The Influence of Heat Transfer on Mass Transfer at Low Pressures

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It is unfortunate that in a number of studies on the evaporation of solids and liquids at low pressures the influence of heat transfer has not been properly taken into account. The result is that the true temperature of the evaporating surface was not used in the analysis of the data and so the reported evaporation coefficients are in error.

A case in point is the very low value for the evaporation coefficient of naphthalene recently reported by Sherwood and Cooke (*5*). This value appears to be low by at least an order of magnitude, owing to a temperature depression of the surface of the evaporating naphthalene sphere which was not considered. The authors indicate that, since the evaporation rate was very small, the evaporative cooling of the surface was negligible. At first glance this seems to be quite reasonable, since only 0.178 g. was evaporated in 1 hr. at the highest rate, and the heat requirement for sublimation amounts to a mere 24 cal. Indeed the very low heat duty of 24 cal./hr. would suggest no problem. However at a pressure of 0.1 μ Hg substantially all heat reaching the sphere must be supplied by radiation from the enclosure walls, and a rather sizable temperature difference is required. With the enclosure maintained at 0°C. the equivalent radiant heat transfer coefficient is about 0.36 cal./(hr.)(sq. cm./°C.). (This is the maximum coefficient when all emissivities are assumed to be 1.0.) Hence the sphere, 1.0 cm. in diameter, evaporating at a pressure of 0.1 μ, would tend to attain a steady-state surface temperature of about −21°C. It is to be noted that the vapor pressure of naphthlene at −21°C. is about 0.38 μ Hg compared with 5.74 μ Hg at 0°C.

With the true vapor pressure of the surface introduced into Equation (1) of their paper and the evaporation coefficient assumed to be unity, the maximum evaporation rate at a pressure of 0.1 μ Hg would be about 0.177 g./hr. This agrees almost exactly with the observed result. Thus it appears that the evaporation coefficient of naphthalene is in reality close to unity, and the low apparent value reported (about 0.056) merely reflected the temperature depression of the naphthalene surface. The same argument also suggests that the true evaporation coefficient of diethyl adipate is close to unity, rather than 0.177 as reported.

While the largest temperature depression of the surface was encountered in the experiments at the lowest pressure, 0.1 μ, where heat transfer to the sphere was most unfavorable, some temperature depression also was involved at the higher pressures studied. This temperature depression tended to decrease with increasing pressure for two reasons: (1) increased diffusional resistance in the gas reduced the evaporation rate and hence the required heat duty, and (2) heat transfer to the sphere was improved at the higher pressures because of increased heat conduction through the gas.

As the evaporation of spheres (or drops) has been studied in a number of cases, a general equation has been developed for predicting the temperature depression of the surface accompanying evaporation into a quiescent gas at low pressures. The equation is shown to reduce to simplified forms for the limiting cases of very low pressures and relatively high pressures. The term *relatively* high pressures is used, as the pressure must be low enough to assure the absence of convection. As a rough guide, the upper pressure limit would be of the order of 1 mm. Hg.

EVAPORATION OF SPHERES AT LOW PRESSURES

The evaporation rate for a sphere in a gas at low pressures has been considered in detail by Bradley, Evans, and Whytlaw-Gray (*1*). Considering the enclosure to be very large and the concentration of the evaporating substance to be zero at the walls of the enclosure, one can develop the following equation for the rate of evaporation:

$$-\frac{dm}{dt} = \frac{4\pi a\, D_v C_s}{\dfrac{D_v}{\alpha_M \Upsilon a} + \dfrac{a}{a + \Delta}} = \frac{4\pi a^2 C_s}{\dfrac{1}{\alpha_M \Upsilon} + \dfrac{a^2}{(a + \Delta)\, D_v}} \tag{1}$$

This equation was developed on the basis of an evaporation model proposed by Fuchs (*2*). In his treatment evaporation from the sphere occurs through a surrounding vacuous shell of thickness Δ at the theoretical vacuum rate. In the steady state, molecules arriving at the shell surface at a distance $a + \Delta$ from the sphere center leave by diffusion through the gas.

