The Maximum Rate of Sublimation of Solids

THOMAS K. SHERWOOD and CONRAD JOHANNES
Massachusetts Institute of Technology, Cambridge, Massachusetts

The rate of evaporation of pure liquids and solids at very low pressures is given by the Hertz-Knudsen equation

$$\dot{m} = \alpha P_s \sqrt{\frac{M}{2\pi R T_s}} = 0.0583 \alpha P_s \sqrt{\frac{M}{T_s}} \qquad (1)$$

This relation was derived from the kinetic theory of gases, with the later introduction of α, defined as the fraction of the gas molecules impinging on a condensing surface which stick and are not reflected. It has generally been assumed that α depends on the specific properties of the substance.

Numerous experimental determinations of α have been reported in the literature, and no attempt will be made to list these here. Values of α ranging from 10^{-9} to unity have been found for solids, but no satisfactory theory based on the properties of the solids has been developed to explain these results. The most apparent generalizations appear to be that α is unity for metals and that reported values of α less than about 0.04 were obtained with substances which exist in different forms in the vapor and in the condensed phase.

Littlewood and Rideal (*8*) questioned the validity of most of the values reported. Their criticisms were directed primarily at the techniques employed to measure the temperature of the surface of the evaporating substance. The surface temperature must be known accurately to allow the correct value of P_s to be inserted in Equation (1) in solving for α. It is clearly of the greatest importance to resolve the question raised by these authors, not only to establish the value of Equation (1) for technical applications but also to provide the experimental basis for the development of a sound theory.

The present paper describes the measurement of α for several solids by a technique which is believed not to be subject to the criticisms leveled by Littlewood and Rideal at other workers.

EXPERIMENTAL PROBLEMS

Most of the data on α are based on measurements of the rate of evaporation at low pressure. It is evident from Equation (1) that this procedure requires accurate determinations of the rate and area of evaporation and of T_s. The vapor pressure at T_s must be known, and furthermore, if the equation is to apply, the pressure and geometry must be such that the evaporating molecules collide neither with each other nor with the walls of the apparatus on their way to the condenser.

Most investigators have measured the loss in weight of a sample over a finite period of time and so have obtained an average rate. Some have employed conduits connecting the vaporization chambers and the condenser, thus introducing an additional resistance to transport which requires an uncertain correction to Equation (1). Where thermocouples are employed they must be mounted so as to avoid both heat conduction along the wires to the junction as well as any effect of the presence of the wires on the surface temperature.

Perhaps the most important error in many of the results, and the one which most concerned Littlewood and Rideal, was due to the difficulty in measuring T_s under dynamic conditions. Not infrequently T_s has been assumed to be equal to the temperature of the containing vessel. Cooke and one of the present authors (*15*) made this mistake, as Madden (*9*) pointed out. In this instance surface cooling due to evaporation resulted in a temperature about 17°C. lower than that of the surroundings, from which the energy of vaporization was being received by radiation. Littlewood and Rideal, in their measurements on the evaporation of benzophenone, calculated the surface cooling to be 6.8°C.

This study attempted to avoid these sources of error by arranging the test specimen quite close to a very cold condenser, noting weight loss at frequent intervals by the use of a torsion balance, providing a uniform supply of heat from beneath the evaporating surface, employing special precautions in the use of fine-wire thermocouples, and using a thermistor bolometer to substantiate the thermocouple measurements of surface temperature.

The novel feature of the investigation was the use of the bolometer which permitted dynamic measurements of the surface temperature with no possibility of influencing its value. The solids employed were naphthalene, biphenyl, camphor, thymol, and hexadecanol.

EXPERIMENTAL

The arrangement of the experimental equipment is shown in Figure 1. Hollow spheres were coated with the test materials and suspended from a helical quartz balance. The containing vessel was a glass cylinder 10 cm. in diameter and 20 cm. in length. This vessel was surrounded by a mixture of solid carbon dioxide and alcohol to make the internal surface an effective condenser. Pressures were maintained at less than 10^{-5} mm. Hg during the test by the pumping system shown.

