Temperature Depressions for Evaporating Spheres at Low Pressures

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The evaporation of naphthalene spheres into air in the micron pressure range may be accompanied by an appreciable surface temperature depression. The magnitude of the effect is shown to depend upon the geometry of the experimental system and the pressure level. Such effects are of interest in studies aimed at determining evaporation coefficients.

In a previous note (7) attention was drawn to the possibility of very significant surface temperature depressions which may be encountered when solids (or liquids) evaporate into gases at low pressures. This situation arises because of the poor heat transport properties of low pressure gas systems. Consequently a substantial temperature difference may exist between the surroundings and the evaporating surface in order to transport the required latent heat of sublimation (or vaporization). The effect becomes more pronounced the higher the evaporation rate and is therefore directly related to the volatility of the evaporating compound.

In the earlier communication (7) a general equation was developed for predicting the steady state temperature depression of the surface of a sphere evaporating into a quiescent gas at low pressures. This derivation was for the case of an infinite enclosure with the concentration of evaporating substance at a great distance from the sphere taken to be zero. In this paper surface temperature-depression measurements are presented for evaporating naphthalene spheres suspended in a thermostatted cylindrical tube, the vapor being continuously removed by transport to an adjoining condenser. The equation previously derived for predicting the temperature depression must be modified to apply to this work because of the difference in geometry.

THE THEORETICAL TEMPERATURE DEPRESSION

The basic argument in developing an equation to predict the steady state temperature depression for this case is similar to that used previously (7). Only the basic argument and pertinent points due to the different geometry will be emphasized in this development.

In the steady state the heat flow to the sphere satisfies the latent heat requirement for evaporation. Thus the rate of heat transfer and the evaporation rate are related by

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

Evaporation from the sphere is presumed to take place through a surrounding vacuous shell at the theoretical vacuum rate. This shell is of thickness Δ, which is of the order of one mean free path length. In the steady state, molecules arriving at the shell surface leave by diffusion up the tube to the condenser. Vapor transport, for this case, takes place by means of a combination of molecular (Knudsen) flow and ordinary diffusion. (At very low pressures Knudsen flow predominates, and at higher pressures ordinary diffusion controls.) The general equation for the evaporation rate may then be shown to be

$$-\frac{dm}{dt} = \frac{C_s}{\dfrac{1}{4\pi a^2 \alpha_M \Upsilon} + \dfrac{1}{\dfrac{4}{3}\sqrt{\dfrac{2\pi RT}{M}}\dfrac{r^3}{L}} + \dfrac{LP_{bm}}{\pi r^2 P D_V}} \tag{2}$$

To derive this equation the vapor pressure at the condenser is assumed to be zero and the resistance for vapor transport along the tube is taken to be the sum of the resistances for molecular flow and for ordinary diffusion. This method of combining resistances is similar to that proposed by Dryer (3). It is clear from this equation that for a given surface temperature (thus fixing C_s) the evaporation rate at a given pressure may be *seriously affected* by the dimensions of the enclosing cylinder.

The heat transfer to a suspended evaporating sphere occurs in three ways: by conduction through the gas to the sphere, by radiation from the enclosure walls, and by conduction through the sphere support. Thus the heat flow to the sphere is given by

$$\frac{dQ}{dt} = 4\pi a^2 (T_w - T_s)(h_c + h_r + h_m) \tag{3}$$

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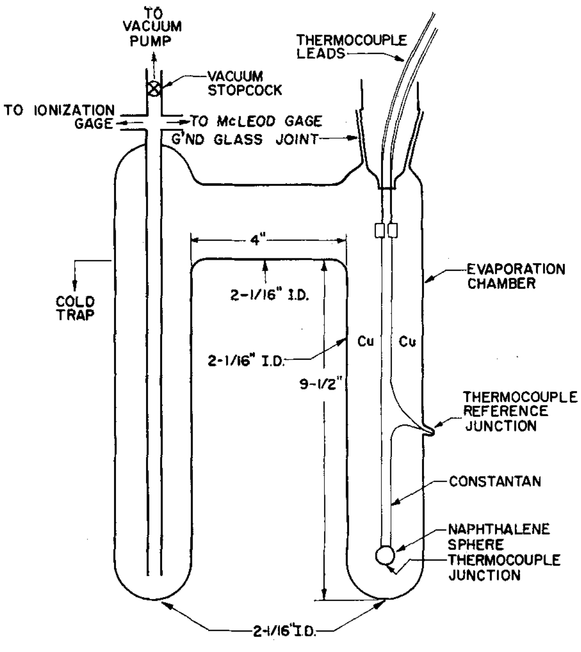

Fig. 1. Apparatus for determining the surface-temperature depression of an evaporating naphthalene sphere.

$$h_c = \frac{1}{\dfrac{(r-a-\Delta)a^2}{r(a+\Delta)k} + \dfrac{1}{\alpha_H \Lambda_0 P \sqrt{\dfrac{273}{T_s}}}} {}^{*} \qquad (3a)$$

$$h_r = \frac{\epsilon \sigma (T_w^4 - T_s^4)}{T_w - T_s} \qquad (3b)$$

$$h_m \cong \frac{k_m A_m}{L_w A_s} \frac{(T_r - T_s)}{(T_w - T_s)}{}^{\dagger} \qquad (3c)$$

