Mass Transfer at Low Pressures

THOMAS K. SHERWOOD and NORMAN E. COOKE

Massachusetts Institute of Technology, Cambridge, Massachusetts

Data are reported for the evaporation of spheres of naphthalene into air, helium, carbon dioxide, and Freon-12, and of liquid diethyl adipate into air at pressures from 0.1 to 3,000μ Hg and at Reynolds numbers from 0 to 1.37. By use of suitable values of the surface-evaporation coefficient and the assumption of additivity of surface evaporation and diffusional resistances, the data are well correlated. The results lend semiquantitative support to the theory of sublimation of crystals developed by Stranski.

Mass transfer between a solid or liquid and a gas at low pressure is a subject of wide scientific and technological interest. Vacuum sublimation of ice ("freeze-drying") has been developed in recent years as a useful process for drying antibiotics, sera, blood plasma, and other heat-sensitive materials (*52, 22, 16, 17, 18*). Metals and inorganic salts are evaporated at low pressures to coat plastics, lenses, and other parts. Objects moving at high velocities in the upper atmosphere attain high temperatures and tend to sublime; for scientific purposes it is desirable to estimate the rate of sublimation of meteors and satellites.

The subject is also one of considerable interest in conjunction with various mass transfer operations in chemical engineering, as knowledge of evaporation at low pressures throws considerable light on the *interfacial*, or surface, resistance to mass transfer, about which relatively little is known.

THEORETICAL BACKGROUND

It is well known that solids and liquids evaporate at a *finite* rate in the absence of any gas-phase diffusional resistance. This rate is given by

$$-\frac{dW}{d\theta} = \alpha A\sqrt{\frac{Mg_c}{2\pi RT}}(P_V - P_A)$$
$$= \alpha A K_1(P_V - P_A) \qquad (1)$$

for which it is convenient, as indicated in the table of nomenclature, to express the gas constant R, the pressures P_V and P_A, and the conversion factor g_c, in pressure units of microns Hg. Equation (1) with P_A equal to zero gives the rate of vaporization into an absolute vacuum.

This expression was first derived by Hertz (23) and later by Knudsen (32) and by Langmuir (33). The same relation has been derived (42) from statistical thermodynamics without the assumption of a particular model of gas behavior, such as the kinetic theory. It follows from a consideration of the rate of impingement of gas molecules on the surface as given by the kinetic theory for saturated vapor and of the assumption that the fraction 1-α of the molecules hitting the surface does not condense. At equilibrium the rates of evaporation and condensation are assumed to be equal, whence it follows that the rate of vaporization into an absolute vacuum must be proportional to the *evaporation coefficient* α. As applied to the case of evaporation, Equation (1) is an expression for the rate of escape of molecules from the surface; no diffusional resistance, as of the vapor through air, is involved.

The difficulty with Equation (1) is the uncertainty regarding the evaporation coefficient α, which has been the subject of a great deal of experimental and theoretical investigation. A few of the many experimental values of α found in the literature are listed in Tables 1 and 2. Considerable evidence exists that α varies greatly with the purity of the material and the degree of surface contamination. Several investigators have reported values of α increasing in successive tests as continuing efforts were made to remove minute traces of impurities, and Hickman (*24*) postulates that α should be unity for pure liquids with absolutely clean surfaces, in support of which he and Trevoy (*25*) have induced water and glycerol to evaporate at rates corresponding to values of α from 0.5 to 1.0, which is twenty to forty times greater than rates reported by earlier workers who took less care to obtain clean surfaces. Evidently the effect of trace contaminants is so great that reported values of α may often be lower than the characteristic values for the substances tested.

All the values of α found in the literature were obtained with essentially pure substances. Data on solutions are completely lacking, though Emmert and Pigford (*15*) deduced a value of α of $1.8 - 7.4 \times 10^{-6}$ for the absorption of carbon dioxide by water and $3.7 - 9.1 \times 10^{-8}$ for oxygen in water.

Attempts to develop useful theoretical expressions for α have met with little success. Thus Polanyi and Wigner (*46*) relate α to the vibrational frequency of the molecules F, the molecular spacing r, and the enthalpy of vaporization L:

$$\alpha = \frac{L}{\pi F^2 r^2} = \frac{1{,}338L}{S^2} \qquad (2)$$

The second form follows from the relation between F and the speed of sound in the liquid, S. Table 1 lists values of α calculated by means of this expression; it is evident that these compare very poorly with the experimental values. Though the two are not equal, Figure 1 suggests the possibility of a functional relationship with a sharp peak near a value of 0.08 for the right-hand side of Equation (2).

More recently Wyllie (*59*) has proposed that α should be numerically identical to the "free angle ratio" of Kincaid and Eyring (*30*). Table 1 lists this ratio for a number of liquids; it may be seen that these do not agree with the reported values of α.