Under high vacuum conditions, where $\Delta \gg a$, and $a/(a + \Delta) \rightarrow 0$, this equation reduces to the familiar form for the evaporation rate in an absolute vacuum:

$$-\frac{dm}{dt} = 4\pi a^2 \alpha_M \Upsilon C_s \tag{2}$$

HEAT TRANSFER TO A SPHERE AT LOW PRESSURES

When one follows the evaporation model of Fuchs, heat conduction to the sphere may be assumed to take place in the following manner. Conduction occurs through the gas up to the outer surface of the vacuous shell and then by free molecule conduction across the vacuous shell to the sphere surface. A similar argument was used previously by Kyte, Madden, and Piret (*4*).

The heat flow to the sphere by conduction through the gas will then be given by an equation analogous to Equation (1),

$$\frac{dQ_c}{dt} = \frac{4\pi a^2 (T_\infty - T_s)}{\dfrac{1}{\alpha_H\ \Lambda_0 P\ \sqrt{\dfrac{T_s}{273}}} + \dfrac{a^2}{(a + \Delta)k}} \tag{3}$$

At low pressures, where $\Delta \gg a$, Equation (3) reduces to

$$\frac{dQ_c}{dt} = 4\pi a^2 \alpha_H\ \Lambda_0 P \cdot \sqrt{\frac{273}{T_s}}\,(T_\infty - T_s). \tag{4}$$

This will be recognized as the equation for heat transport by free molecule conduction. At the other extreme, where the gas pressure is relatively high, $\Delta \ll a$, Equation (3) reduces to

$$\frac{dQ_c}{dt} = 4\pi a k (T_\infty - T_s) \tag{5}$$

the usual equation for heat conduction to a sphere through a surrounding infinite medium.

The total heat transfer to a sphere will include simultaneous radiant heat transfer. Hence the total heat transfer may be represented by

$$\frac{dQ}{dt} = \left[h_r + \frac{1}{\dfrac{1}{\alpha_H\ \Lambda_0 P\ \sqrt{\dfrac{T_s}{273}}} + \dfrac{a^2}{(a + \Delta)k}} \right] \cdot 4\pi a^2 (T_\infty - T_s) \tag{6}$$

HEAT BALANCE

In the steady state the heat transfer to the sphere will satisfy the latent heat requirement for evaporation (or sublimation). Hence

$$-\frac{dm}{dt} = \frac{1}{L_v}\frac{dQ}{dt} \tag{7}$$

thus

$$\frac{4\pi a^2 C_s}{\dfrac{1}{\alpha_M \Upsilon} + \dfrac{a^2}{(a + \Delta)\, D_v}}$$

$$= \left[h_r + \frac{1}{\dfrac{1}{\alpha_H \; \Lambda_0 P \sqrt{\dfrac{T_s}{273}}} + \dfrac{a^2}{(a + \Delta)k}} \right] \cdot \frac{4\pi a^2 (T_\infty - T_s)}{L_v} \qquad (8)$$

Equation (8) may be rearranged to give

$$C_s = \left[\frac{1}{\alpha_M \Upsilon} + \frac{a^2}{(a + \Delta) \; D_v} \right] \left[h_r + \frac{1}{\dfrac{a^2}{(a + \Delta)k} + \dfrac{1}{\alpha_H \; \Lambda_0 P \sqrt{\dfrac{T_s}{273}}}} \right] \cdot \frac{(T_\infty - T_s)}{L_v} \qquad (9)$$

The heat balance, Equation (9), gives one relationship for C_s and hence p_s as a function of the surface temperature. Simultaneous solution of this equation with the vapor-pressure–temperature relationship for the substance enables one to determine the surface temperature.