Substituting Equations (2) and (3) in Equation (1) one gets the following equation for the concentration of vapor in equilibrium with the sphere surface:

$$C_s = \frac{T_w - T_s}{L_V} \left[\frac{1}{\alpha_M T} + \frac{1}{\dfrac{2}{3}\sqrt{\dfrac{RT}{2\pi M}\,\dfrac{r^3}{La^2}}} + \frac{4La^2 P_{bm}}{D_V P r^2} \right] (h_c + h_r + h_m) \qquad (4)$$

This general equation relates C_s and T_s as governed by heat and mass transfer considerations. Another relation for C_s as a function of T_s is obtained from the vapor pressure-temperature relationship for the evaporating substance. Simultaneous solution of these two equations gives the steady state temperature depression of the evaporating sphere as a function of pressure. To apply this equation information is required on the evaporation coefficient, the transport properties of the system, and the enclosure dimensions.

EXPERIMENTAL

The steady state temperature depression of an evaporating naphthalene-coated sphere was determined in the Pyrex glass vacuum apparatus shown in Figure 1. Measurements were made over the pressure range 0.5 to 100μ Hg with a 0.85-cm. diameter sphere.

The right (evaporation) leg was immersed in a flask filled with crushed ice and water to maintain the wall temperature at 0°C., while the left (condensing) leg was immersed in a flask filled with crushed dry ice and acetone to condense the evaporated naphthalene. A copper-constantan thermocouple (30 gauge) served to measure the surface temperature and also to suspend the sphere as shown in Figure 1, the reference junction being immersed in a well depressed in the side of the glass wall. The electromotive-force difference of the two thermocouple junctions, as determined with a potentiometer, gave the surface temperature depression.

The coated sphere was prepared in the following way. A 0.75-cm. diameter hollow brass sphere served as the base support for the coating. Thermocouple wire was coiled one and one-half turns around the sphere and glued to insure good thermal contact. The assembly was then coated by immersion in molten naphthalene which solidified upon withdrawal. The final coated diameter was about 0.85 cm., which required repeated immersions in molten naphthalene to build up the coating thickness. By this procedure the thermocouple junction and about 4 cm. of each wire were completely covered by the naphthalene coating.

The vacuum chamber was evacuated by means of a three-stage oil diffusion pump in series with a mechanical vacuum pump. Pressures were measured with an ionization gauge or a McLeod gauge, depending upon the pressure level.

EXPERIMENTAL RESULTS

The measured and predicted temperature depressions for the 0.85-cm. diameter naphthalene coated sphere are shown in Figure 2. The solid line represents the predictions for the temperature depression as a function of pressure based on Equation (4), coupled with the vapor pressure-temperature relationship. The open circles are the experimental measurements, and the agreement is quite good.

In evaluating Equation (4) the evaporation coefficient of naphthalene was taken to be unity and the emissivity equal to 0.85 (*8*). The thermal conductivities Λ_0* (*4*) and k (*5*) were

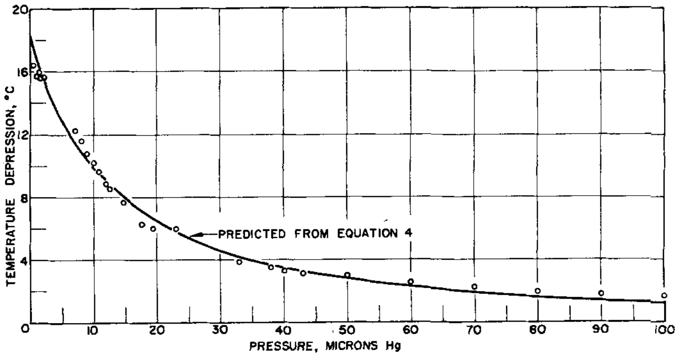

Fig. 2. Surface temperature depression measurements for an evaporating naphthalene sphere.

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* The first term of the denominator of h_c arises from the assumption that conduction through the gas up to the surface of the vacuous shell is approximated by conduction between concentric spherical shells of radii, r and $a + \Delta$. The second term is for free molecule conduction between the vacuous shell and the sphere surface. When $\Delta \geqq r - a$, ordinary conduction vanishes and the first term of the denominator is zero: h_c then becomes equal to $\alpha_H \Lambda_0 P \sqrt{\dfrac{273}{T_s}}$.

† At low pressures and for small thermocouple wires heat transfer to or from the circumference of the thermocouple is neglected.

* $\Lambda_0 = \dfrac{2.664}{\sqrt{M}} \left(\dfrac{\gamma + 1}{\gamma - 1}\right) \dfrac{\text{cal.}}{\text{sq.cm.-sec.-°C.-atm. pressure}}$

the values for air, and Δ (*6*) was taken as the mean free path length of air. The thermal accommodation coefficient was assumed to be unity. The vapor pressure-temperature relationship for naphthalene, used in conjunction with Equation (4), was the equation of Bradley and Cleasby (*1*). Application of the Clapeyron equation to their equation shows that the latent heat of sublimation is 135 cal./g. In the experiments summarized in Figure 2 the path length to the condensing surface was 30.5 cm.

