

# Onsager Heat of Transport Measured at the *n*-Heptanol Liquid–Vapor Interface

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The Onsager heat of transport  $Q^*$  has been determined by measuring the effect of a temperature gradient at the interface on the apparent vapor pressure of the liquid. Results for *n*-heptanol extend to pressures that are low enough for the separation between the liquid and the warmer surface above it to be less than one mean free path. At low pressure, the dependence of  $\Delta P$  on  $\Delta T$  is found to be linear, in contrast to the curves obtained when the separation is greater than a mean free path. As with aniline, the heat of transport is negative and its magnitude approaches the latent heat of vaporization at low pressures. The results are discussed in relation to three anomalous effects that have been predicted or observed during steady-state evaporation and also in relation to the problem of determining rates of air–sea exchange for atmospheric gases.

## Introduction

The flux  $J$  of gas through a region in which there are simultaneous fluxes of heat and matter is given by the equation

$$J = -\frac{L_{22}}{\delta} \left( \frac{Q^*}{RT} \frac{\Delta T}{T} + \frac{\Delta P}{P} \right) \quad (1)$$

where  $\delta$  is the width of the (thin) region across which the temperature and pressure changes are  $\Delta P$  and  $\Delta T$ ,  $R$  is the ideal gas constant and  $Q^*$  is the Onsager heat of transport.<sup>1,2</sup> The requirement that eq 1 should reduce to Fick's law of diffusion in the absence of a temperature gradient enables us to identify the coefficient  $L_{22}$  as the product of the average diffusion coefficient  $D$  and concentration  $C$  in the narrow region, where  $\Delta P/P = \Delta C/C$ . In practice,  $Q^*$  is best obtained from the stationary-state equation

$$\frac{Q^*}{RT} = -\frac{\Delta P}{P} \frac{T}{\Delta T} \quad (2)$$

which holds when the flux of matter is zero, i.e., the rates of evaporation and condensation are equal.<sup>3–5</sup> For gas–liquid interfaces in general, the situation in which a flux of matter across the interface is not accompanied by a flow of heat is quite rare, so eq 1 evidently has very wide applicability.

The relative importance of the temperature and pressure gradients in deciding the magnitude and direction of the gas flux of eq 1 depends on the size of the factor  $Q^*/RT$ . Our initial experiments with aniline<sup>5</sup> showed that  $Q^*$  is of similar magnitude to the latent heat of vaporization, so that  $Q^*/RT$  is typically greater than 10, that the effect of  $Q^*$  is significant for values of  $\delta$  up to more than 30 mean free paths in the gas phase, and that a positive temperature gradient results in a positive pressure gradient in the stationary state, which means that the sign of  $Q^*$  is negative. If  $Q^*$  is defined as the heat which is absorbed on one side of the region and released on the other, this

