Evaporation of Liquid Droplets Containing Surface Impurities

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The evaporation of a single droplet into still air has been summarized by Green and Lane (*1*) and by Orr (*2*). If the drop does not become too small, the rate of evaporation follows the Langmuir equation (*3*), which can be written as

$$N = \frac{D}{r}(c_o - c_g) \tag{1}$$

or

$$\frac{dS}{dt} = \frac{8\pi DM(c_o - c_g)}{\rho} \tag{2}$$

Equation (2) shows that the rate of change of surface area of a drop, *dS/dt*, is constant during the evaporation. Experimental results show that *dS/dt* is not a constant in certain cases; an example is given in Figure 2. The rate of evaporation is smaller than that predicted by the Langmuir equation, especially when the drop becomes small. To explain this phenomenon, Fuchs (*4*) proposed a model which was refined and tested experimentally by Bradley et al. (*5*). Further research in this field was more or less based on Fuch's model (*6* to *8*). In Fuch's model, the diffusion is considered to start at a distance Δ from the droplet surface, and Bradely et al. (*5*) related Δ to the mean free path of the diffusing molecules. The spherical shell of thickness Δ is considered as a vacuous space. However the physical picture of this model is unreal. Monchick and Reiss (*9*) pointed out that "the distance Δ is never clearly defined and the limits of validity of the treatment are not apparent."

It is well known that surface impurities retard the rate of evaporation in a flat surface (*10*), but there is no quantitative discussion of the effect of surface impurities on the evaporation of a droplet. Such a detailed discussion is given in this report, which also discusses the effect of surface tension.

EFFECT OF SURFACE IMPURITIES AND SURFACE TENSION

The effect of curvature on the vapor pressure of a liquid is described by the Kelvin equation (*11*), which may be written for a spherical surface as

$$\ln \frac{p_o'}{p_o} = \frac{2\sigma M}{rRT\rho} \tag{3}$$

For air-water at 20°C. $(p_o' - p_o)/p_o$ is 0.11% if $r = 10^{-4}$ cm. but 11% if $r = 10^{-6}$ cm. Therefore, if the size of the drop is not too small, the effect of surface tension on the vapor pressure is negligible. At low pressure, where the ideal gas law is valid, the concentrations may be written as

$$c_o' = \frac{p_o'}{RT} \tag{4}$$

$$c_o = \frac{p_o}{RT} \tag{5}$$

Substitution of Equations (4) and (5) into Equation (3) gives

$$c_o' - c_o = c_o\left[\exp\left(\frac{2\sigma M}{rRT\rho}\right) - 1\right] \tag{6}$$

A more important effect on the rate of evaporation is the accumulation of surface impurities, which form a layer or coating, on the surface. As the drop diameter decreases during the evaporation, the thickness of the impurity layer increases. Since the amount of surface impurities in turn is proportional to the surface area of the initial drop, one may write

$$4\pi r^2 d = K_1 \, 4\pi r_o^2 \tag{7}$$

or

$$d = K_1 \frac{r_o^2}{r^2} \tag{8}$$

where we have assumed that the thickness of the impurity layer, *d*, is much smaller than the diameter of the drop; K_1 is a constant.

In the following treatment we assumed that the resistance to diffusion through the impurity layer is proportional to its thickness. We also neglected the effect of curvature. Hence

$$N = K_2 \frac{c_o' - c'}{d}$$

A combination of this with Equation (8) gives

$$N = K_3 \frac{r^2}{r_o^2}(c_o' - c') \tag{9}$$

where K_2 is a constant of proportionality and $K_3 = (K_2/K_1)$. Figure 1 describes this model. The rate of evaporation from the surface can be obtained by integrating the diffusion equation with the boundary conditions, c' at the surface and c_g at infinity. The result is