It should be pointed out that no claim can be made as to the absolute value of the evaporation coefficient on the basis of the reported temperature-depression measurements. Uncertainties in the absolute pressure at the low-pressure end and other assumptions involved in the evaluation of Equation (4) preclude drawing any reliable conclusions. The greatest effect of α_M on temperature depression occurs at the low-pressure end. Thus if $\alpha_M = 0.5$, the predicted temperature depression at zero pressure limit would be 15.4°C. compared with 18.2°C., with $\alpha_M = 1.0$ assumed. The data of Figure 2 suggests that α_M rests somewhere between 0.5 and 1.0. Some thirty-five additional measurements where the pressure was less than 1μ Hg, with four sphere sizes (0.85, 0.64, 0.56, and 0.51-cm. diameter) used, support the conclusion that α_M is greater than 0.5. However since the aim of the present work was only to confirm the temperature-depression effect and not to pin point the value of the evaporation coefficient, it seems best to simply indicate the approximate magnitude of the latter.

DISCUSSION OF RESULTS

It is clear from Equation (4) that the temperature depression and the evaporation rate are very sensitive to the system geometry. Thus the temperature depression will be greater for a given pressure if any of the following changes are made: reduction of the sphere radius, a decrease in the path length to the condenser, and a decrease in the heat conduction to the sphere by a reduction of the size of the thermocouple support. This is demonstrated by an experiment wherein all three factors were decreased. A sphere, 0.56 cm. in diameter, was suspended by means of 36 gauge thermocouple wire and the path length to the condenser reduced to 17.8 cm. The measured temperature depression at 0.5μ Hg pressure was 19.2°C., compared with 16.4°C. obtained with the 0.85-cm. diameter sphere, 30 gauge thermocouple, and 30.5-cm. path length to the condenser.

Conversely if the tube radius leading to the condenser is decreased and/or the path length increased, resistance to mass transport increases and the evaporation rate falls off, as does the temperature depression. This is dramatically illustrated by an experiment in which the 0.85-cm. diameter naphthalene sphere sublimed inside a vacuum chamber separated from the condenser by a ½-in. I.D. tube, 10 in. long. The steady state temperature depression of the evaporating naphthalene was found to be only 1.3°C. at 0.75μ Hg pressure. When the passage diameter to the condenser was large, as was the case for the experiments summarized in Figure 2, the steady state temperature depression was 16.1°C. at the same pressure. This shows rather strikingly that even at low pressures the evaporation rate can be seriously affected by the mass transport problems, as pointed out recently by Burrows (*2*).

In the experiments summarized in Figure 2 the resistances to mass transport offered by surface evaporation, Knudsen flow, and ordinary diffusion are given, respectively, by the three terms of the denominator of Equation (2). For the experimental conditions leading to the results of Figure 2, and with $\alpha_M = 1.0$ assumed, the relative weights of these three terms are 1: 0.46:0.44 P_{bm} (μ Hg). Thus at the low pressure limit, where $P \to 0$, ordinary diffusional resistance disappears, and Knudsen flow resistance accounts for about one-third of the total resistance to mass transport. At the other extreme, $P = 100\ \mu$, essentially all resistance is accounted for by ordinary diffusion (the third term). Thus the relative importance of the three terms depends upon the evaporation coefficient, the system geometry, and the pressure level.

SUMMARY

Experimental temperature depression measurements on evaporating naphthalene spheres at low pressures agree quite well with predictions based on heat and mass transfer considerations. The system geometry is shown to markedly affect the temperature depression and hence the evaporation rate.

ACKNOWLEDGMENT

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NOTATION

a = sphere radius
A_m = cross-sectional area of thermocouple wire
A_s = sphere surface area
C_s = concentration of evaporating substance in gas in equilibrium with sphere surface
D_v = diffusivity of evaporating substance in gas
h_c = coefficient for heat transfer by gas conduction
h_r = coefficient for radiant heat transfer
h_m = coefficient for heat transfer by conduction through sphere support
k = gas thermal conductivity
k_m = thermocouple wire thermal conductivity
L = path length to the condenser
L_v = latent heat of evaporation (or sublimation) per unit mass of evaporating substance
L_w = length of copper thermocouple wire from sphere to contact at room temperature
M = molecular weight of evaporating substance
P = gas pressure
P_{bm} = log mean partial pressure of inert gas
r = tube radius leading to condenser
T_r = room temperature (absolute scale)
T_s = sphere surface temperature (absolute scale)
T_w = evaporation chamber wall temperature (absolute scale)

Greek Letters

α_M = evaporation coefficient
α_H = thermal accommodation coefficient
Δ = distance of order of one mean free-path length
ϵ = emissivity
Λ_0 = free molecule conductivity at 0°C.
σ = Stefan-Boltzmann constant
$\Upsilon = \sqrt{\dfrac{RT_s}{2\pi M}}$
γ = ratio of heat capacities, c_p/c_v

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