By virtue of their more ordered structure, the sublimation of solids is more complex

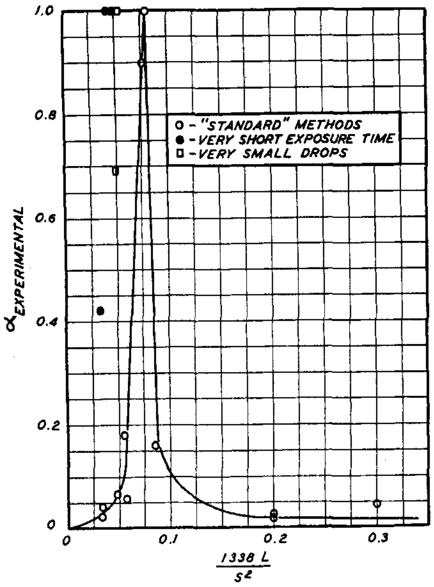

Fig. 1. Comparison of evaporation coefficients with theory of Polanyi and Wigner.

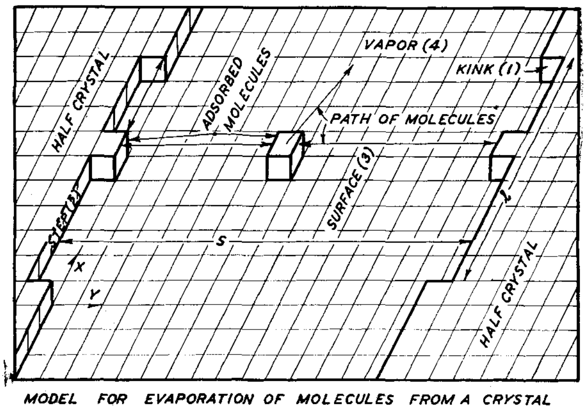

Fig. 2. Diagram illustrating process of separation of molecules from crystal surface.

than the evaporation of liquids. With increasing understanding of crystal growth and structure it has become evident that molecules can join and leave the crystal only at certain definite points on the surface and that diffusion of molecules over the surface occurs when crystals form, evaporate, or dissolve. The fact that the molecule must diffuse over the surface before it can pass into the vapor can materially reduce the rate of sublimation (*51*).

In Figure 2 the incomplete layer of molecules on top of complete layers is the *half crystal*. The boundary of the half crystal is a *step*, which contains *kinks* due to the incompleteness of the row of molecules. As the crystal sublimes, the molecule separates at the kink, moves out across the step, leaves the step to move across the plane, and finally leaves the plane and enters the vapor phase. The sequence is one of diffusional processes, each of which involves a resistance.

With this general picture as a model, Knacke, Stranski, and Wolff (*31*) derived an expression for α in terms of the several diffusional resistances:

$$\frac{1}{\alpha} = \frac{K_{pv}}{K_{sp}}\left[1 + \frac{K_{sp}}{K_{ks}}\right] + \frac{1}{K_{pp}} \qquad (3)$$

Here K is a rate coefficient; subscript pv refers to the path from plane to vapor, sp to the path from step to plane, ks to that from kink to step, and pp to that across the plane. This result is of little practical use but represents the beginning of a valid theory. It explains the low value of 10^{-6} for α for claudetite (As_2O_3), since a primary valence bond must be broken and K_{ks} is very small. It suggests that α might increase with ambient gas velocity in cases where K_{pp} is small, as impinging gas molecules may assist transfer across the plane. As will be shown, this is the case for naphthalene, the flat molecules of which lead to small values of K_{pp} (as compared with the other K's).

DIFFUSIONAL RESISTANCE

The molecular resistance to diffusion away from the evaporating surface becomes dominant at pressures above a few millimeters of mercury, and various empirical equations involving dimensionless groups have been developed for application to flow over surfaces of different shapes. For spheres the Fröessling (*19*) equation with the constant recommended by Ranz and Marshall (*48*) is

$$-\frac{dW}{d\theta} = \frac{2D_0MA}{PRTD} \cdot (1 + 0.30\, Re^{1/2}Sc^{1/3})(P_V - P_A) = \frac{K_2A}{P}(P_V - P_A) \qquad (4)$$

where D_0 is the molecular diffusion coefficient at atmospheric pressure, sq. cm./sec.; D is the diameter of the sphere, cm.; Re is the Reynolds number based on the sphere diameter; Sc is the Schmidt group, $\mu/\rho D_v$; and P is the total pressure in microns Hg.

In the general case molecules must first escape from the surface and then be transported by molecular diffusion into the main body of the gas stream. It would appear to be a logical assumption that the resistances to both rate processes should be additive, with the individual resistances determined by Equations (1) and (4):

$$-\frac{A(P_V - P_A)}{dW/d\theta} = \frac{1}{\alpha K_1} + \frac{P}{K_2} \qquad (5)$$

Because of the diffusional resistance, the rate will be less than the absolute rate of escape from the surface; let this fraction be β:

$$\frac{1}{\beta} = \frac{1}{\alpha} + \frac{K_1}{K_2}P \qquad (6)$$

Here β is the ratio of the actual rate of evaporation to the absolute rate of escape as given by Equation (1) for an α of unity; K_1 is defined by Equation (1); and K_2 is defined by Equation (4).

If K_1 is small, the rate of escape from the surface becomes controlling and the ratio β approaches the evaporation coefficient α. If K_2 is small or the pressure large, diffusion away from the surface becomes controlling, and the value of α is not important. The diameter of the sphere appears in the denominator of K_2, and so the diffusional resistance may be relatively unimportant for very small spheres or drops, when the rate of evaporation is determined primarily by α, which conceivably varies with the radius of curvature. It may be noted that the ratio β does not depend on the vapor pressure and should not be affected by the increase in vapor pressure as the drop becomes very small.

