Absolute Evaporation Rates for Some Polar and Nonpolar Liquids

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A method was developed for providing continuously wiped and, therefore, clean liquid surfaces in vacuo. By means of a mass spectrometer detector, the absolute evaporation flux from such clean surfaces was measured for diethylene glycol, glycerine, dibutyl phthalate, and oleic acid. The molecular flux from equilibrium vapor was also measured by the same detector. The ratio of the former to the latter, the evaporation coefficient, was found in each case to be close to unity and independent of the temperature.

SCOPE

The evaporation coefficient α is identified with the ratio of net evaporation rate from a unit area of surface to the arrival rate of molecules from vapor in equilibrium with that surface. For simple and nonpolar molecules, it is now widely accepted that for liquid surfaces α is always unity. When experimental values less than unity have been encountered, further experiments have usually revealed either that the surface was not clean or that its true temperature was lower than measurements had indicated. In the case of polar molecules such as water, there have remained doubts that α is necessarily unity. Values substantially less than unity have been obtained from careful experiments, and some theoretical considerations have supported the idea that all liquids need not necessarily evaporate at the maximum possible rate associated with a value of unity for α.

Because its relatively low vapor pressure eases the problem of determining surface temperature, the polar liquid glycerine has been the subject of several experimental investigations of its vacuum evaporation rate. Trevoy (1953) found that α had a value within 10% of unity. Wyllie (1949), Heideger and Boudart (1962), and McFeely and Somorjai (1972) found much lower values ranging from 0.05 to 0.34. It is of practical import to obtain true values of α because of their implications with respect to design of molecular stills and high performance condensers. They are of scientific interest because of what they may reveal about the nature of liquids and liquid surfaces. Therefore, we undertook the present study. One particular feature of our experiment was a novel method for generating clean liquid surfaces and directly comparing their evaporative flux with the flux from vapor in equilibrium with liquid surface at the same temperature.

CONCLUSIONS AND SIGNIFICANCE

Our measurements showed a probable value of α very close to unity for the four liquids which we studied: diethylene glycol, glycerine, dibutyl phthalate, and oleic acid. Moreover, there was no variation with temperature over a fairly wide range. We conclude that if their surfaces are clean, liquids of complex and polar molecules along with their simple and nonpolar counterparts will always evaporate at the maximum possible rate corresponding to an α of unity. We also conclude that there is no activation energy associated with evaporation or condensation.

Consider a liquid surface in equilibrium with its vapor. According to elementary kinetic theory, the rate of arrival of molecules from the vapor phase on a unit area of the surface is given by $n\bar{v}/4$, where n is the number density of molecules in the equilibrium vapor and $\bar{v}$ is their average velocity. Some fraction α of such arriving molecules will stick to the surface or condense. Another fraction $(1 - \alpha)$ will simply reflect. The quantity α is sometimes called the sticking probability or the condensation coefficient. Because at equilibrium the net rate of condensation $\alpha n\bar{v}/4$ must equal the net rate of evaporation, α has also been referred to as the evaporation coefficient. If it is assumed that the intrinsic rate of evaporation for a given surface temperature is independent of the actual gas-phase pressure, then measurements of evaporation or condensation rates under nonequilibrium conditions can give information on the value of α. This assumption, or its equivalent, is customary in absolute rate theory. It is clearly suspect for vaporization-condensation kinetics at very high vapor pressures when the molal volume in the condensed phase is nonnegligible with respect to the molal volume of the vapor.

It was Hertz (1882) who first introduced the concept of a maximum evaporation rate inferrable from the vapor pressure. His own measurements indicated that evaporation of mercury in vacuo occurred at about 10% of this maximum rate. In a more careful experiment, Knudsen (1915) found that the evaporation of mercury from droplets falling from the tip of a pipette into an evacuated chamber achieved the maximum possible value only if the mercury had been distilled several times. Without purification the rate was slower by three orders of magnitude. Knudsen introduced the concept of the evaporation coefficient and suggested the possibility that some substances might never attain the theoretical rate, that is, that α might be intrinsically less than unity. Volmer and Estermann (1921) confirmed Knudsen's findings with a value of α for mercury at or very near unity over a