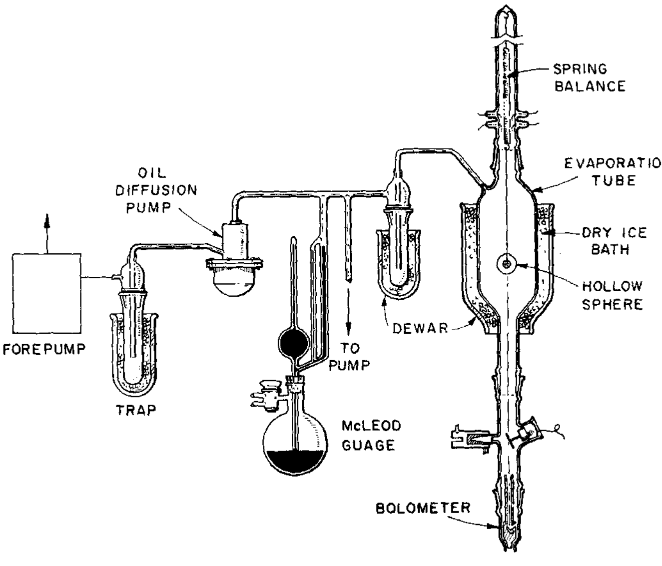

Fig. 1. Experimental equipment.

Conrad Johannes is with C. E. N. Grenoble, Service de Chimie, B. P., No. 269, Grenoble, France.

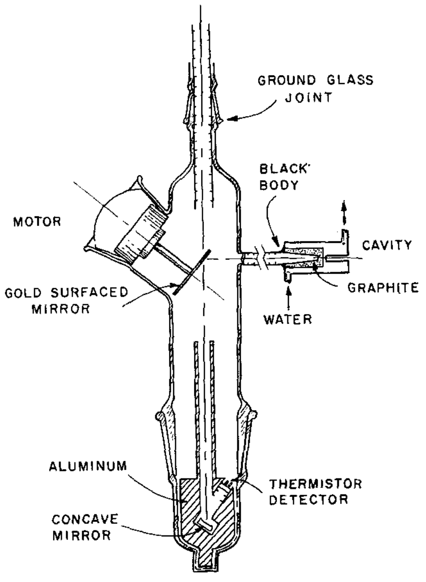

Fig. 2. Thermistor bolometer used in measuring temperatures of evaporating substances.

Very thin hollow spheres of copper 1.27 to 1.90 cm. in diameter were formed by plating copper on a wax sphere coated with Aquadac. The wax was then removed. After 25-μ copper and constantan thermocouple wires were attached, the leads for several centimeters from the junction were carried around but out of electrical contact with the sphere and the whole was dipped in molten test material. The coating thickness was built up to about 2 mm. by dipping repeatedly. The sample was not used unless the resulting coating was very smooth and regular. Sphere diameters were measured both with calipers and by use of a photographic technique.

A small coil of resistance wire suspended in the center of the hollow copper sphere supplied heat to the evaporating shell. A constant voltage was applied to the resistance wire. Throughout each test both current and voltage were recorded at intervals.

The quartz balance extended 1 mm. with a weight addition of 1 mg. Movements of the balance were read with a telescope fitted with a filar micrometer to increase precision. It was calibrated by means of standard weights, with the test sphere, 40-μ heater leads, and thermocouple leads in place. (The presence of the four fine wires changed the balance calibration about 10%.) Thermocouple readings were made with a potentiometer. These readings were recorded at frequent intervals throughout the tests, which varied in length from 8 to 170 min.

The thermistor bolometer was sighted on a 9.5-mm.-diam. circular area at the bottom of the test piece. It was arranged in the evacuated space as shown in Figure 1.

The design of the bolometer is shown in Figure 2. Radiant energy from the evaporating surface was collimated in a tube fitted with disks having 9.5-mm. holes. The chopper shown consisted of a gold-faced mirror with holes near the periphery, set at 45 deg. to the beam, and rotated by a small synchronous motor. This caused the thermistor detector to receive radiant energy alternately from the specimen and from a blackbody cavity held at a measured constant temperature.

The detector consisted of two identical thermistor elements, one receiving the radiation pulses and the other, shielded from radiation, serving to compensate for ambient temperature changes.

The chopped radiant energy generated an a-c signal at the junction of the detector circuit, shown in Figure 3. A high-gain low-noise amplifier was used to allow the signal to be read with an a-c voltmeter. The response of the detector was 315 v./w.; this was amplified 5,000-fold to give the voltmeter reading.