TABLE 1. VALUES OF THE EVAPORATION COEFFICIENT OF LIQUIDS

Substance	α experimental	α calc. by Eq. (2)	Free angle ratio, ψ	Remarks	Reference
Benzene	0.9	0.078	0.85		*5*
Carbon tetrachloride	1.0	0.079	1		*3, 5, 47*
Chloroform	0.16	0.086	0.54		*5*
Dibutyl phthalate	1.0	0.052	6.8×10^{-4}	Very small droplets	*7*
Diethyl adipate	0.18	0.050	0.54		This work
Diethyl hexylphthalate	1.0	0.042	6.1×10^{-5}	Short exposure time	*25*
Ethanol	0.24	0.20	0.020		*10*
Mercury	1.0	0.047	1	Short exposure time (*32*); small droplets (*58*)	*32* *58*
Methanol	0.045	0.30	0.05		*5*
Potassium	1.0	——	1		*43, 45*
Water	0.42	0.033	0.04	Very short exposure time	*24*
Water	0.04	0.033	0.04		*1, 4*

TABLE 2. VALUES OF THE EVAPORATION COEFFICIENT FOR SOLIDS

Substance	α Experimental	Notes	Reference
Ammonium chloride	3.9×10^{-4}	*	*53*
Benzoic acid	0.09–0.51		*2*
Cadmium	0.388–0.65	T = 417.6° to 507.6°C.	*6*
Camphor	0.139–0.190		
Ice	0.94 ± 0.06	−85° to −60°C. Very careful work	*57*
Ice	0.44	$T = -54.8$°C.	*56*
Iodine	0.055–0.208	40°C. $\leq T \leq$ 70°C.	*35*
Mercuric bromide	0.64		*39*
Mercurous chloride	10^{-4}	*	*41*
Mercury	0.85–0.94	−64°C. $\leq T \leq$ −41.5°C.	*58*
Monoclinic arsenic oxide	10^{-6}	*	*54, 55*
Naphthalene	0.036–0.135	40°C. $\leq T \leq$ 70°C.	*35*
Naphthalene	0.0562–0.162	Variation due to nature of ambient gas and flow conditions. 0°C.	This work
Nickel	$0.75 < \alpha < 1$	Ring heated by an induction current	*28*
Phosphorous (red)	1.57×10^{-9} 4.67×10^{-8}	480°C. $\geq T \geq$ 305°C.* *	*37, 38*
Platinum	1	Hot-wire technique	*29*
Potassium	1	Vapor pressure of some faces greater than saturation vapor pressure	*26*
Potassium perrhenate	0.80	T = 768° to 742°K.	*44*
Sulfur	1	α varied from crystal face to crystal face as did vapor pressure of each face	*49*

---

*These four substances all apparently exist in one form in the solid and in an entirely different form in the vapor.

The concept of additivity of diffusional

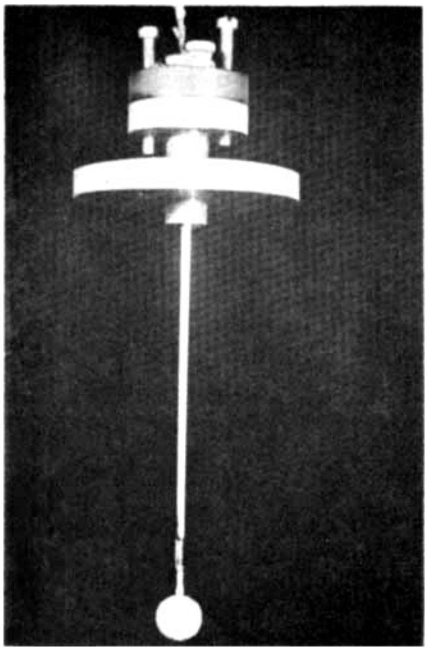

Fig. 3. Test sphere of naphthalene.

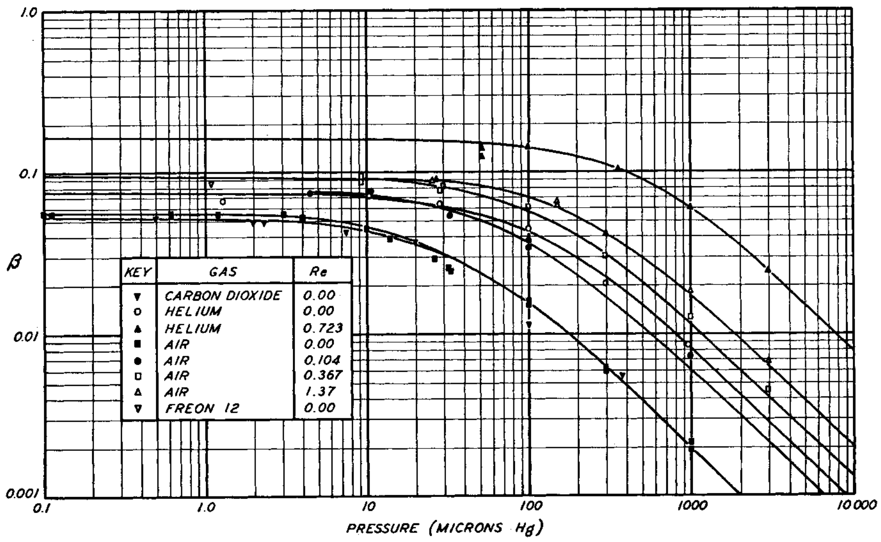

Fig. 4. Relative sublimation rates for naphthalene.

and surface-escape resistances has been employed previously by Langmuir and Langmuir (*34*), Carman (*11*), and others but never properly tested. Fuchs (*20*) and later Bradley and co-workers (*7, 8*) introduced a modification to allow for the ratio of the molecular mean free path to the dimensions of the experimental equipment. Monchick and Reiss (*40*) developed equations based on the non-equilibrium character of the gas phase and suggested that the apparent evaporation coefficient should change as drop size or pressure become very small.