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range of surface temperatures. Since then, a large number of measurements with metals and other nonpolar liquids indicate that a value of α near unity is almost universal. In those cases where values substantially less than 1 have been initially reported, subsequent attempts to confirm low values have invariably resulted in raising the accepted value to near unity. Summary reviews of evaporation and condensation measurements have been prepared by Knacke and Stranski (1956), Paul (1962), Hirth and Pound (1963), and Pound (1972). The cumulative result of all these studies has been a large body of opinion which holds that whenever a value of α is encountered which is apparently less than unity, either the surface is dirty or the surface temperature is less than it seems to be. These conclusions do not apply to solids. It is well known that the overall process by which a gas-phase molecule finally becomes incorporated in the substrate crystal lattice is much more complicated than in the case of liquids and involves at least two steps, either of which may be rate limiting. Values of α substantially less than unity have been well established for crystalline solids.

In the case of polar liquids, the situation is less clear cut. Until recently, the most careful studies of water have reported values of α much less than unity, some of them grouping about values as low as 0.02 to 0.04 (Alty, 1931; Delaney et al., 1964). Water combines a relatively high vapor pressure with a very high heat of vaporization. At conditions far from equilibrium, when the net rates are rapid, the consequent large heat fluxes to or from the surface have made it very difficult to determine the surface temperature. At slower rates near equilibrium, there is the problem of insuring that the surface remains clean during the longer time required to make the measurement. With the advent of new techniques, results with water have shown a progressive increase in α. Recent measurements show values well over halfway to unity (Nabavian and Bromley, 1963; Bonacci et al., 1976; Maa, 1969, 1970).

Because it has a much lower vapor pressure than water, glycerine is an experimentally more tractable polar liquid which has been studied by several investigators. By measuring the weight loss from a stagnant pool of liquid, Wyllie (1949) determined the vacuum evaporation rate of glycerine and obtained the value for α of 0.052 at 18°C. Trevoy (1953) condensed and collected the vapor from the surface of a jet of glycerine in vacuo and found that α was within 10% of unity in the temperature range from 18° to 5°C. Then, Heideger and Boudart (1962) measured the time rate of pressure change in an initially evacuated vessel enclosing a pool of glycerine. By comparing the rate when the pool was completely exposed to the vacuum and when it was covered except for a small hole, as in a Knudsen cell, they were able to determine α without an independent knowledge of the vapor pressure. Moreover, they did not need an absolute calibration for their pressure gauge (NRC Alphatron). It was necessary only that it have a linear response over the pressure range encountered. There was an apparent dependence of α upon pressure which the investigators attributed to sorption-desorption effects on the chamber wall. Their conclusion was that the limiting value of α as pressure approached steady state equilibrium represented a true characteristic property of glycerine. This limiting value was 0.05, independent of temperature over the range studied (14 to 25°C) and in good agreement with the results of Wyllie. The confidence of Heideger and Boudart in their result was further enhanced by their observation that fairly vigorous stirring of the liquid with a submerged four-bladed rotor did not affect the apparent value of α even when the rotor blades broke through the surface

The most recent investigation of the evaporation of polar liquids was by McFeely and Somorjai (1972). They measured the vacuum vaporization rates of glycerin, diethylene glycol, and triethylene glycol over a range of temperatures by following the weight loss with time of a small pan of liquid suspended on a microbalance. Surface temperature was determined by means of a small thermocouple supported by surface tension. The temperature dependence of the rate indicated an activation enthalpy lower than the latent heat of vaporization for glycerine but higher in the case of the other two liquids. At 300°K, α was 0.34 for glycerine, 0.05 for diethylene glycol, and 0.46 for triethylene glycol.

It seemed to us that the problem was sufficiently important and the results of these various investigators were sufficiently disparate to justify further study. Accordingly, we undertook the investigation reported here.

