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

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

$$= \frac{e\sigma(T_\infty^4 - T_s^4)}{T_\infty - T_s}$$

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.

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