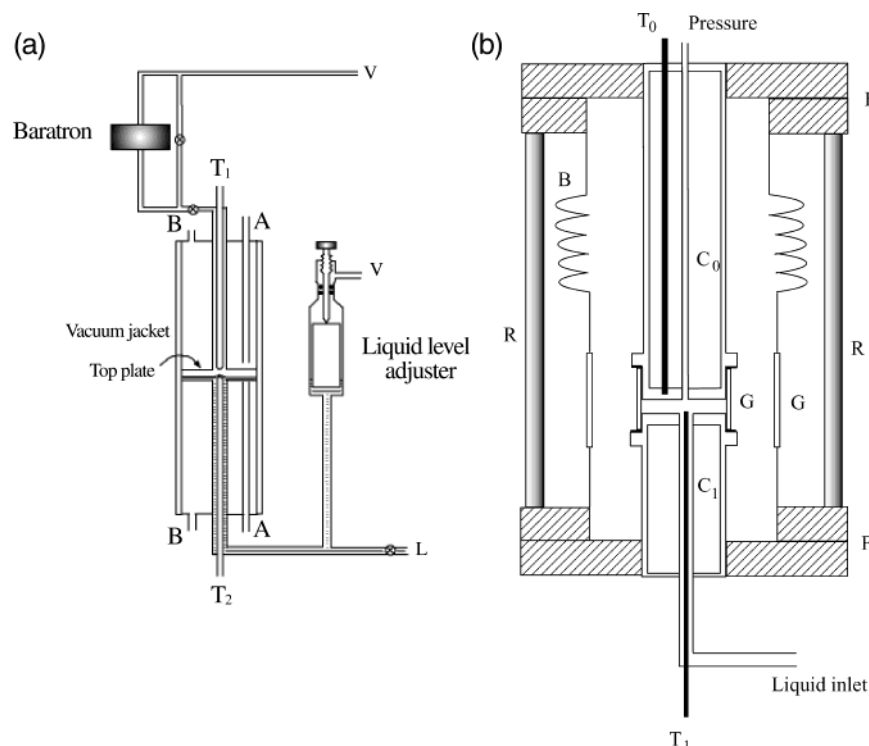
observation requires that positive fluxes of heat and matter and positive gradients of temperature and pressure are directed *away* from the liquid. It appears that this requirement can be understood in terms of a physical mechanism based on the effect of the temperature gradient on the effective height of the free-energy barrier to evaporation,<sup>6</sup> but a detailed quantitative treatment is still lacking. Our initial experiments also revealed the unexpected phenomenon of a cool liquid distilling onto a warmer surface<sup>7</sup> and provided indirect support for the well-known theoretical paradox<sup>8</sup> of inverted gas-phase temperature gradients during trap-to-trap distillation.<sup>9</sup> Recently, studies of evaporating liquids by Ward and co-workers<sup>10–13</sup> have demonstrated the existence of anomalous temperature profiles that deviate in the opposite direction from the predictions of classical kinetic theory. In the present paper, we show that both kinds of anomalous temperature profiles can be understood on the basis of the dependence of apparent vapor pressure on the temperature difference across the Knudsen zone at the surface of the liquid.

The main purpose of this paper is to give the results of our experiments with *n*-heptanol. Heptanol has the advantage of possessing a much lower triple-point vapor pressure than aniline, which allows measurements to be made with values of  $\delta$  that are less than one mean free path. An unexpected outcome is that the dependence of  $\Delta P$  on  $\Delta T$  corresponding to eq 2 is found to be perfectly linear for values of  $\delta$  less than about one mean free path, which suggests that the curvature observed for larger values of  $\delta$  is an experimental artifact. It seemed likely that the curvature might result from the fact that the glass from which the apparatus was made is a relatively poor conductor of heat so that horizontal temperature gradients could exist in the cell, gradients that might give rise to unwanted gas-phase circulation and/or turbulence. Therefore we changed to a metal apparatus; however, curves were also obtained with the metal apparatus at higher pressures, so the question of the origin of the curvature remains open. A referee has pointed out that a mechanism exists by which small vortices can arise spontaneously in a moderately dense gas<sup>14</sup> so that the curvature we observe at higher pressures might be inescapable.

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**Figure 1.** (a) The Pyrex apparatus used in most of the measurements. A and B are connections leading to and from the alcohol circulating system, T1 and T2 are thin-walled tubes to hold thermistors, V indicates vacuum connections,  $\otimes$  indicates the position of a greaseless stopcock, and L connects to the sample-handling line. Further description is given in the text. (b) The metal apparatus. F = stainless steel Conflat flanges; R = stainless steel rods; B = stainless steel bellows. Each letter G indicates a length of glass tubing, the outer length being part of a double-ended Pyrex-Kovar seal that, together with the bellows, forms an outer vacuum jacket. The inner length of glass butts against Buna-n gaskets at top and bottom to isolate the central liquid compartment from the vacuum jacket. C<sub>0</sub> and C<sub>1</sub> are the temperature-control compartments (alcohol inlet and exit tubes not shown). Tubes T<sub>0</sub> and T<sub>1</sub> hold either thermistors or platinum-resistance thermometers.