Radiant energy received by the detector is proportional to the quantity $[T_b^4 - \epsilon T_s^4 - (1 - \epsilon) T_w^4]$. The emissivity was determined by adjusting T_s (equipment not evacuated but condenser wall cold) until no signal was received; ϵ for naphthalene was found in this way to be 0.88. Separate measurements with an emissometer gave a value of 0.90.

In connection with the evaporation tests the use of the bolometer did not require knowledge of the emissivity value. It was calibrated in place against thermocouple readings of the temperature of coated test pieces supported in the equipment at atmospheric pressure. Typical calibration results are shown in Figure 4.

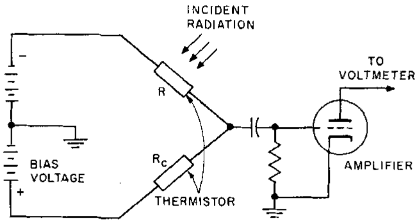

Fig. 3. Bolometer circuit diagram.

The bolometer, calibrated in this way, was used in several evaporation tests. The observed surface temperatures agreed so closely (±0.1°C.) with the simultaneous thermocouple readings however that most of the data were obtained with only the thermocouples. Thus the bolometer served primarily as a check on the technique employed in using thermocouples for surface temperatures.

VAPOR PRESSURES

The Knudsen effusion technique was employed to measure vapor pressures of the five test substances over the temperature range of interest. The cup was 1.27 cm. in diameter, and the cover was thin metal foil. An 0.032-cm. hole was used, for which the correction for finite foil thickness was only 0.3%.

The vapor-pressure data obtained are represented closely by

$$\log_{10} P \text{ (mm.)} = \frac{A}{T} + B \qquad (2)$$

with the following constants:

	A	B
Naphthalene	−3,965	11.55
Biphenyl	−3,918	11.003
Camphor	−2,855	8.926
Thymol	−4,780	14.24
Hexadecanol	−1,840	0.756

These results agree well with data in the literature.

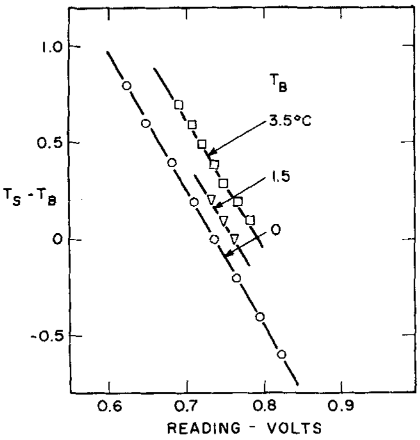

Fig. 4. Bolometer calibration curves.

PRECISION

Since the pressure during each test was maintained below 10^{-5} mm. Hg, the mean distance from the evaporating surface to the cold condenser surface was less than 1% of the mean free path of the evaporating molecules. The vapor pressure at the condensing surface was less than 10^{-4} times that at the evaporating surface. Evidently the conditions were such that the maximum rate of sublimation was obtained.

The balance permitted reading a loss of 10^{-6}g. with a precision of ±2%. This is the loss in about 1 sec. in the case of the least volatile substance (hexadecanol). Since evaporation rates held constant during periods of 6 to 100 min., the rates during these periods were subject to negligible error.

The electrical input to the internal heating element was varied during the initial periods of the tests but was held constant during the constant-rate periods for which the reported values of α were calculated. The transient thermal effects during these periods were negligible.

The installation of the fine thermocouple wires has already been described. At the measured heat fluxes the calculated temperature drop through the coating of test substance was never more than 0.3°C.; this calculated correction was subtracted from the thermocouple readings to obtain the surface temperature.

A good indication of the reliability of the thermocouple measurements of surface temperature is provided by the following comparison of temperatures

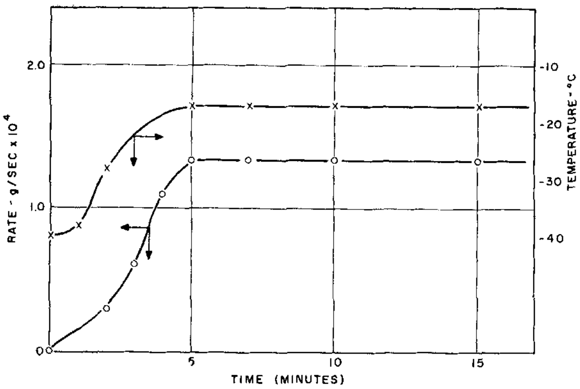

Fig. 5. Representative test with naphthalene.