Crout (*14, 21, 50*) showed that as evaporation occurs the distribution of molecular velocities near the surface could not be the same as the equilibrium distribution and that, as a consequence, the rate of evaporation from a flat surface should be limited by the speed of sound in the vapor. Crout's theory would appear to apply only when the space above the evaporating surface has a minimum dimension of at least three mean free paths, since this length of travel by the molecules is necessary to reestablish a normal equipartition of energy in the vapor molecules. For the naphthalene used in the present work the mean free path at the lowest pressures was 16 cm., or more than three times the diameter of the tube employed, and so Crout's theory was not tested.

Application of Equation (5) requires that the ambient partial pressure P_A be known. In many cases there is an additional resistance to transport of vapor from the space surrounding the evaporating material to the point at which P_A is measured or controlled. Data are reported in the literature (*59*) on the evaporation of liquids placed in the bottom of a small cylindrical cup placed in an evacuated space; such data were obtained in the course of the present study for diethyl adipate. With such an arrangement it is necessary to take account of the resistance to escape owing to the return to the liquid of some of the molecules impinging on the inner vertical walls of the cup. Clausing's treatment (*13*) of this process is entirely analogous to that of Hottel and Keller (*27*) for thermal radiation between parallel planes separated by nonconducting but reradiating walls, and the numerical results are the same.

EXPERIMENTAL PROCEDURE

Small (1.0 cm.) spheres of naphthalene were sublimed at pressures from 0.1 to 3,000μ total pressure in air, helium, carbon dioxide, and Freon-12. Rates of evaporation were measured in stagnant gas and in gas flowing over the sphere at Reynolds numbers up to 1.37.

The principal part of the apparatus consisted of a 5.08-cm. I.D. copper tube in which the test spheres were mounted. Dried gas entered through a controlled leak to an intermediate-pressure chamber, then through a sonic orifice to a flow-straightening section upstream of the test position. The latter consisted of a 12-cm. bundle of 0.63-cm. copper tubes each 12.8 cm. long. Downstream from the bundle of tubes the gas entered the 5.08-cm. copper tube through a reducing nozzle. Both nozzle and copper test section were internally polished.

The test sphere was centered in the test section 26 cm. downstream from the nozzle and 22.9 cm. upstream from the discharge into a 15.3-cm. steel pipe. The latter was evacuated by means of a large oil-diffusion pump (15.3-cm. throat) in series with a 100-cu. ft./min. mechanical pump. The entire flow-measuring, flow-straightening, and test sections were surrounded by a water bath maintained at 0°C. Pressure was measured by means of two McLeod gauges and one Alphatron gauge at taps 3.8 cm. downstream from the test sphere.

The naphthalene spheres were formed on a stainless steel stock carrying a thermocouple and were machined smooth. One of these is shown in Figure 3. When a test was made, the sphere was weighed and placed in the apparatus, the pressure adjusted, and the sphere removed and reweighed after approximately 0.178 g. had been estimated to be evaporated. Test periods varied from 0.4 to 29.1 hr. The weight-time relationship having been established, the observed times were adjusted to a constant weight loss of 0.1779 g., this being the observed loss in 1 hr. in the case of naphthalene at 0.10μ with no gas flow.

Since both the rate of evaporation and gas flow were very small, the evaporative cooling of the surface was negligible, and both gas and sphere surfaces were within 0.1° of 0°C. in all tests. At this temperature the vapor pressure of the naphthalene as used was measured by the effusion technique and found to be 5.74μ, agreeing well with an extrapolation of the data of Bryant (*9*) obtained by an air-saturation method at higher temperatures. The vapor pressure of diethyl adipate was found similarly to be 1.46μ at 0°C. The diffusion coefficient for naphthalene in air at 1 atm. was taken (*12*) to be 0.0639 sq. cm./sec. and that for diethyl adipate as 0.0199 sq. cm./sec.

RESULTS

The data obtained were compared with Equation (6), as it was anticipated that the concept of additivity of surface-escape and diffusional resistances might prove valid.

The rate was found to be independent of pressure below about 1μ, and so the results at 0.1μ were assumed to involve no diffusional resistance. The adjusted test time θ_2 is the ratio of the time at pressure P to the time for the same weight loss at 0.1μ (1 hr. for naphthalene), whence from Equations (5) and (6),

$$\theta_2 = \frac{\alpha}{\beta} = 1 + \alpha \frac{K_1}{K_2} P \qquad (7)$$

The data were found to fall on straight lines when plotted as θ_2 vs. P, an indication that α was independent of pressure. In the case of stagnant air, α was found from the intercept to be 0.0625 and from the slope to be 0.0561; the latter is doubtless the better value.

