the vaporization of a non-porous solid which completely lines a Knudsen cell of total interior area A (when a $\ll$ A) -- if the assumption $\alpha_v = \alpha_c$ = constant were correct. It should, perhaps, be pointed out that the spherical cavity also reduces to the same equation as derived by Motzfeldt's steady-state model when α_v is assumed different from α_c in both derivations.

PROCEDURES TO OBTAIN P_e AND α

On the basis of Eq. (2), Motzfeldt[1] suggested that a plot of P_m

against $P_m W_a a/B$ would be a straight line with intercept P_e and slope

$-(1/\alpha + 1/W_B - 2)$. The result of the general effective area case, Eq.

(9), can be rearranged to

$$P_m = P_e - P_m W_a a \left(\frac{1}{\alpha A'} - \frac{2}{B} + \frac{1}{W_B B} \right) \tag{22}$$

Equation (22) immediately points out two dangers in the suggested procedure.

If the ratio $W_a a/B$ were varied by changing the cell cross-sectional area,

B, the intercept of the plot would not be P_e unless the effective vapori-

zing area had changed in direct proportion to B. Also, if the orifice

area, a, were varied, P_m plotted against $P_m W_a a/B$, and a straight line

obtained (this appears unlikely for reasons discussed below) the vapori-

zation coefficient still could not be calculated from the slope of this

plot. At best, the product $\alpha A'/B$ would be obtained where A' might be

vastly different from B.

The discussion in the preceding paragraph implicitly accepts the

assumptions made in the derivation of Eq. (9). It is instructive to

examine the effect on Eq. (9) of the removal or modification of these

assumptions; and thus examine the effect of these assumptions on such

procedures to obtain P_e and α as are implied by Eq. (9) and (22). Equation

(22) suggests that a plot of P_m against $P_m W_a a$ will be a straight line

with intercept P_e when a = 0. It is intuitively clear that P_m must

approach P_e as a approaches zero. Use of the Clausing factor, W_B, in the

derivation ignores the radial dependence of the vapor density inside the

cell, the non-uniform distribution of the molecules reflected from the

of the cell, and the departure from a cosine spatial distribution of the
molecules vaporizing from a porous sample with a low condensation coeffi-
cient. Carlson's[8] and Balson's[9] analyses of the flow of vapor in a
Knudsen cell show that the resistance to flow of the Knudsen cell varies
as the orifice area is varied. This means that W_B in Eq. (9) is not a
constant but, rather, a function of the orifice area, a. This being so,
a plot of P_m against $P_m W_a a$ will deviate somewhat from a straight line.

For substances which have very small vaporization coefficients the
$\alpha A'$ term in Eq. (9) is much larger than the B and $W_B B$ terms so that these
latter terms, and their uncertainties, can be neglected. This is the
situation of primary interest in this paper. Usually when α_v is close to
unity the orifice area can be made small enough so that the measured
pressure is very close to the equilibrium pressure.

It was assumed in deriving Eq. (9) that the vaporization and conden-
sation coefficients are independent of pressure and, therefore, that
$\alpha_v = \alpha_c$ at all pressures. Neither theory nor experiment has yet given
a description of the behavior of α_v and α_c for molecular substances.
However, both theory and experiment indicate that α_v and α_c are not
constants independent of pressure. Knacke, Schmolke, and Stranski[18]
predict the vaporization coefficient of an ionic crystal to be a function
of the undersaturation of the vapor and of the crystal face vaporizing.
Jaeckel and Peperle[19] have measured Knudsen cell pressures of single
crystal faces of NaCl, KI, Sb_2S_3, and sulfur with different cells and
orifice areas. Their results show that the value of α calculated from
Eq. (1) varies with the orifice size.