$$N = \frac{D}{r}(c' - c_g) \tag{10}$$

Although this is of the same form as the Langmuir equation, Equation (1), the actual concentration at the surface has been used. If surface impurities are not present, Equation (10) reduces to Equation (1). The quasisteady state approach has been used in the derivation of Equation (10). The validity of this approach has been checked by Luchak and Langstroth (*12*), who showed that at low diffusion flux the time-variable boundary approach gives almost the same results as the quasisteady state approach. Combination of Equations (6), (9), and (10) gives

$$N = \frac{D}{r}\,\frac{(c_o - c_g) + c_o\left[\exp\left(\frac{2\sigma M}{rRT\rho}\right) - 1\right]}{1 + \frac{K_4 r_o^2}{r^3}} \tag{11}$$

where $K_4 = D/K_3$. Comparison of Equation (11) with the Langmuir equation, Equation (3), shows that the term $K_4 r_o^2/r^3$ represents the effect of surface impurities and that the term $c_o\left[\exp\left(\frac{2\sigma M}{rRT\rho}\right) - 1\right]$ represents the

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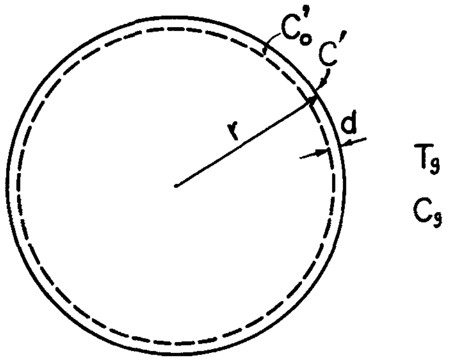

Fig. 1. A model for the evaporation of a drop.

effect of surface tension. However, Equation (11) is not valid at the very end of the evaporation, when the curvature of the impurity layer must be considered and the linear resistance assumption is questionable. If the drop does not become too small, say $r = 10^{-4}$ cm., the term representing the surface tension effect can be dropped; hence

$$N = \frac{D}{r} \frac{c_o - c_g}{1 + \dfrac{K_4 r_o^2}{r^3}} \tag{12}$$

This equation will be used in later sections.

RATE OF EVAPORATION AND LIFETIME OF DROPLETS

A material balance on the drop during evaporation gives

$$N = -\frac{\rho}{M} \frac{dr}{dt} \tag{13}$$

Substituting Equation (13) into Equation (12), we obtain

$$dt = -\frac{\rho}{DM\,(c_o - c_g)} \left(r + \frac{K_4 r_o^2}{r^2} \right) dr \tag{14}$$

Integration of the above expression from $t = 0$, $r = r_o$, to $t = t$, $r = r$ gives

$$t = \frac{\rho}{DM\,(c_o - c_g)} \left[\frac{1}{2} (r_o^2 - r^2) + K_4 r_o^2 \left(\frac{1}{r} - \frac{1}{r_o} \right) \right] \tag{15}$$

In the integration of Equation (14), c_o (or the temperature of the drop) is treated as a constant. The validity of this assumption is based on the experimental results of Johnson (*13*), who measured the temperature of a water drop by suspension of the drop on a thermocouple. If the drop did not become too small, the variation of temperature was about 1°C. Therefore c_o can be considered as a constant during the evaporation. A more detailed discussion about the temperature of the drop will be given in a later section.

The rate of evaporation of a drop under given conditions is shown equivalently by Equation (15), which relates the time and the radius of the drop. Since certain physical properties are difficult to measure, Equation (15) is rewritten in the following form:

$$t = K_5\,(r_o^2 - r^2) + K_6 \left(\frac{1}{r} - \frac{1}{r_o} \right) \tag{16}$$

where

$$K_5 = \frac{\rho}{2DM\,(c_o - c_g)}$$

$$K_6 = \frac{\rho K_4 r_o^2}{DM\,(c_o - c_g)}$$

The parameter K_5 can be estimated from physicochemical data and the operating conditions, whereas parameter K_6 can be evaluated only from experiment. The data of Bradley et al. (5) for the evaporation of a drop of dibutyl phthalate are shown in Figure 2, along with a curve computed from Equation (16). Because of the uncertainty of the diffusion coefficient, both K_5 and K_6 are evaluated from the experimental data. Figure 2 shows that this model correlates very well the experimental data.