Figure 4 summarizes the data on naphthalene in the form of a graph of β ($0.0561/\theta_2$) vs. pressure. The asymptotes at low pressure are the indicated values of the evaporation coefficient α, listed in Table 3. Decrease in β with increase in pressure indicates the increasing importance of the diffusional resistance.

The solid curves of Figure 4 are calculated from the theory of additivity of resistances, by use of Equation (6), with K_1 as defined by Equation (1). For finite gas flow the Ranz and Marshall value of K_2 was used, as given by Equation (4). With zero gas flow the naphthalene escaped by diffusion down the copper tube from the test sphere to the large exhaust conduit, where its partial pressure was essentially zero. In this case K_2 was obtained by adding the resistance to diffusion through the 22.9-cm. stagnant gas column to the diffusional resistance to evaporation from the sphere, as given by Equation (4).

The only data from the present study used in placing the lines on Figure 4 are the values of α obtained as described above. (Vapor pressure is not involved in β.) The excellent agreement with the experimental points would seem to be convincing proof of the additivity of surface evaporation and diffusional resistances. An alternative analysis is shown in Figure 5, where the observed and calculated values of β are compared directly.

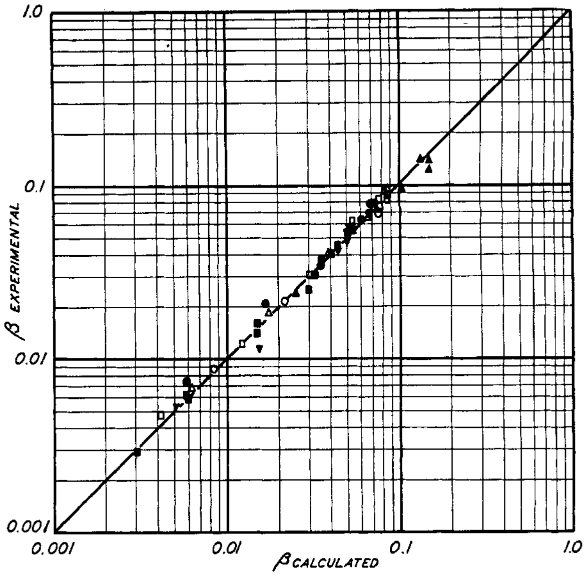

Fig. 5. Comparison of experimental and calculated sublimation rates.

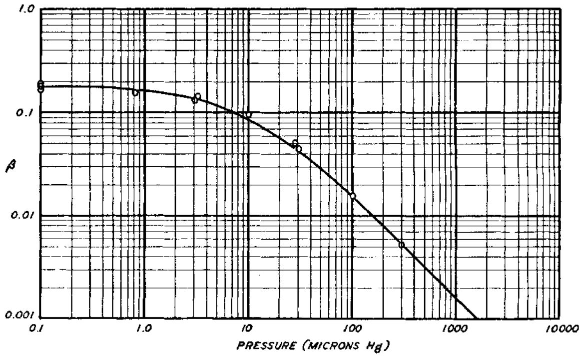

Fig. 6. Data on relative evaporation rates for diethyl adipate.

Figure 6 shows similar results for the evaporation of carefully degassed liquid diethyl adipate from a stainless steel cup 1.11 cm. deep and 1.19 cm. in diameter. The calculated curve is based on a value of α of 0.177, with allowance for the reflection of molecules from the sides of the cup. This last effect corresponded to a resistance of 8 to 22% of that at the liquid surface, depending on the liquid level.

Monchick and Reiss (*40*) report data on the evaporation of very small drops of diamyl sebacate in a cloud chamber, and Birks and Bradley (*7*) give data on the evaporation of small drops of dibutyl phthalate. These data are plotted in Figure 7 as

$$\frac{\alpha}{\beta} \text{ vs. } \alpha \frac{K_1}{K_2} P = \frac{\alpha D P}{2 D_0} \sqrt{\frac{g_c R T}{2 \pi M}}$$

with the values of α, P_V, and D_0 reported by these investigators. The results of this investigation for evaporation of naphthalene into stagnant air, helium, and carbon dioxide are also replotted, along with the theoretical line representing Equation (6). The general agreement of the data is good, and the results lend additional support to the basic theory represented by Equation (6). Only in the lower left corner of Figure 7 is the indicated agreement with theory sensitive to the value assumed for α. There is no evident trend indicating α to vary with the radius of curvature.

Several observations regarding the results of the present study may be made, in addition to an appraisal of the validity of the resistance theory. As the curves shown in Figure 4 are each based on a single value of α, it is evident that this coefficient is independent of pressure

TABLE 3. SUMMARY OF EXPERIMENTAL VALUES OF THE EVAPORATION COEFFICIENT

Evaporating substance	Gas	Reynolds number	α
Naphthalene	Air	0.00	0.0561
Naphthalene	Air	0.104	0.0773
Naphthalene	Air	0.367	0.0947
Naphthalene	Air	1.37	0.0960
Naphthalene	Helium	0.00	0.0758
Naphthalene	Helium	0.723	0.162
Naphthalene	Carbon dioxide	0.00	0.0526
Naphthalene	Freon-12	0.00	0.086 approx.
Diethyl adipate	Air	0.00	0.177

over the experimental range. Furthermore, the constancy of α over months of time for numerous test samples suggests that surface contamination, if present, was at least constant. The inference is that the values obtained are characteristic of the materials.

