

A method is proposed for determining the degree of evaporation of a drop of solution under conditions where the evaporation is slow and the effect of diffusion within the drop can be neglected. An equation and criterion are derived which determine the evaporation of a drop of solution under these conditions. The range of criterial values corresponding to these conditions was determined experimentally.

As is well known [1], the evaporation of a drop of chemically uniform liquid in stationary air is well described by the equations

$$I = 4\pi R D_a (C_s - C_\infty), \quad (1)$$

$$R = R_0 \sqrt{1 - \frac{2D_a(C_s - C_\infty)\tau}{\rho R_0^2}}, \quad (2)$$

$$\tau_1 = \frac{\rho R_0^2}{2D_a(C_s - C_\infty)}. \quad (3)$$

As applied to a drop of solution (even in the simplest case of an ideal solution of a nonvolatile material), the problem is complicated by the fact that the concentration of saturated solvent vapor at the surface of a drop of solution is less than at the surface of a drop of solvent and decreases in proportion to the reduction of solvent κ in the surface layer of the evaporating drop. What is particularly important in addition is that significant gradients of κ may arise because of the slowness of diffusion in liquids within an evaporating drop of solution so that the value of κ at the surface of a drop may differ considerably from the average value $\bar{\kappa}$. The chief difficulty in constructing a theory for the evaporation of a drop of solution is that an exact solution of the nonstationary problem is complicated and the simplifications which led to Eq. (1) (quasistationary problem) are unacceptable.

However, with slow evaporation of a drop of solution (for example, typical of evaporation of a sea-water drop in air, of evaporation of a drop of pesticide during spraying of agricultural crops, etc.), the solvent concentration κ within a drop may become equalized. We consider an approximate solution of the problem for this limiting case.

Nonstationary evaporation of a drop of solution in stationary air is determined by the equation for solvent diffusion within the drop, by the equation for vapor diffusion outside the drop, by the equations of motion for the phase interface, by the equations of heat transfer, and by the appropriate initial and boundary conditions. By analysis of this system of equations and of the uniqueness condition by the methods of similarity theory, the solution can be represented in the form of a criterial relation containing eight unknown criteria. A large number of experiments would be required for an experimental determination of this relation. In order to reduce the volume of research, we attempt to predict the nature of this relation by means of an approximate solution of the problem.

We assume that vapor diffusion outside the drop is described by Eq. (1), i.e., it corresponds to a quasistationary process, and that the diffusion of solvent within the drop also takes place at concentration gradients corresponding to the quasistationary process,

$$I = 4\pi R D_l \Delta \kappa. \quad (4)$$

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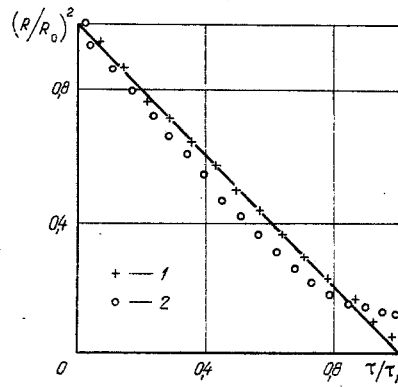


Fig. 1. Dynamics of drop evaporation in stationary air: 1) water drop; 2) drop of 2% aqueous solution of NaCl; solid curve was calculated from Eq. (2).

In order to avoid values of the concentration κ tending to infinity when $r \rightarrow 0$ under quasistationary conditions, we eliminate from consideration a region containing the center of the drop; for example, we consider only the region $R > r > R/2$, which contains 7/8 of the volume of the drop. The solvent concentration difference in this region is

$$\Delta\kappa = \kappa \left(\frac{R}{2} \right) - \kappa(R) = B\bar{\kappa}, \quad (5)$$

where the average concentration (neglecting differences between the densities of solution and solvent) is

$$\bar{\kappa} \approx \rho - \left(\frac{R_0}{R} \right)^3 \kappa'_0. \quad (6)$$

The solvent concentration at the surface of the drop is

$$\kappa(R) \approx \bar{\kappa} - \frac{\Delta\kappa}{2} = \bar{\kappa} \left(1 - \frac{B}{2} \right). \quad (7)$$

We find an expression for the criterion $B = \Delta\kappa/\bar{\kappa}$ characterizing the degree of nonuniformity of solvent concentration within an evaporating drop.