METHOD AND APPARATUS

In our view, the critical problem was to provide a clean surface at a known temperature in an evacuated chamber. As have others before us in the surface field, we finally took a leaf out of Langmuir's notebook. It will be recalled that in his studies with monomolecular films on water he found that he could literally wipe the water surface clean by dragging a bar or a piece of folded paper across it. An analogous effect was achieved by Trevoy (1953) when he passed liquid glycerine through a small nozzle to form the cylindrical free jet from whose surface he measured the evaporation rate. Indeed, we did some preliminary experiments with such liquid jets, but for a number of reasons, including outgassing difficulties, we gave up and built the modified Knudsen cell shown in Figures 1 and 2. It comprised a rectangular box 12.7 cm × 10.2 cm × 7.6 cm. The sides were 6.4 mm plates of aluminum, the bottom a 2.54 cm block of aluminum, and the top a 6.4 mm plate of Plexiglas which provided visual access to the interior. In the bottom block were a pair of parallel 6.4 mm holes through which heat transfer liquid could be circulated to provide temperature control. Through the rear end plate of the box was passed a shaft which outside the box was connected by a flexible nylon coupling to a 5W synchronous electric motor geared down to turn at 10 rev/min. Inside the box the shaft terminated in a rotor which comprised a circular disk 5.7 cm in diameter and 6.4 mm thick. In the center of the rotor was a simple thrust bearing opposed by a set screw in the front end plate of the box. The set screw could be turned and locked from the outside so that the front face of the rotor could be positioned at a desired fixed distance from the front end wall of the box. A 144 deg. sector was cut out of the disk leaving

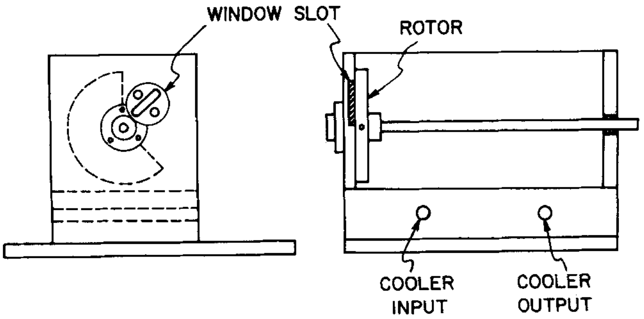

Fig. 1. End on and side views of the apparatus.

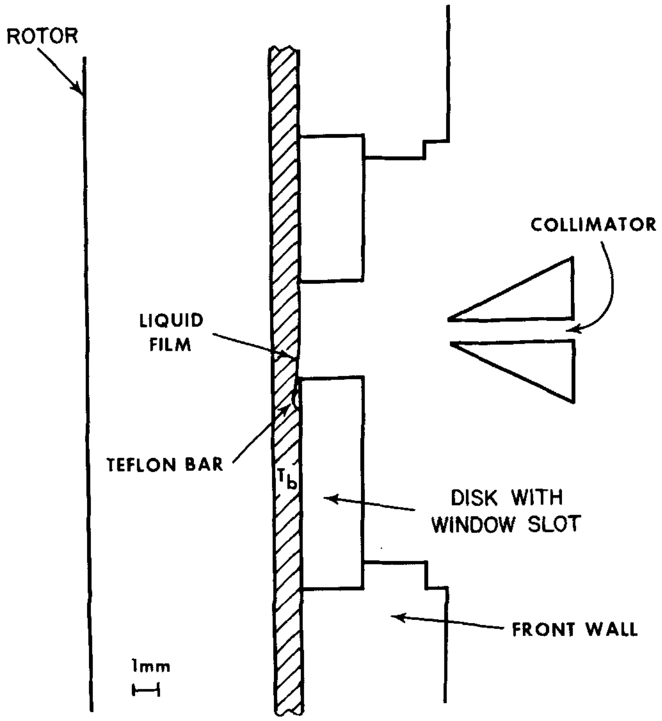

Fig. 2. Detail showing liquid film at window, the wiping bar, and the collimator.

about 40% of its frontal area open. Inset in the front end plate of the box was a 2.54 cm diameter disk of 3.2 mm thick aluminum into which was milled a window slot 19 mm long and 4.8 mm wide. Parallel to the slot and 2.5 mm away from its edge was milled a groove into which was pressed a 19 mm length of 1.5 mm teflon tubing. The groove was deep enough so that outermost teflon surface extended about 0.5 mm above the surface of the disk. The disk with its slot and teflon bar was located in the front end plate of the box in such a way that the center of the slot was at a radial distance of 19 mm from the center of the rotating disk and at about 2 o'clock when viewed head on from outside the box. Best results were obtained when the disk was turned so that edges of the slot were parallel to that radius of the rotor which passed through the center of the slot.