LIMITING CASES

At very low pressures conduction through gas becomes negligible, and all heat transfer is by radiation. Also since D_v varies inversely with gas pressure, the term $a^2/[(a + \Delta)D_v]$ becomes very small. For this case Equation (9) reduces to

$$C_s = \frac{h_r (T_\infty - T_s)}{\alpha_M \Upsilon L_v} \qquad (10)$$

At higher pressures, $\Delta \ll a$, $1/(\alpha_M \Upsilon) \ll a/D_v$, and $[1/(\alpha_H \Lambda_0 p \sqrt{T_s/273})] \ll a/k$, Equation (9) becomes

$$C_s = \frac{a}{D_v} \left[h_r + \frac{k}{a} \right] \left(\frac{T_\infty - T_s}{L_v} \right) \qquad (11)$$

If in addition the sphere diameter is small, radiant heat transfer will be small compared with that by conduction, and Equation (11) simplifies further to

$$C_s = \frac{k}{D_v} \left(\frac{T_\infty - T_s}{L_v} \right) \qquad (12)$$

Equation (12) with a slight modification was used by Johnson (*3*) in analyzing measurements of the surface temperature of evaporating water drops. (In Johnson's case the left-hand side of the equation was given as $C_s - C_\infty$, where C_∞ is the concentration of water vapor in the ambient gas. In the present case C_∞ was assumed to be zero by use of a suitable absorbent.)

A few measurements have been made of the temperature depression of a hollow sphere, coated with naphthalene, evaporating in air inside an 18-in.-diameter bell jar. In the pressure range 500 to 800 μ Hg the results agree rather well with the prediction of Equation (11). Further experimental work is in progress to cover a wider pressure range. The assistance of the National Science Foundation under grant G1617 is gratefully acknowledged.

NOTATION

a = sphere radius
C_s = concentration of evaporating substance in gas in equilibrium with sphere surface
D_v = diffusivity of evaporating substance in gas
e = emissivity
h_r = coefficient for radiant heat transfer $\equiv \dfrac{e\sigma(T_\infty^4 - T_s^4)}{T_\infty - T_s}$
k = gas thermal conductivity
L_v = latent heat of evaporation (or sublimation) per unit mass of evaporating substance
M = molecular weight of evaporating substance
P = gas pressure
T_∞ = temperature of enclosure walls
T_s = temperature of evaporating surface, sphere surface temperature

Greek Letters

α_H = evaporation coefficient
α_H = thermal accomodation coefficient
Δ = distance of order of one mean free-path length
Λ_0 = free molecule heat conductivity at 0°C.
σ = Boltzmann's constant
$\Upsilon = \sqrt{\dfrac{RT_s}{2\pi M}}$

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Reply

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Professor Madden's suggestion that the surface temperature of the naphthalene sphere employed in our study must have fallen considerably below 0°C. seems to be correct. We had reached the same conclusion shortly after our article appeared in print, when we noted the paper by Littlewood and Rideal (*1*). In effect these authors questioned practically all the values of accommodation coefficients reported in the literature, suggesting that few, if any, had been based on reliable measurements of surface temperature. This led us to repeat an earlier calculation of the temperature depression owing to evaporation, and we found that we had indeed made an error in the calculation of some two years previous which had indicated the effect to be trivial. To rectify the situation work was undertaken along two lines.

First, following a suggestion of H. C. Hottel, Conrad Johannes initiated an experimental study to employ a radiometer for the accurate measurement of the surface temperature of a solid subliming at low pressure. The necessary equipment is complex, and it will be some time yet before the results can be reported.

Second, the data which we had obtained were analyzed carefully to see whether the accommodation coefficient might not be calculated by allowing for the cooling of the surface of the naphthalene spheres.

In a series of eleven tests below 3 μ the rate of sublimation decreased during the first hour but remained quite constant at 0.0344 cm. (radius)/hr. during the subsequent 1-hr. period. When one assumes the surroundings to be at 0°C., the following values of the equilibrium surface temperature and accommodation coefficient are calculated for various assumed values of the emissivity of the surface:

Emissivity	0.927	0.878	0.833	0.794
Temperature, °C.	−16	−17	−18	−19
Accommodation coefficient	0.336	0.381	0.434	0.494

If the emissivity is taken to be 0.85 (*2*), the calculated accommodation coefficient is about 0.41—considerably greater than the value which we reported but much smaller than the value unity, suggested by Professor Madden.

This discussion would appear to emphasize the point of Littlewood and Rideal's paper: that reliable values of accommodation coefficients require accurate measurements of the surface temperature of the evaporating substance.

LITERATURE CITED

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