As shown in Table 3, α for naphthalene in air increases regularly from 0.0561 to 0.0960 as *Re* increases from 0 to 1.37; a somewhat greater effect of *Re* is indicated for naphthalene in helium. In line with the theory of Stranski and coworkers, this result indicates that the flow of ambient gas may assist the transfer of molecules across the plane of the crystal (increase K_{vp}), the resistance to which is relatively large in the case of the flat naphthalene molecules. If K_{vp} is assumed to be a function of *Re*, Equation (3) may be put in the form

$$\frac{1}{\alpha} = A_1[1 + A_2A_3] + A_4f(Re) \quad (8)$$

where A_1, A_3, and A_4 depend only on the nature of the evaporating surface, and A_2 is a function of the interaction of foreign molecules with those of the crystal surface. Taking $f(Re)$ as 1.0 when *Re* is zero yields

$$\frac{1}{\alpha_0} - \frac{1}{\alpha} = A_4[1 - f(Re)] \quad (9)$$

where α_0 is the value of α with no gas flow. Figure 8 is a plot of the left-hand side of this expression vs. $1/Re$, from which the empirical form of $f(Re)$ may be developed. The intercept of 8.0 suggests that the highest values of α with flow over naphthalene are about 0.1 in air and 0.19 in helium.

It is also noted that α is smaller in air or carbon dioxide than in helium or Freon-12, the values for the latter two gases differing by less than 15%. It is difficult to imagine a mechanism by which the very dissimilar molecules helium and Freon-12 might produce nearly the same effect if both interfered with surface diffusion by adsorption on the surface. One can only speculate that neither helium nor Freon-12 affects the rate at all, but that air and carbon dioxide interfere in some way.

Recent chemical engineering literature has been concerned with the *interfacial*, or surface-evaporation, resistance, and it is of interest to note the magnitude of this effect in the case of evaporation into air at 1 atm. Figure 9 is a graph showing the surface-evaporation resistance as a percentage of the total resistance to mass transfer for air flow over a 1-cm. sphere of naphthalene, α being taken as 1.0. Corresponding values of the surface resistance for other values of α may easily be obtained: at 1 atm. the percentage is seen to be 2.5 at $Re = 10^7$; if α were 0.1 the value would be 2.5(1/0.1)/(0.975 + 0.25), or 20.4%. Evidently α must be very much smaller than the

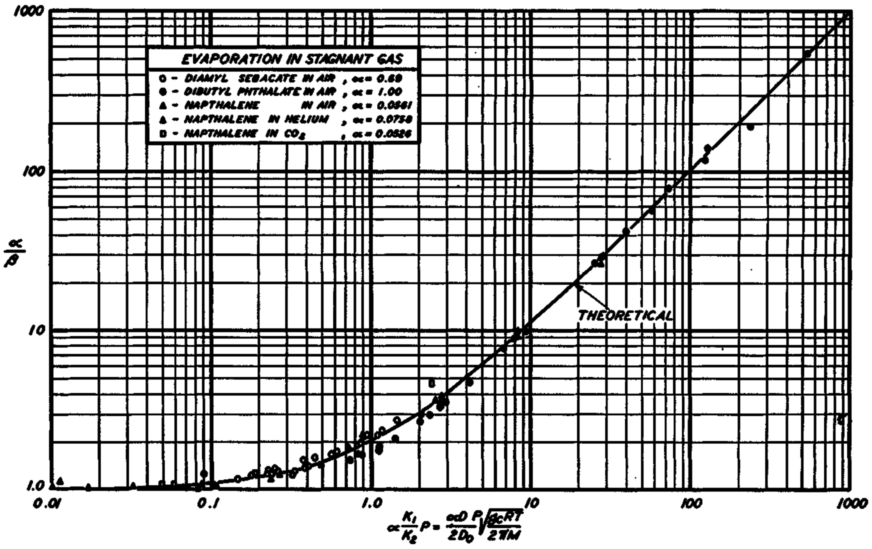

Fig. 7. Comparison of present data on naphthalene with data from the literature on small liquid drops.

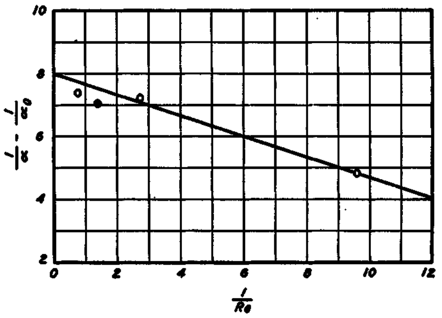

Fig. 8. Effect of gas-flow rate on evaporation coefficient.