When the box was filled with liquid to a level just below the shaft, the turning rotor would pick up a layer of liquid and drag it past the slot. Just before reaching the slot the liquid film would encounter the teflon bar which wiped away the outermost layer so that the liquid surface which reached the slot was freshly exposed and presumably clean. A chromel-alumel thermocouple was cemented into a small brass tube which extended from the outside surface of the box so that the junction was flush with the inside surface of the box at a point 6.4 mm above the slot. Because the box walls and the rotating disk were made of aluminum, which is a good conductor, the thermocouple reading was taken to be a fairly reliable measure of the temperature of the liquid film.

The box assembly with its motor was mounted on an aluminum plate on which was also mounted a quadrupole mass spectrometer equipped with a fourteen stage copper-beryllium multiplier. The inlet aperture to the ion source of the mass spectrometer was at a perpendicular distance of about 4.5 cm from the liquid surface on the rotating disk. A collimator slit was mounted about 6.4 mm from the liquid surface so that the mass spectrometer saw only the vapor flux from a 6.4 mm × 0.8 mm area in the center of the window slot. Between the collimator and the spectrometer was a rotating slotted wheel which chopped the flux at 250 Hz. It also chopped the light beam from a small light bulb to a photodiode to provide a reference signal for the lock-in amplifier (PAR 122) whose output was displayed on a strip chart recorder (Mosely 7101A). Before arriving at the lock-in amplifier, the output from the mass spectrometer multiplier was fed directly to a field effect transistor amplifier which acted as a cathode follower and then through a low noise preamplifier (PAR CR-4).

To make a measurement involved the following procedure. The liquid to be studied was thoroughly outgassed by warming in a flask evacuated by a mechanical vacuum pump. It was then poured into the box so that the level was just below the shaft. The thrust bearing was adjusted with the rotor turning so that the liquid layer on the disk was from 0.5 to 1.5 mm thick, and there was a clearance of a millimeter or so between the liquid surface and the face of the disk containing the window slot. The whole assembly was then placed on a cylindrical chamber evacuated by an 81 cm oil diffusion pump (NRC H-32-SP) backed by a large mechanical pump (Stokes 412-H). The nominal speed of 32 000 l/s was halved by a freon cooled optical baffle but was sufficient to maintain the background pressure during an experiment at a value less than 2.66×10^{-3} N/m^2.

After the pressure in the vacuum system reached a steady state value, usually about 8×10^{-5} N/m^2, the chopper and rotor motors were turned on and the mass spectrometer was tuned to a mass peak appropriate for the liquid being studied. After a few minutes the system reached a steady state cycling. The output signal was then continuously recorded as the temperature in the box was gradually raised (or lowered) by circulating fluid from an external thermostat through the base of the box. The thermocouple temperature was recorded by hand on the strip chart at appropriate intervals. When the rotor was dragging a liquid layer past the window slot, the mass spectrometer signal corresponded to rate of evaporation from the liquid surface. When the open sector of the rotor passed the window slot, the mass spectrometer signal corresponded to the flux from equilibrium vapor in the box behind the rotor. The ratio I_s/I_v was directly the apparent evaporation coefficient, where I_v is the signal due to the equilibrium vapor when the open sector was passing the window and I_s is the signal due to the vaporization of the liquid when the liquid surface was in the window. Note that the effective area was identical for both signals and that the result did not depend upon an independent knowledge of the vapor pressure. Nor was it necessary to calibrate the mass spectrometer. The only requirement was that its sensitivity at a particular mass peak remain constant over the time needed for the rotor to make half a revolution, that is, about 3 s. The actual signals were very reproducible over a period of many rotor revolutions.

In what follows we will attempt to respond to the three main questions which in our view can be raised about the method and the credibility of our results.

1. Was the pressure of the vapor in the box behind the rotor the equilibrium vapor pressure? In this connection the first problem is whether the temperature was uniform throughout the box. We note that the walls and bottom of the box were relatively thick aluminum which is a good thermal conductor. Moreover, in some experiments with thermocouples at three different locations, we found they all gave the same temperature within less than a degree. It is also to be wondered whether there was sufficient time for vaporization to bring the

vapor pressure to its equilibrium value, a process which can be notoriously slow. That equilibrium was maintained was evidenced by the fact that we obtained the same values for α within experimental error at a particular temperature whether it was recorded while the temperature was rising or while it was falling. It is also noteworthy that the area of the aperture was only 0.2% of the area of the liquid surface in the box. Moreover, when we attached several disks to the shaft in the box so that the effective liquid surface area was greatly increased while the shaft was turning, there was no observable effect on the measured value of α. We concluded that equilibrium obtained between the vapor and the liquid in the box.