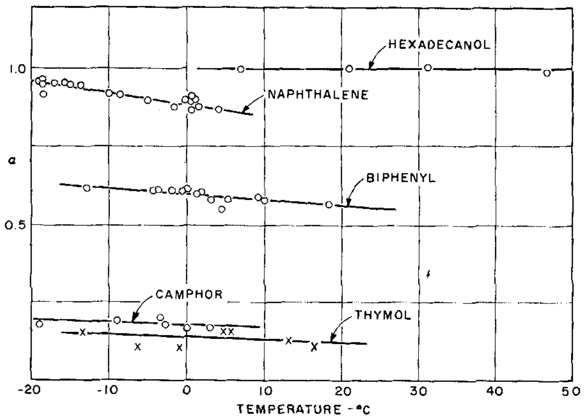

Fig. 6. Summary of experimental data on evaporation coefficients.

measured by the bolometer and by thermocouples at the same rates of evaporation from a sphere of naphthalene having a surface area of 11.58 sq. cm.:

Evaporation rate, g./sec. × 10⁴	Temperature, °C. Bolometer	Temperature, °C. Thermocouple
3.24	4.0	4.0
2.7	1.5	1.6
2.5	0.6	0.6
2.5	−0.4	−0.2

The bolometer measurements were made with no thermocouple on the test piece. The thermocouple measurements were interpolated from other tests in which thermocouples were employed with heat input varied to cover the same range of evaporation rates. Evidently the presence of the thermocouple had little effect on the rate.

The mean error in surface temperature is perhaps 0.3°C.; since P_s changes rapidly with temperature, this suggests an error of about 3.5%. The uncertainty in the vapor pressures is of the same order. Overall reproducibility of calculated evaporation coefficients (at a fixed surface temperature) was found to be ± 4%.

The test materials were purified by two recrystallizations and in some cases by a subsequent sublimation. Melting points agreed with literature values. All five materials formed smooth coatings. Tests with benzoic acid and anthracene were rejected, since these substances gave rough surfaces of very small needle-like crystals. Evaporation coefficients for these two substances were of the order of 0.01, presumably being low because of the large temperature drop along the projecting needles.

RESULTS

The nature of the test data is illustrated by the data on one test with naphthalene, shown in Figure 5. This graph shows both evaporation rate and surface temperature as functions of time. The constant electrical input of 0.30 w. to the heater was turned on at zero time. Essentially constant conditions were established in 5 min.; reported values of α are for the subsequent period.

By control of the heater current it was possible to cause an initial temperature decrease; in some instances the constant period was established immediately. Conditions became erratic toward the end of the test as bare spots of copper appeared. In some cases pieces of the test substance fell off the sphere at this time.

Figure 6 summarizes the results obtained with the five materials (values of α of 0.21 at −27.3 deg., and 0.19 at −28.1 deg. for camphor are not shown). A definite and unexplained effect of surface temperature is indicated, which is evidently not due to experimental error. Rate increases with temperature, and a progressive error in T_s might be suspected. Values of α however are not in order of the evaporation rates for the several substances; naphthalene evaporates ten times faster than biphenyl at the same temperature, but hexadecanol evaporates very slowly.

The results may be summarized very briefly by tabulating the values of α at 0°C.:

	α at 0°C.
Hexadecanol	1.00
Naphthalene	0.88
Biphenyl	0.60
Camphor	0.18
Thymol	0.14

The value of 0.88 for naphthalene is not far from Alty's approximate value of unity; the value for camphor agrees closely with Alty's average value of 0.172; the result for hexadecanol agrees with that of Littlewood and Rideal. No previous values for biphenyl or thymol are known.

It was of interest to compare the electrical input to the heater with the heat flux calculated by the relation

$$q = \frac{A_s \sigma (T_s^4 - T_w^4)}{\frac{1}{\epsilon} + \frac{A_s}{A_w}\left(\frac{1}{\epsilon} - 1\right)} + \dot{m} \lambda A_s \qquad (3)$$

The agreement was fair; the average difference was less than 10%.