Let r_f be the final radius of the drop which contains only nonvolatile impurities. The lifetime, t_f, of a drop of initial radius r_o is then

$$t_f = \frac{\rho}{DM\,(c_o - c_g)} \left[\frac{1}{2} (r_o^2 - r_f^2) + K_4\, r_o^2 \left(\frac{1}{r_f} - \frac{1}{r_o} \right) \right] \tag{17}$$

In general, r_o is much larger than r_f and the final volume of the drop is proportional to the number of surface impurities; that is

$$r_f = K_7\, r_o^{2/3} \tag{18}$$

Equation (17) is then reduced to the following approximate form:

$$\frac{t_f}{r_o^2} = K_8 + K_9\, r_o^{-2/3} \tag{19}$$

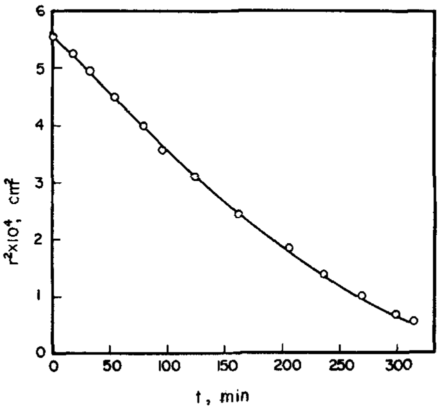

Fig. 2. Rate of evaporation of a drop. o Data of Bradley et al. (5), for the evaporation of dibutyl phthalate at 20°C., 0.309 mm. Hg, —Equation (16) with $K_5 = 4.62 \times 10^5$, $K_6 = 0.82$.

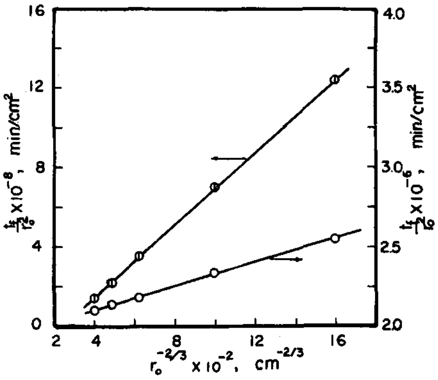

Fig. 3. Lifetime of water droplets; o water, ⦶ water coating with long-chain alcohols. Data of Eisner et al. (6), for the evaporation of water at 20°C., 80° relative humidity.

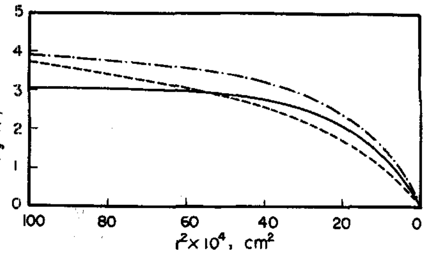

Fig. 4. Temperature of a droplet during evaporation: —Johnson's data (*13*), water, T_g = 23.9°C., 68% relative humidity, – – – Calculated from Equation (22), with $\frac{D \Delta H_v}{k_g}$ = 2.4 × 10^6, °C./g./cc. (--- $K_4 = 0.025$, –·– $K_4 = 0.015$).

where

$$K_8 = \frac{\rho}{2\,DM\,(c_o - c_g)}$$

$$K_9 = \frac{\rho K_4}{K_7\,DM\,(c_o - c_g)}$$

The data of Eisner et al. (*6*) shown in Figure 3, are seen to be fitted by Equation (19).