2. Was the liquid surface on the rotor from which the vapor flux was measured truly clean? At a pressure of 10^{-6} torr, the background pressure during most of the experiments, it would take between 1 and 2 s, depending on species in the background gas, to form a monolayer on a clean surface if the sticking probability were unity. The time for an element of surface area to travel from the edge of the slit to the center of the field of view of the mass spectrometer was 0.2 s at a rotor speed of 10 rev/min. Thus there could not have been more than about 0.2 of a monolayer of contamination from the background gas. Moreover, when we changed motors and turned the rotor at 4 instead of 10 rev/min, we found no appreciable change in the observed value of α. Perhaps the most persuasive evidence that the surface was effectively clean was provided after the fact by the result that the apparent value of α was always close to unity.

3. What was the true effective surface temperature? We took as the nominal surface temperature that which was indicated by the thermocouple near the window slot. As has already been mentioned, the walls and base of the box were good thermal conductors, and simultaneous readings with thermocouples at different locations showed no appreciable differences so that the temperature gradients in the system must have been small. However, we did observe a small decrease in apparent values of α as the temperature increased. This effect was more pronounced in those liquids which had higher vapor pressures and, therefore, required higher heat flux rates to the surface. Accordingly, we undertook a simple analysis of the heat flux which led to small corrections which were applied to the raw data. The essential features of the analysis are set forth in what follows. Recall that the apparent (uncorrected) experimental value of α is simply the ratio of the measured evaporative flux from the liquid surface to the measured effusive flux from the equilibrium vapor in the box, that is, $\alpha' n_s \overline{v_s} / n_b \overline{v_b}$, where subscript s relates to the surface properties, subscript b refers to the bulk properties in the box, and α' is the true evaporation coefficient of the liquid. In terms of temperature and vapor pressure, we can thus write

$$\alpha = \alpha' p_s (2mkT_s)^{-1/2} / p_b (2mkT_b)^{-1/2}$$

or

$$\alpha' = \alpha (p_b/p_s)(T_s/T_b)^{1/2} \tag{1}$$

We assume that when the surface of the liquid film becomes exposed to the vacuum system, as it emerges into the window slit, vaporization begins and proceeds at a constant rate equal to the maximum value ($\alpha = 1$) at T_b for which the vapor pressure is p_b. From this rate and a knowledge of the heat of vaporization, we arrive at the rate of heat flux to the surface Q. We assume that this heat arrives by conduction from the substrate bulk liquid. We then apply the solution to the one-dimensional heat conduction equation (Welty et al., 1969) in the form

$$T_s = T_b - (1.13\, Q/K)(Kt/\rho C_p)^{1/2} \tag{2}$$

The evaporation time t is the time for an element of liquid surface to pass from the bottom edge of the slit to the area seen by the detector, about 0.2 s at a rotor speed of 10 rev/min.

This solution assumes that the heat is supplied only by conduction from the underlying fluid to a penetration depth of

$$\xi = (6Kt/\rho C_p)^{1/2} \tag{3}$$

At this depth, the temperature gradient is presumed to become negligible. It is critically important, therefore, that this depth be less than the thickness of the liquid film on the rotor. Otherwise, the aluminum rotor would contribute to the heat flow and because of its higher conductivity and density, Equation (2) would have to be modified. We estimate that the film thickness was usually at least 0.5 mm. The penetration depth from Equation (3) was never more than 0.35 mm.

The surface temperature obtained by this first application of Equation (2) is too low because it assumes a constant heat flux, whereas because of the decreasing surface temperature, the heat flux decreases with time. Consequently, we then took the arithmetic mean of T_b and the calculated T_s and applied Equation (2) again to arrive at a second estimate of T_s. This iteration was continued until differences in successive values of T_s became negligible. The value of T_s finally obtained was used in Equation (1) to obtain a value of the evaporation coefficient α' corrected for the lowering of surface temperature due to evaporation while the liquid surface was exposed to the vacuum system.