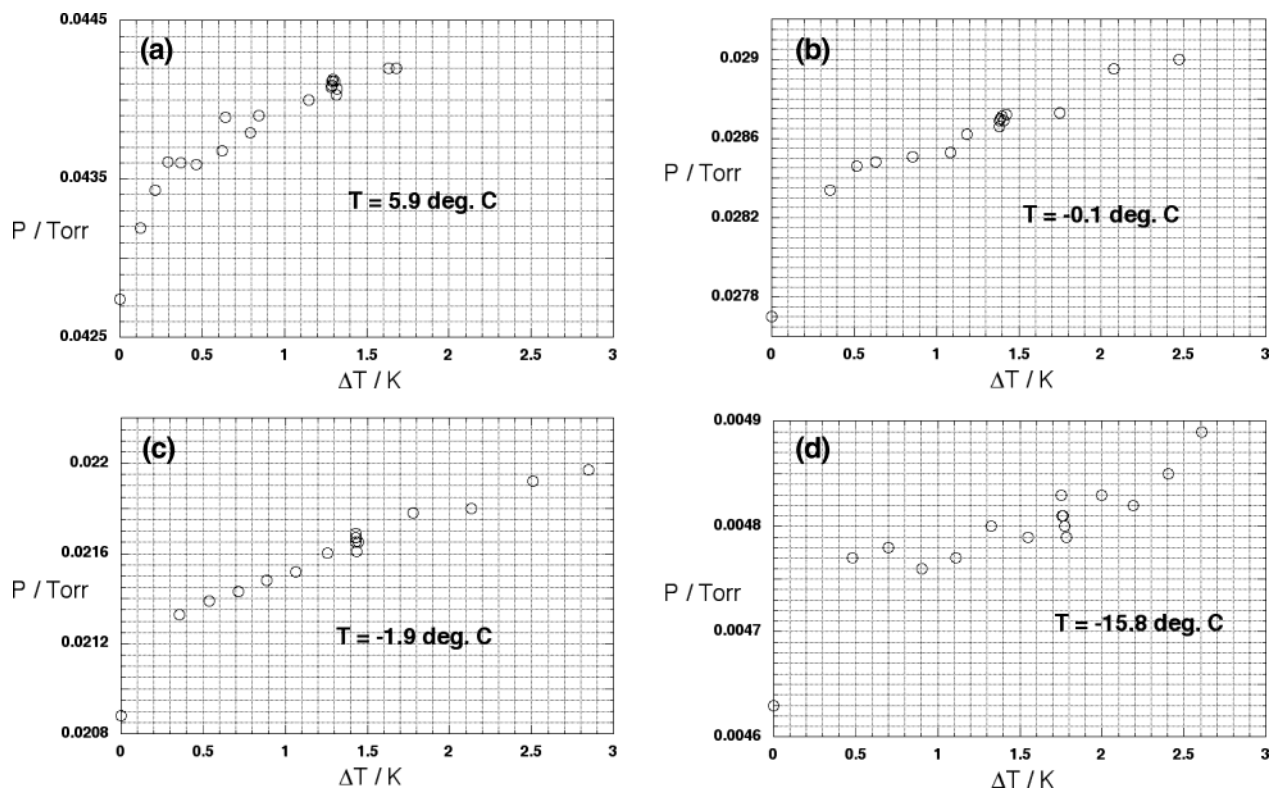
## Experimental Section

Figure 1a is a diagram of the central part of the glass apparatus, which is a vacuum-jacketed Pyrex cylinder about 20 cm long, having two large (~400 mL) compartments with inlets A and outlets B through which ethanol can be pumped from a Haake DC5-K75 circulating Cryostat via computer-controlled heaters that provide independent temperature regulation to within a few hundredths of a degree Celsius for each compartment. Greaseless vacuum stopcocks with Buna-n O-rings are represented by  $\otimes$  in the diagram. The level of the liquid sample can be set to within 0.1 mm by adjusting the depth of the plunger in the external float chamber. In practice, a variation of  $\pm 0.5$  mm in liquid level has no significant effect on the results. The nominal gap between the liquid surface and the ground-glass bottom surface of the upper temperature-control chamber (termed the "top plate") is 4.1 mm. The connection to the liquid supply and purification system is labeled L. Connections to a vacuum system with a 4-in. (10-cm) diffusion pump are labeled V. Temperatures are monitored by thermistors immersed in the circulating liquid and measured by thermistors inserted into thin-walled glass tubes at T1 and T2. The quantity  $\Delta T$  in eq 2 is the temperature difference between the vapor at the level of the top plate and the surface of the liquid.