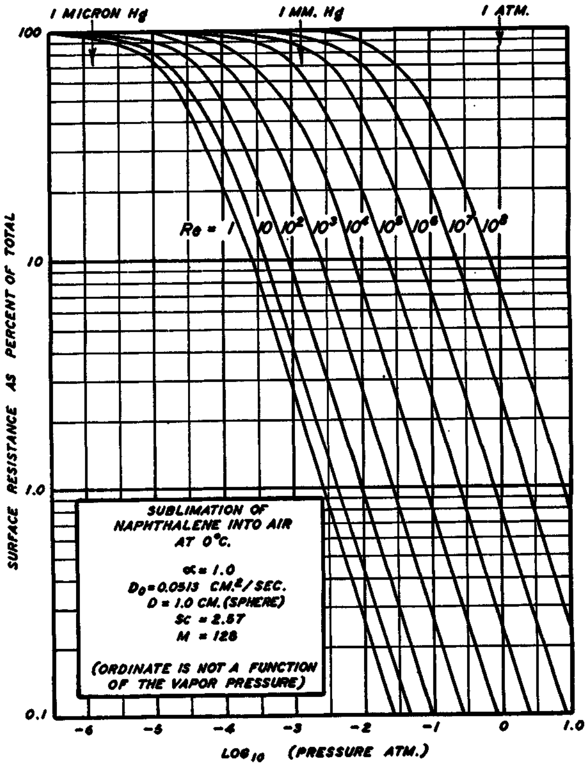

Fig. 9. Illustration of the relative importance of surface-evaporation and diffusional resistances.

values here reported for the surface resistance to be important at 1 atm. in the usual range of Reynolds numbers.

SUMMARY

Values of the evaporation coefficient α were measured for naphthalene subliming into air, helium, carbon dioxide, and Freon-12, and for liquid diethyl adipate evaporating in air. The results are given in Table 3. The evaporation coefficient was found to be independent of pressure over the range 0.1 to 3,000μ of mercury, but to be higher in helium and Freon-12 than in air or carbon dioxide. Results obtained at Reynolds numbers up to 1.37 indicate that α increases with Re.

The data lend excellent support to the concept of additivity of surface evaporation and diffusional resistances, being capable of prediction on the basis of the available correlations for evaporation from single spheres together with experimental values of evaporation coefficients. The results agree in a semiquantitative fashion with the general theory of sublimation developed by Stranski and coworkers.

ACKNOWLEDGMENT

The work described was carried out under contract DA-19-020-ORD-3244 with the Office of Ordnance Research, Department of Defense. Funds for the purchase of the vacuum pumps employed were supplied by the National Research Corporation Scientific Trust.

NOTE:—The original data are not tabulated, but are on file as the 1956 Sc.D. thesis of Norman E. Cooke in the Library of the Massachusetts Institute of Technology, Cambridge, Massachusetts. Photostat or microfilm copies may be ordered from the library.

NOTATION

A = surface area, sq. cm.
A_1, A_3, A_4 = functions of the nature of the surface of the evaporating solid substance
A_2 = function of interaction of foreign molecules with those of the crystal surface
D = diameter of sphere, cm.
D_V = diffusivity, sq. cm./sec.
D_0 = diffusivity at 1 atm., sq. cm./sec.
F = vibrational frequency of molecule, sec.$^{-1}$
g_c = conversion factor = 1.333 g. mass/(μ Hg)(cm.)(sec.^{2})
G = mass flow rate, g./(sec.)(sq. cm.)
$K_1 = \sqrt{\dfrac{Mg_c}{2\pi RT}}$
$K_2 = \dfrac{2D_0M}{RTD}(1 + 0.30\, Re^{1/2}Sc^{1/3})$; *see* Equation (4)
$K_{pv}, K_{sp}, K_{ks}, K_{pp}$ = rate constants in Equation (3)
L = enthalpy of vaporization, g. cal./g.
M = molecular weight, g./g. mole
P = pressure, μ Hg
P_A = partial pressure of evaporating substance in ambient gas, μ Hg
P_V = vapor pressure, μ Hg
r = molecular spacing, cm.
R = gas constant = $62.37 \times 10^6 \mu$ Hg/(cc.)(g./mole)(°K.)
Re = Reynolds number, DG/μ
S = speed of sound in liquid, m./sec.
Sc = Schmidt number, $\mu/\rho D_v$
T = absolute temperature, °K.
W = mass, g.
α = evaporation coefficient (sometimes referred to as *accommodation coefficient*)
α_0 = value of α in stagnant gas
β = ratio of actual rate of mass transfer (evaporation) to the limiting rate of escape of molecules from the surface, as given by Equation (1) for $\alpha = 1.0$
μ = gas viscosity, g./(sec.)(cm.)
ψ = free-angle ratio
ρ = gas density, g./cc.
θ = time, sec.
θ_2 = ratio of the time of evaporation of 0.1779 g. at pressure P to the time for the same weight loss at 0.1μ