RESULTS AND DISCUSSION

Determinations of evaporation coefficient were made in accordance with the above procedure for diethylene glycol, glycerine, oleic acid, and dibutyl phthalate over a range of temperatures. The results are summarized in Table 1. Several runs were made on each liquid, a run consisting in gradually increasing or decreasing the temperature over the range shown. Temperatures were recorded on the strip chart at frequent intervals. From the chart for each run, a value of α associated with a particular temperature could be obtained. Those values from each run at a temperature within a degree or so of some nominal temperature were averaged to give the values shown in the table. The associated temperatures were also averaged to give the temperature indicated in the table. Both α (uncorrected) and α' (corrected for surface cooling) are shown along with the heat flux to the surface at the indicated maximum rate of evaporation calculated from available vapor pressure data assuming an α of unity. Also shown is a Knudsen number, the ratio of the mean free path in the equilibrium vapor to the width of the window slot. It is clear in many cases, especially at the higher temperatures, that these Knudsen numbers were appreciably less than unity. Consequently, there must have been some collisions between the molecules as they passed through the window. However, it is well known that the mass flux through an aperture, particularly along the center line, is much more insensitive to Knudsen number than is velocity distribution which itself remains fairly undistorted down to Knudsen numbers as low as 0.1 (Phipps and Scott, 1973). Moreover, whatever collisional effects there may have been were the same for both effusion and vaporization. Consequently, we do not think that they distorted the apparent values of α by an appreciable amount.

TABLE 1. EVAPORATION RATE DATA

	Temp., °C	α	α'	Kn	Q (cal/cm^2 s)	Max. vap. rate (mole/cm^2 s)
Glycerin	19.1	0.97	0.97	68	5.5×10^{-4}	1.6×10^{16}
	20.9	0.91	0.91	64	8.5	2.4
	20.9	0.91	0.91	64	8.5	2.4
	27.5	0.94	0.94	27	1.6×10^{-3}	4.5
	30.2	0.90	0.90	19	2.0	5.7
	35.4	0.89	0.89	12	4.1	1.2×10^{17}
	39.9	0.91	0.92	7.2	6.3	1.8
	40.5	0.96	0.97	6.9	7.0	2.0
	40.5	0.93	0.94	6.9	7.0	2.0
	49.5	0.92	0.93	6.9	7.0	2.0
	51.5	0.96	0.98	2.3	2.2×10^{-2}	6.0×10^{17}
	57.0	0.92	0.96	1.4	3.9	1.1×10^{18}
	62.1	0.91	0.96	.69	6.4	1.9
Oleic acid	36.7	0.77	—	61	6.9×10^{-5}	1.9×10^{15}
	47.7	0.77	—	19	2.3×10^{-4}	6.3
	57.5	0.71	—	7.1	6.2	1.7×10^{16}
	64.7	0.81	—	3.8	1.3×10^{-3}	3.6
	66.3	0.88	—	3.3	1.6	4.3
	68.7	0.84	—	2.6	1.9	5.3
	71.3	0.86	—	2.0	2.6	6.8
	71.5	0.89	—	1.9	2.5	6.9
	71.8	0.90	—	1.9	2.5	7.0
	73.2	0.86	—	1.8	2.9	8.0
	73.6	0.86	—	1.7	3.0	8.4
	74	0.85	—	1.6	3.1	8.6
Diethylene glycol	4.5	0.90	0.98	0.19	8.0×10^{-2}	3.9×10^{18}
	6.7	0.97	1.07	0.18	0.11	5.2
	8.0	0.95	1.06	0.16	0.12	5.7
	9.3	0.89	1.01	0.15	0.13	6.0
	11.0	0.93	1.06	0.13	0.15	7.2
	13.6	0.88	1.04	0.11	0.18	8.4
	15.5	0.91	1.09	0.095	0.21	1.0×10^{19}
	20.3	0.88	1.08	0.069	0.34	1.4
	23.8	0.78	1.01	0.055	0.39	1.9
	25.0	0.83	1.1	0.050	0.42	2.0
	30.2	0.85	1.2	0.039	0.62	3.0
	34.1	0.73	1.02	0.028	0.80	3.9
	37.3	0.74	1.05	0.022	0.96	4.6
Dibutyl phthalate	32	0.95	0.95	8.8	1.1×10^{-3}	3.4×10^{16}
	65	0.90	0.92	0.55	1.9×10^{-2}	6.0×10^{17}
	68.5	0.85	0.89	0.44	2.3	7.8
	71.3	0.82	0.85	0.36	3.0	1.0×10^{18}
	76.2	0.91	0.96	0.24	4.1	1.4
	78.4	0.89	0.95	0.21	4.8	1.6
	81.1	0.90	0.96	0.17	5.8	1.9
	84.3	0.87	0.95	0.13	7.1	2.4
	87.3	0.79	0.88	0.11	8.9×10^{-2}	3.0
	90.5	0.81	0.92	0.092	0.11×10^{0}	3.7
	93.3	0.75	0.87	0.075	0.14	4.5
	96.2	0.75	1.04	0.063	0.16	5.4
	100.2	0.71	0.88	0.047	0.21	7.0×10^{18}
	103.1	0.74	0.93	0.040	0.25	8.0
	108.8	0.72	0.97	0.029	0.31	1.2×10^{19}