THEORY

The principal purpose of this study was to answer the question posed by Littlewood and Rideal, so the theoretical approaches to the phenomenon of maximum evaporation rate will not be discussed. Herzfeld (*5*), Polanyi and Wigner (*13*), and Neumann (*11*) have developed theories based on statistical mechanics. Frank and others (*4, 17, 7, 16, 6*) base a theory on the assumed mechanism of escape of a molecule from a crystal, and Bradley and others (*16, 2, 10, 14, 3, 12*) have described phenomenological theories in which no attempt is made to predict α. None of these theories has been developed sufficiently to provide a basis for a quantitative prediction of α.

Alty (*1*) suggests that α decreases with increase in dipole moment of the evaporating pure liquid or solid. This view is supported by the results for four of the five substances of the present study; hexadecanol however does not conform.

CONCLUSIONS

Apparently for the first time evaporation coefficients have been obtained based on measurements of surface temperature by a method which cannot conceivably affect the temperature being measured. Values of α differing from unity by much more than the experimental error have been found. It is concluded that Littlewood and

Rideal cannot have been right in suggesting that all reported values of α less than unity are the result of errors in measuring surface temperature. α appears to be a property of the evaporating substance, decreasing in value with increasing temperature.

NOTATION

A = constant in Equation (2)
A_s = area of surface of test piece, sq. cm.
A_w = area of condenser surface, sq. cm.
B = constant in Equation (2)
$\dot{m}$ = evaporation flux, g./(sec.)(sq. cm.)
M = molecular weight of evaporating substance
P = vapor pressure, mm. Hg.
P_s = vapor pressure at surface temperature, mm. Hg.
R = gas constant
T = temperature, °K.
T_b = temperature of blackbody cavity, °K.
T_s = temperature of surface, °K.
T_w = temperature of surrounding condenser, °K.
α = evaporation coefficient, defined by Equation (1)
ϵ = emissivity of coated test specimen
σ = Stefan-Boltzmann constant
λ = enthalpy of sublimation, cal./g.

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Transfer Functions of Heat Exchangers

JAMES P. HSU
IBM Corporation, Chicago, Illinois

and NATHAN GILBERT
University of Cincinnati, Cincinnati, Ohio

In the course of research the authors have collected a number of transfer functions for various types of heat exchangers. For the convenience of analysis the heat exchangers may be classified into several basic types described in subsequent pages. In each case certain assumptions are made when one writes down the differential equations of the heat exchanger, which constitute the so-called *mathematical model* of the exchanger. If a particular heat exchanger is being classified, it is important to know the nature of temperature variation and the relative directions of flow of the exchanging fluid streams. If the heat exchanger in question matches one of the types described, then the transfer functions listed may be used to obtain its theoretical frequency and transient responses.

To obtain the frequency response the Laplace transform variable s in the transfer function, $G(s)$ is replaced by $j\omega$, and the moduli and arguments of $G(j\omega)$ for different values of ω are, respectively, the amplitude ratios of the output to the input and the phase angles between them. To obtain the transient response for a unit step input it is necessary to invert the function $G(s)/s$, and this procedure is not always easy. Most of the transfer functions presented here appeared previously in the literature, but some were obtained by the present authors. This paper will present to the research workers in this field a convenient collection of available transfer functions, thus eliminating the necessity of duplicating the burdensome mathematical work.

The following notes apply to the notation and procedures used in all cases. The independent time variable t and space variable x are nondimensionalized to τ and ξ, and the system parameters are grouped in dimensionless forms denoted by a's and b's. Certain uniformity and symmetry of notations are incorporated in this presentation so that the reader, in passing from one type of heat exchanger to another, will have little difficulty in interpreting the notations encountered. The temperature variables θ's and ϕ's in all the differential equations denote the time varying part of the temperatures, that is the part representing the deviations or perturbations of the temperatures from their steady state values; therefore when one assumes that the system is in the steady state at the time $t = 0$, the initial values of all these variables are zero.

To derive the transfer functions of the heat exchanger the inlet temperature of one fluid stream is regarded as the input or forcing function of the exchanger and the outlet temperature of the same or other fluid stream as the output function of the exchanger. The transfer function is defined as the ratio of the Laplace transform of the output function to that of the input function, provided that the system is initially in the steady state. The same transfer function may be regarded as the Laplace transform of the output function when the input function assumes a unit impulse function $\delta(t)$. This definition is used to formulate the boundary conditions for the heat exchanger to obtain the desired transfer functions. The differential equations are linearized and

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James P. Hsu is with the IBM Corporation, Camden, New Jersey.