Hirth and Pound[20] have considered the vaporization of perfect metal
crystals to monatomic vapors. For such substances $\alpha_c = 1$. They calculate

$\alpha_v = (2/3) \cdot (P/P_e) + 1/3$. Their result might be taken to suggest a function for molecular substances with low condensation coefficients such as

$$\alpha_v = \frac{P}{P_e}(1\text{-}m)\,\alpha_c + m\,\alpha_c \qquad\qquad (23)$$

where α_c and m are constants (≤ 1) independent of P . This function has α_v vary from α_c at equilibrium to $m\,\alpha_c$ under Langmuir conditions. The discussion of the effective vaporizing area above indicates the effective area to be a function only of α_c and not of α_v. Because of this the effective area model resulting in Eq. (9) can easily be extended to include Eq. (23). The solution, surprisingly, is exactly the same as Eq. (9) with α replaced by the vacuum vaporization coefficient, $m\,\alpha_c$. This suggests that α_v is the appropriate coefficient for Eq. (9). The rate determining step in the vaporization of a molecular substance with a low vaporization coefficient is expected to be very different from the rate step considered by Hirth and Pound. Thus there is no justification for an equation of the form of Eq. (23), particularly for the assumption that α_v varies while α_c is constant. As the actual variation of α_v and α_c with pressure is, at present, a matter of conjection it seems unlikely that a plot of P_m vs. $P_m W_a$a will be a straight line even when the B and W_BB terms are negligible.

This last conclusion contains a further warning. It is only possible to extrapolate to P_e with confidence after experiments with a number of orifices have defined the curvature of the plot used and when the measured pressures are reasonably close to the equilibrium pressure. If these conditions are not met, the resulting long extrapolation necessary to obtain P_e is hazardous.
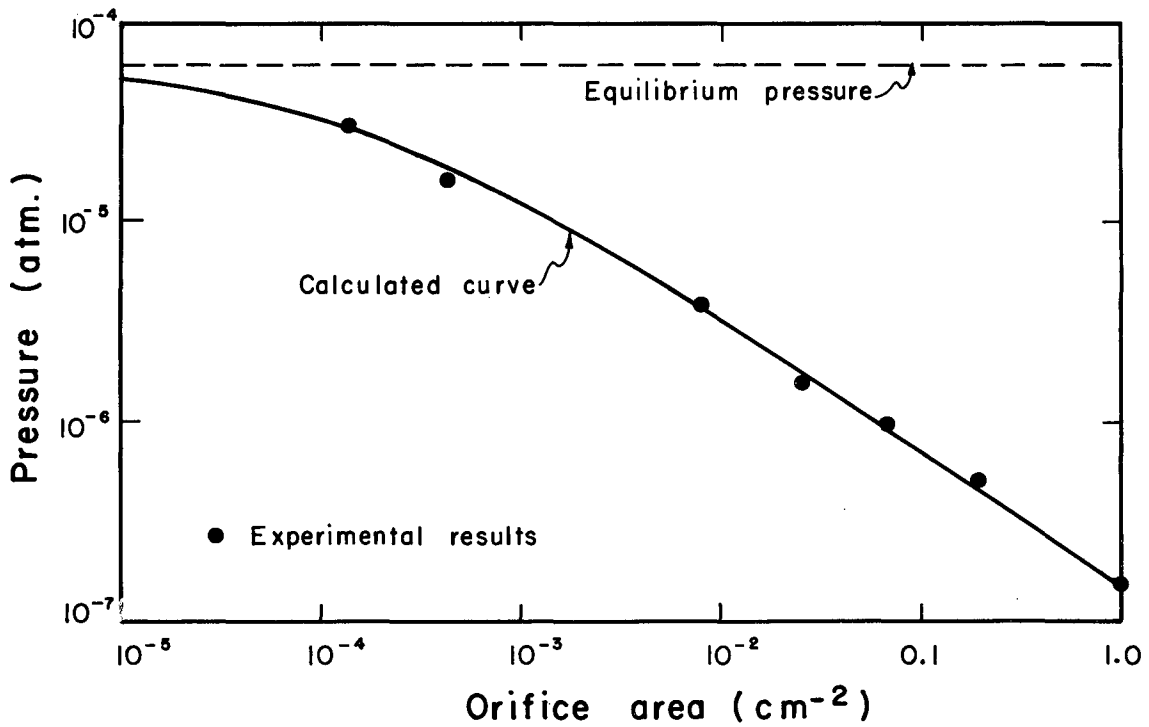
AN EMPIRICAL EQUATION