It is clear that even the uncorrected values of α show very little dependence upon temperature. After the surface cooling correction is applied, the temperature dependence disappears altogether. This temperature independence allows us to average all the values in the table, each of which was itself an average of several measurements. We thus obtain for diethylene glycol $\alpha' = 1.06 \pm 0.05$, for glycerine $\alpha' = 0.94 \pm 0.02$, for dibutyl phthalate $\alpha' = 0.93 \pm 0.04$, and for oleic acid $\alpha' = 0.86$ at temperatures above 60°C. At lower temperatures, the vapor pressure of this latter material was so low that noise made the values suspect.

The value of α' greater than unity in the case of diethylene glycol is not likely to be correct. The penetration depth was greatest for this liquid and may have equalled or exceeded the film thickness at the higher temperatures. Thus our correction procedure may have resulted in a surface temperature which was too low. The only previous measurement on this liquid was by McFeely and Somorjai (1972). As already noted, they found a value for α of 0.05 at room temperature. In the case of oleic acid, there was evidence that the rotor was not wet very well and had dry spots on the surface. In such an event, the effective area of the evaporating surface would have been less than the effective area for effusion and could account for the relatively low value of α for this material. Because of its low vapor pressure, the cooling correction for oleic acid was negligible and was ignored. We were unable to find any record of previous measurements on this material. For dibutyl phthalate, the only nonpolar liquid of those we studied, Birks and Bradley (1949) found that α was 1.00 ± 0.05, in good agreement with our result.

Our result for glycerine agrees with that of Trevoy but is at odds with those of the others who have studied this material. It becomes appropriate to ponder these differences. Trevoy's method and ours are characterized by very short exposure times of the liquid surface to the background gas in the vacuum system, that is, less than 1 s. In the methods used by the other investigators, the vaporizing surface was exposed to the background gas for at least several minutes. The background pressures are not always reported, but it seems unlikely that they were lower than 13.3×10^{-5} N/m^2 torr, and, as we have pointed out, at this pressure it takes only about a second to form a monolayer. The major ingredient of background gas in most vacuum systems is water vapor. Consequently, we speculate that when a glycerine surface is exposed to even a reasonably high vacuum background for periods of minutes it is likely to become covered with many monolayers of water molecules. To the extent that these molecules dissolve in the glycerine, they would substantially lower its vapor pressure in the surface layer and thus give rise to low values of α. This effect may even have been at work in our own measurements and may account for the fact that α' was slightly less than unity.

From these results as a whole, we are tempted to conclude that the true value of evaporation coefficients is indeed very close to unity for all liquids, even those whose molecules are polar and have a complex structure. Certainly the lack of temperature dependence makes it difficult to argue that evaporation in these cases is an activated process.

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NOTATION

C_p = specific heat capacity of liquid
I = mass spectrometer signal
K = thermal conductivity of liquid
Kn = Knudsen number, mean free path/window width
Q = heat flux per unit surface area to sustain evaporation
S = density of liqud
t = time liquid surface is exposed to vacuum
α = evaporation coefficient
α' = true experimental value of α corrected for evaporative cooling
ξ = penetration depth of cooling due to evaporation
ρ = mass density

Subscripts

s = surface property
b = bulk property
v = equilibrium vapor

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