LITERATURE CITED

1. Alty, T., *Phil. Mag.*, **15**, 82 (1933).
2. ———, *Proc. Roy. Soc.* (*London*), **A161**, 68 (1937).
3. ———, and C. A. McKay, *ibid.*, **A149**, 104 (1935).
4. Alty, T., and F. H. Nicoll, *Can. J. Research*, **4**, 547 (1931).
5. Baranaev, M., *J. Phys. Chem.* (*U.S.S.R.*), **13**, 1635 (1939).
6. Bennewitz, K., *Ann. Phys.*, **59**, 193 (1919).
7. Birks, J., and R. S. Bradley, *Proc. Roy. Soc.* (*London*), **A198**, 226 (1949).
8. Bradley, R. S., M. G. Evans, and R. W. Whytlaw-Gray, *Proc. Roy. Soc.* (*London*), **A186**, 368 (1946).
9. Bryant, H. S., Jr., Sc.D. thesis, Mass. Inst. Technol., Cambridge (1956).
10. Bucka, H., *Z. physik. Chem.*, **195**, 260 (1950).
11. Carman, P. C., *Trans. Faraday Soc.*, **44**, 529 (1948).
12. Chipolone, M. D., S. M. thesis, Mass. Inst. Technol., Cambridge (1955).
13. Clausing, P., *Ann. Phys.*, **5F12**, 961 (1932).
14. Crout, P. D., *J. Math. and Phys.*, **15**, 1 (1936).
15. Emmert, R. E., and R. L. Pigford, *Chem. Eng. Progr.*, **50**, 87 (1954).
16. Flosdorf, E. W., "Biological Applications of Freezing and Drying," Chap. 2, Academic Press, Inc., New York (1954).
17. ———, "Freeze-Drying," Reinhold Publishing Corp., New York (1949).
18. ———, and S. Mudd, *J. Immunol.*, **29**, 389 (1935).
19. Froessling, N., *Gerlands Beitr. Geophys.*, **52**, 170 (1938).
20. Fuchs, N., *Physik. Z. Sowjetunion*, **6**, 224 (1934).
21. Giddings, H. A., and P. D. Crout, *J. Math. and Phys.*, **15**, 124 (1936).
22. Harris, R. J. C., ed., "Biological Applications of Freezing and Drying," Academic Press, Inc., New York (1954).
23. Hertz, H., *Ann. Phys.*, **17**, 177 (1882).
24. Hickman, K. C. D., *Ind. Eng Chem.*, **46**, 1442 (1954).
25. ———, and D. J. Trevoy, *Ind. Eng. Chem.*, **44**, 1882 (1952).
26. Hock, F., and K. Neumann, *Z. physik. Chem.*, **NF2**, 241 (1954).
27. Hottel, H. C., and J. D. Keller, *Trans. Am. Soc. Mech. Engrs.*, **55–56**, 39 (1933).
28. Johnston, H. L., and A. L. Marshall, *J. Am. Chem. Soc.*, **62**, 1382 (1940).
29. Jones, H. A., I. Langmuir, and G. M. Mackay, *Phys. Rev.*, **30**, 201 (1927).
30. Kincaid, J. F., and H. Eyring, *J. Chem. Phys.*, **6**, 620 (1938).
31. Knacke, O., I. N. Stranski, and G. Wolff, *Z. physik. Chem.*, **198**, 157 (1951).
32. Knudsen, M., *Ann. Phys.*, **47**, 697 (1915).
33. Langmuir, I., *Phys. Rev.*, **2**, 329 (1913).
34. ———, and D. B. Langmuir, *J. Phys. Chem.*, **31**, 1719 (1927).
35. Marcellen, R., *Compt. Rend.*, **158**, 1674 (1914).
36. Marshall, A. L., K. W. Dornte, and F. J. Norton, *J. Am. Chem. Soc.*, **59**, 1161 (1937).
37. Melville, H. W., and S. C. Gray, *Trans. Faraday Soc.*, **32**, 271 (1936).
38. *Ibid.*, 1026 (1936).
39. Metzger, F., and E. Miescher, *Nature*, **142**, 572 (1938).
40. Monchick, L., and H. Reiss, *J. Chem. Phys.*, **22**, 831 (1954).
41. Neumann, K., *Z. physik. Chem.*, **A191**, 284 (1942).
42. *ibid.*, **A196**, 16 (1950).
43. *Ibid.*, **NF2**, 215 (1954).
44. ———, and V. Costeanu, *Z. physik. Chem.*, **A185**, 65 (1939).
45. Neumann, K., and K. Schmoll, *Naturwissenschaften*, **39**, 131 (1952).
46. Polanyi, M., and E. Wigner, *Z. physik. Chem.*, **A139**, 439 (1928).
47. Pruger, W., *Z. Physik*, **115**, 202 (1940).
48. Ranz, W. E., and W. R. Marshall, *Chem. Eng. Progr.*, **48**, 173 (1952).
49. Rideal, E., and P. M. Wiggins, *Proc. Roy. Soc.* (*London*), **A210**, 291 (1951).
50. Schrage, R. W., "A Theoretical Study of Interphase Mass Transfer," Columbia Univ. Press, New York (1953).
51. Sears, G. W., *J. Chem. Phys.*, **24**, 868 (1956).
52. Shackell, L. F., *Am. J. Physiol.*, **24**, 325 (1909).
53. Spingler, H., *Z. physik. Chem.*, **B52**, 90 (1942).
54. Stranski, I. N., and U. Winkler, unpublished, quoted in Knacke, O., I. N. Stranski, and G. Wolff, *Z. Elektrochem.*, **56**, 476 (1952).
55. Stranski, I. N., and G. Wolff, *Z. Elektrochem.*, **53**, 1 (1949).
56. Strickland-Constable, R. F., and E. W. Bruce, *Trans. Inst. Chem. Engrs.* (*London*), **32**, 192 (1954).
57. Tschudin, K., *Helv. Phys. Acta.*, **19**, 91 (1946).
58. Volmer, M., and I. Estermann, *Z. Physik*, **7**, 1 (1921).
59. Wyllie, G., *Proc. Roy. Soc.* (*London*), **A197**, 383 (1949).