Figure 3 shows that coating with long-chain alcohol gives a large resistance to diffusion. If droplets are free from surface impurities, the lifetime is proportional to r_o^2 as can be derived from the Langmuir equation. However, Figure 3 shows that even for pure water there is a small resistance at the surface. This is due to the fact that it is very difficult to free any liquid from surface impurities.

It should be recognized that during the final phase of evaporation, Equation (17) violates the assumption of a thin layer of impurity. Nevertheless, the final relationship between time and initial radius [Equation (19)] correlates very well the limited data of Eisner et al. Perhaps the success of Equation (19) can be explained by the fact that Equation (17) is an integrated result and that the time during the final phase of evaporation is short compared with the total evaporation time. A complete analysis of the process during the final phase of evaporation may be worthy of study but is beyond the scope of this communication.

TEMPERATURE OF THE DROP

With the above model the temperature of the droplet can be derived as follows. Since for low diffusion flux, liquid has a much higher thermal conductivity than gas, the temperature of the drop can be assumed to be uniform up to the surface. Integration of the heat conduction equation for the gas phase with temperature T at the surface of the drop and with temperature T_g at infinity gives the rate of heat transfer Q as

$$Q = \frac{k_g}{r}\,(T_g - T) \tag{20}$$

where k_g is the thermal conductivity of the gas phase. Since the sensible heat of liquid is much smaller than the latent heat ΔH_v, sensible heat is neglected. Application of a heat balance during evaporation gives

$$T_g - T = \frac{D\Delta H_v}{k_g\left(1 + \dfrac{k_4 r_o^2}{r^3}\right)}\,(c_o - c_g) \tag{21}$$

where Equation (12) has been used. If surface impurities are absent, Equation (21) becomes

$$T_g - T = \frac{D\Delta H_v}{k_g}\,(c_o - c_g) \tag{22}$$

The above expression shows that $(T_g - T)$ is independent of the radius of the drop. However, Johnson's experiments (*13*) showed that $(T - T_g)$ decreased slightly at the early period of evaporation and decreased rapidly as $r \to 0$. He explained that the phenomenon was due to the introduction of the thermocouple used to suspend and to measure the temperature of the droplet. It is much more complicated if the effect of the thermocouple, as well as of the surface impurities, is considered. Figure 4 compares Equation (21) and Johnson's data. The deviation may be due to the introduction of the thermocouple. Nevertheless, one may conclude that the temperature of the drop is essentially constant except at the end of the evaporation.

DISCUSSION

For low diffusion flux the mechanism of the evaporation of a droplet can be described by this simple model, although when the droplet decreases, the evaporation phenomena are more complicated. The effects of surface impurities have been discussed quantitatively with some reasonable assumptions. Equations from this simple model agree with experimental data in the literature. Hoffman and Gauvin (*14*) studied extensively the evaporation of droplets at high diffusion flux. Evaporation at an intermediate diffusion flux remains an area to be explored.

NOTATION

c_o = concentration of diffusing substance at the drop surface corresponding to p_o, mole/unit volume
c_o' = c_o corrected by surface tension effect, corresponding to p_o'
c' = actual concentration of diffusing substance at the surface, mole/unit volume
c_g = concentration of diffusing substance in surroundings, mole/unit volume
D = diffusion coefficient in gas phase, (length)^2/unit time
d = thickness of surface impurities
ΔH_v = heat of evaporation/mole
$K_1, K_2, \ldots K_9$ = parameters
k_g = thermal conductivity of gas phase
M = molecular weight of diffusing substance
N = rate of evaporation, mole/unit area/unit time
p_o = vapor pressure of diffusing substance at the drop temperature over a flat surface
p_o' = p_o corrected by surface tension effect
Q = rate of heat transfer to the drop/unit area
R = gas constant
r = radius of drop
r_o = initial radius of drop
r_f = final radius of drop
S = surface area of drop
T = absolute temperature of drop
T_g = absolute temperature of surroundings
t = time
t_f = lifetime of drop
ρ = density of drop
σ = surface tension

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