For a few measurements, the glass cell was replaced by the metal cell shown in Figure 1b. The key to this diagram is in the figure caption. Stainless steel was chosen instead of brass or copper because, in our earlier experiments, aniline appeared to interact chemically with brass. The purpose of changing to the metal apparatus was to determine whether the observed curvature of plots of  $\Delta P$  vs  $\Delta T$ , postulated as being due to gas circulation arising from small temperature differences over the

upper glass surface of the liquid compartment, could be eliminated by using a metal system. The ratio of thermal conductivities of stainless steel and Pyrex glass is about 30, which should have been a large enough factor to make an appreciable difference if the curvature of the  $\Delta P$  vs  $\Delta T$  plots at high pressures were due to such circulation. The metal cell was designed to use a pair of Pt100 platinum-resistance thermometers, but for preliminary measurements, sufficient to establish whether the plots were curved or straight, a pair of thermistors encased in thin stainless steel tubes were used instead. As noted in the Introduction, the results obtained with the metal cell were very similar to those obtained with the glass apparatus. This does not rule out gas-phase turbulence or circulation as the cause of the curvature but does appear to eliminate temperature gradients across the upper plate as a major source of turbulence.

The absolute calibration of the thermistors has been found to vary significantly with time, so the relative thermistor calibrations, which have a direct impact on the measured  $Q^*$  values, were checked frequently. The gas pressure above the test liquid was measured with a 0–0.2 Torr MKS Baratron type 223B differential transducer. The Baratron output and thermistor voltages were taken to a computer via a programmable-gain 12-bit analog-to-digital converter. Because the Baratron was being used to measure pressures of the order of only a few percent of its full-scale reading, the pressure readings were smoothed by a 12-point running average. Eight or ten measurements were taken at each data point in a typical series of measurements of  $\Delta P$  and  $\Delta T$ . Small drifts in the pressure readings were measured by returning to the same temperature values at regular intervals during an experimental run. Variations in the base pressure due to small variations in liquid temperature



**Figure 2.** Typical results for  $n$ -heptanol at higher pressures and temperatures. The liquid surface temperature is marked on each graph.

were compensated with the aid of the enthalpy of vaporization ( $65.7 \text{ kJ mol}^{-1}$ ) calculated from the temperature dependence of the vapor pressure as observed with  $\Delta T = 0$ . The  $n$ -heptanol was the middle fraction distilled from a sample of CP-grade material which had been left to stand overnight in contact with barium hydride to remove water. It was rigorously freed of dissolved gas by a large number of *freeze-pump-thaw-boil* cycles, of which the *boil* component was found to be essential if the process was to be completed within a reasonable time (less than a week).

## Results and Discussion

Figure 2 shows typical results for  $n$ -heptanol in the glass cell at pressures such that the 4.1-mm distance  $\delta$  from the liquid surface to the top plate was greater than one mean free path. The liquid temperatures are marked on the graphs. In the absence of a listed collision diameter for  $n$ -heptanol, a value of  $5 \times 10^{-8} \text{ cm}$  was assumed for the mean free path calculation. The dependence of  $\Delta P$  on  $\Delta T$  in these graphs is seen to be nonlinear and of the same form as those previously found for aniline. As for aniline,  $Q^*$  is negative and of comparable magnitude to the latent heat of vaporization.