As has been seen there are many uncertainties in models of the type considered in this paper. This is particularly due to the lack of experimental information on the variation of α_v and α_c with pressure. It is therefore tempting to try to obtain helpful information from experiments which have been published. Brewer and Kane[4] report the results of Knudsen measurements on the vapor pressure of porous arsenic at $575°K$. The vapor pressure was measured for seven different orifice sizes which differed by a factor of 10,000 while the other geometrical and experimental variables were held constant. Their results are illustrated in Fig. 3. If an attempt is made to treat these measurements by an equation such as (9), α is found to vary regularly and to a great degree.

However, Brewer and Kane's results can be represented within experimental error by a simple, one-parameter, empirical equation:

$$\frac{P_e}{P_m} = 1 + (\frac{a}{k})^{2/3} \tag{25}$$

The line drawn through the experimental results in Fig. 3 represents this equation. P_e, P_m, and a are taken directly from their paper. The value of k used to calculate the line (1.3×10^{-4}) is the average of the k values calculated from the measurements. The fit of the seven experimental points to this simple equation is remarkable considering the complexity of the situation inside the Knudsen cell and the large range of variable covered.

Comparing Eq. (25) with Eq. (9) suggests association of the empirical constant k with $\alpha A'$. It would be very interesting to determine if Eq.

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Fig. 3. Knudsen cell data for arsenic at 575°K. The exper-
imental results and equilibrium pressure are from Brewer
and Kane.[4] The calculated curve represents the empirical
equation, $P_e/P_m = 1 + (a/k)^{2/3}$, with $k = 1.3 \times 10^{-4}$.

(25) applies to experimental results on other substances having low

vaporization coefficients. It would also be instructive to find a model

for vaporization in a Knudsen cell which leads to an equation of the form

of Eq. (25).

CONCLUSIONS

The model used to describe the vaporization of porous solids with

low vaporization coefficients is subject to many uncertainties. A par-

ticular difficulty is the unknown variation of the vaporization and

condensation coefficients with the undersaturation of the ambient vapor.

The model does, however, focus attention on the effective vaporizing

area of a solid sample and shows that vaporization coefficients for

porous samples can not be obtained from the slope of a plot of P_m against

$P_m W_a$. The model also demonstrates that attempts to vary the cell dimen-

sions or the sample vaporizing area will not necessarily extrapolate to

P_e.

Uncertainty regarding the behavior of α_v and α_c with pressure suggests

that Knudsen measurements on substances with low vaporization coefficients

can only be extrapolated to the equilibrium pressure reliably when experi-

ments have been carried out with a number of orifice sizes and when the

measured pressures are close to the equilibrium value. This very uncer-

tainty also suggests that experimental data should be carefully examined

to see what light they throw on this unknown behavior.

A simple, empirical equation accurately represents the variation with

orifice area of Knudsen measurements on arsenic. It would be very in-

teresting to ascertain if this equation has more general validity.

LIST OF RECURRING SYMBOLS

a   cross-sectional area of orifice of Knudsen cell

A   total vaporizing area

A'   effective vaporizing area

B   cross-sectional area of Knudsen cell

G = $(2\pi RMT)^{1/2}$

k   empirical constant

P_e equilibrium pressure

P_m measured pressure

q   number of moles of vapor effusing through orifice of Knudsen cell in unit time

r   number of moles vaporizing in unit time

W   Clausing factor for orifice (W_a) or cylindrical cell (W_B)

α condensation coefficient (α_c) and/or vaporization coefficient (α_v) when these are equivalent and constant

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