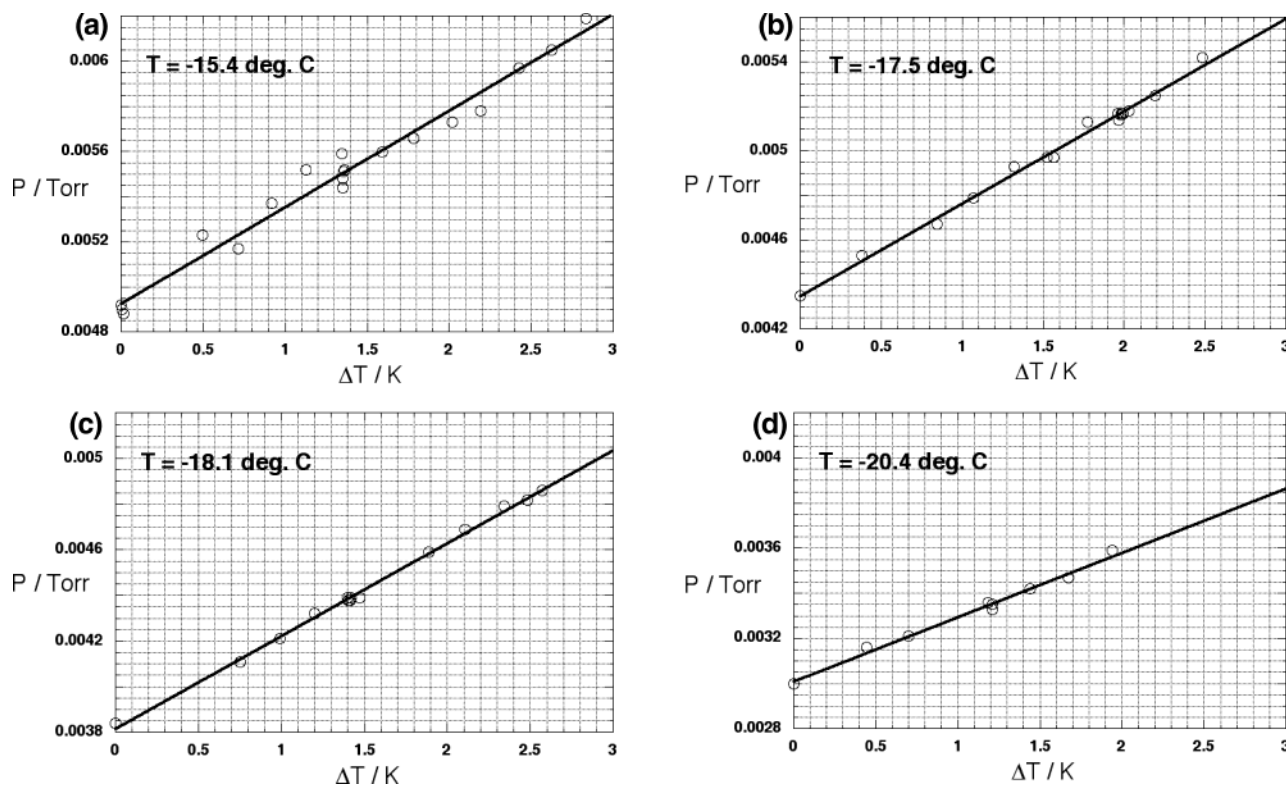
The heptanol results obtained for  $\delta$  less than one mean free path were linear, as shown in Figure 3. A comparison of the curves in Figures 2 and 3 reveals that the two data sets actually overlap, the  $-15.8 \text{ }^\circ\text{C}$  curve of Figure 2 corresponding to a slightly smaller number of mean free paths than the  $-15.4 \text{ }^\circ\text{C}$  line of Figure 3, which suggests that the curvature is an artifact. We initially suspected that the curvature had its origin in a slow gas circulation that was liable to be set up by small departures from uniformity in the temperature of the top plate, which was made of Pyrex glass. Such circulation would affect  $Q^*$  by increasing the effective value of  $\delta$ . However, as already noted, changing to the metal apparatus of Figure 1b has made no difference, so the origin of the curvature at higher pressures

remains unknown. Some form of turbulence still seems the most likely cause.

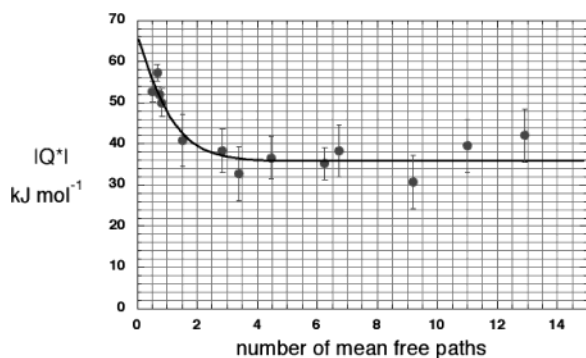
Figure 4 shows the dependence of  $|Q^*|$  for  $n$ -heptanol on  $\delta$  measured in mean free paths. For the experiments that gave curved plots, the heat of transport was calculated from the average of the  $\Delta P$  values obtained with  $\Delta T$  less than  $0.5 \text{ }^\circ\text{C}$ . The curve in Figure 4 is drawn to indicate the trend and has no theoretical basis. The results indicate that  $|Q^*|$  approaches quite closely to the latent heat of vaporization as  $\delta$  tends toward zero. If we consider a small volume of gas located a short distance below the top plate, the fraction of molecules arriving directly from the liquid surface with the velocity distribution appropriate to the temperature of the liquid surface, relative to those arriving from the top plate with the velocity distribution appropriate to the temperature of a liquid film adsorbed on the top plate, passes through a maximum at  $\delta$  equal to two mean free paths and falls to zero when  $\delta$  goes to zero.<sup>9</sup> If the pressure changes that we have measured near the top plate had their origin in the effect of proximity to the liquid surface on processes occurring in the gas phase, they would have to vary in proportion to the fraction of molecules arriving directly from the liquid surface. The results in Figure 4 show that this is not the case, and we therefore conclude that the changes in the effective vapor pressure result from the effect of the temperature gradient on processes occurring in the capillary-wave zone at the surface of the liquid. Model calculations<sup>6</sup> show that a possible explanation can be found in terms of the effect of the temperature gradient on the barrier to evaporation, where the negative sign of  $Q^*$  indicates that, as might have been anticipated, the barrier is a free-energy barrier with temperature coefficient  $-\Delta S$ , rather than an enthalpy barrier with temperature coefficient  $\Delta C_p$ .

Our experimental results so far are limited to the two pure liquids aniline and  $n$ -heptanol and are also restricted to positive values of  $\Delta T$  because steady condensation on the upper plate prevents a stationary state being established when  $\Delta T$  is





**Figure 3.** As in Figure 2, but under conditions where  $n_L$ , the gap between the liquid surface and the top plate, measured in mean free paths, is less than 1.

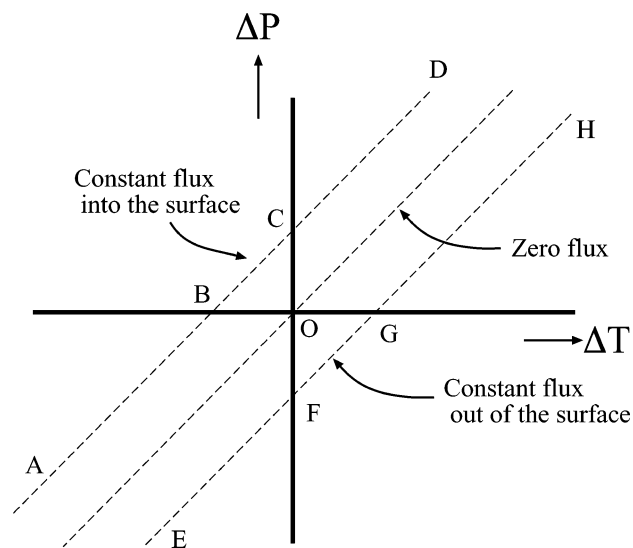


**Figure 4.** Variation of the measured heat of transport for *n*-heptanol with the number of mean free paths in the gap above the liquid.

negative. However, our observation of the distillation of cool aniline onto a warmer surface (a phenomenon that was also observed with *n*-heptanol) implies that eq 2 does indeed hold for negative values of  $\Delta T$ .<sup>7</sup> Planned experiments with systems comprising a nonvolatile solvent and a volatile solute will enable this point to be checked directly.

If the heat of transport arose solely from effects occurring in the capillary-wave zone, the magnitude of  $Q^*$  would be expected to be somewhat less than the latent heat of vaporization, because a molecule in the capillary-wave zone is not fully accommodated into the body of the liquid. However, for a one-component liquid–vapor system, this argument loses most of its force because, in the steady state, the addition of a new molecule to the capillary zone has to be balanced by the accommodation of another molecule into the bulk liquid. The same argument applies to a two-component system, but this too needs to be tested by experiment.

The observations by Ward and co-workers<sup>10–14</sup> of large temperature excursions near the surface of an evaporating liquid, where the deviations are in the opposite direction to those



**Figure 5.** Postulated dependence of  $\Delta P$  on  $\Delta T$  for steady-state gas fluxes into and out of the liquid surface and for the stationary state with zero gas flux.

predicted by Pao,<sup>8</sup> provide a further instance of nonintuitive behavior at the gas–liquid interface, additional to the inverted temperature gradients predicted by classical kinetic theory<sup>8</sup> and our observations of the distillation of a cool liquid onto a warmer surface.<sup>7</sup> All of these processes can be understood on the basis of the diagram in Figure 5, which plots the pressure difference against the temperature difference across the Knudsen layer and represents a slight elaboration of the similar diagram in ref 9. The point O corresponds to the equilibrium vapor pressure, with  $\Delta P$  and  $\Delta T$  both zero. The line through O is the locus of possible stationary states as observed in our experiments. Of the other two lines, the top one corresponds to the effect of applying a pressure difference greater than the stationary-state value, so

as to produce a steady flux into the liquid, and the bottom line corresponds to maintaining a pressure difference smaller than the stationary-state value, so that there is a steady flux out of the liquid. These changes amount to moving away from the stationary state by adjusting the second term in eq 1. Alternatively, but less intuitively, the lines could be regarded as related through temperature changes applied across the interface and giving rise to a nonzero gas flux via the first term in eq 1 or, more generally, as the locus of points with constant gas flux for different values of  $\Delta P$  and  $\Delta T$ .

In Figure 5, the paradoxical behavior discovered by Pao<sup>8</sup> corresponds to the region E–F, with  $\Delta P$  and  $\Delta T$  both negative, at the surface of the evaporating liquid and region C–D, with  $\Delta P'$  and  $\Delta T'$  both positive, at the surface of the condensing liquid. When  $|\Delta T| + |\Delta T'|$  is greater than the temperature difference between the two liquids, the gas-phase temperature profile is inverted, which results in a small conductive heat flux in the opposite direction to the larger latent heat flux from the warm liquid to the cooler one. So far this sort of anomalous behavior has not been observed experimentally.

The observed distillation of a cool liquid onto a warmer surface<sup>7</sup> corresponds to region G–H, with  $\Delta P$  and  $\Delta T$  both positive, at the surface of the evaporating liquid and region A–B, with  $\Delta P'$  and  $\Delta T'$  both negative, at the warmer surface of the condensing liquid. If  $|\Delta P| + |\Delta P'|$  is greater than the equilibrium vapor pressure difference between the two liquid surfaces, liquid distills from the cool surface to the warmer one. In this case, the flux of latent heat has to be smaller than the conductive heat flux that drives the process.

The experiments of Ward et al.<sup>10–12</sup> correspond to the region F–G at the surface of an evaporating liquid, with  $\Delta P$  negative and  $\Delta T$  positive. In a two-surface system, this would be paired with region B–C at the surface of a condensing liquid, with  $\Delta P'$  positive and  $\Delta T'$  negative, but the corresponding condensation experiment has not been done. The sizes of the regions B–C and F–G increase with increasing vapor flux, so the observation of this kind of behavior depends on the presence of a large gas flux. The other “anomalous” phenomena occur in regions that are semi-infinite, which suggests that they ought to be easier to observe. With all of the regions in Figure 5 accounted for, we can conclude that no other forms of anomalous behavior at the interface remain to be discovered.

One of the many locations in which transport of vapor across a gas–liquid interface is very important is the surface of the ocean. The rate and direction of air–sea exchange of CO<sub>2</sub> have been calculated from the partial pressure difference between an air sample taken 10 m above the surface and a bulk water sample taken at a depth of the order of 1 m, with no reference

to the temperature gradient at the surface.<sup>15</sup> Subsequently the effect of greater solubility in the surface layer (the “cool skin of the ocean”) was taken into account,<sup>16</sup> but evidently this is only part of the story. In the limit where  $Q^*$  approaches the latent heat of vaporization, the effective vapor pressure is the same as it would be if the liquid surface were at the temperature of the gas on the other side of the Knudsen layer, approximately one mean free path away. Depending on the origin of the air mass in question, this temperature can be very different from the temperature of the ocean surface. Many complicating factors are involved,<sup>17</sup> and absolute field measurements are notoriously difficult,<sup>18</sup> but it does seem likely that a correct prediction of the direction of air–sea exchange of minor atmospheric constituents such as CO<sub>2</sub> can be made on the basis of the assumption that the effective vapor pressure corresponds to the vapor pressure for the temperature at the top of the Knudsen zone and that a correct calculation of the rate of air–sea exchange, under conditions where the rate is limited by transfer across the interface, should include both of the terms inside parentheses in eq 1.

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