Using Eq. (7), we write Eq. (1) in the form

$$I = 4\pi R D_a \frac{C_s}{\kappa(R)} \left[\bar{\kappa} \left(1 - \frac{B}{2} \right) - \kappa_\infty \right]. \quad (8)$$

Using Eq. (5) and equating Eqs. (4) and (8), we obtain

$$D_a \frac{C_s}{\kappa(R)} \left[\bar{\kappa} \left(1 - \frac{B}{2} \right) - \kappa_\infty \right] = D_l B \bar{\kappa},$$

whence the desired degree of nonuniformity of concentration is

$$B = \frac{\kappa \left(\frac{R}{2} \right) - \kappa(R)}{\bar{\kappa}} = 2 \left(\frac{1 - \frac{\kappa_\infty}{\bar{\kappa}}}{1 + \frac{2\kappa(R)}{C_s} \cdot \frac{D_l}{D_a}} \right)$$

or, using Eq. (6),

$$B = 2 \left\{ \frac{1 - \kappa_\infty \left[\rho - \left(\frac{R_0}{R} \right)^3 \kappa'_0 \right]^{-1}}{1 + \frac{2\kappa(R)}{C_s} \cdot \frac{D_l}{D_a}} \right\}. \quad (9)$$

TABLE 1. Experimental Conditions and Results for Determination of Rate of Evaporation of Drops of Water and of NaCl in Water

No.	Liquid	R_0 , cm	τ_1 sec	Air temperature, t , °C	Wet-bulb temperature, °C	$C_0 \cdot 10^4$, g/cm ³ [2]	$C_\infty \cdot 10^4$, g/cm ³
1	Water	0,0895	2580	17,4	9,4	9,07	4,00
	2% NaCl	0,0900	—	17,4	9,4	9,07	4,00
2	Water	0,0838	2475	17,6	9,6	9,20	4,20
	2% NaCl	0,103	—	17,6	9,6	9,20	4,20
3	Water	0,0940	2550	18,0	10,0	9,40	4,46
	2% NaCl	0,103	—	18,0	10,0	9,40	4,46

When $C_\infty = \kappa_\infty = 0$,

$$B = \frac{2}{1 + \frac{2\kappa(R)}{C_s} \cdot \frac{D_l}{D_a}} \quad (10)$$

For the initial period of evaporation [$\kappa(R) \approx \kappa_0$, $C_s \approx C'_s$, $R \approx R_0$, $(\rho - \kappa'_0) \approx \kappa_0$]

$$B_0 \approx 2 \left(\frac{1 - \frac{C_\infty}{C'_s}}{1 + \frac{2\kappa_0}{C'_s} \cdot \frac{D_l}{D_a}} \right) \quad (11)$$

When $C_\infty = 0$,

$$B_0 \approx \frac{2}{1 + \frac{2\kappa_0}{C'_s} \cdot \frac{D_l}{D_a}} \quad (12)$$

For ideal solutions, the saturated-vapor concentration C_s at the surface of the drop is proportional to the solvent concentration $\kappa(R)$, i.e., $B \approx B_0$ throughout evaporation. [However, one should keep in mind that as the drop of solution evaporates, its surface temperature increases somewhat because of the slowing down of evaporation and when the dissolved material crystallizes the temperature increases because of release of the heat of crystallization. Because of this, the quantity $\kappa(R)/C_s$ does not remain constant but decreases somewhat.]

We consider slow evaporation of a drop of ideal solution taking place at negligibly small gradients of solvent concentration within the drop.

Using the Raoult law, Eq. (1) is written in the form

$$I_l = 4\pi R D_a (N C_s - C_\infty),$$

where the solvent mole fraction N (neglecting differences between the molecular weights of solvent and dissolved material) is

$$N \approx 1 - \frac{\kappa'_0 \left(\frac{R_0}{R} \right)^3}{\rho},$$

i.e.,

$$I_l = 4\pi R D_a \left\{ C_s \left[1 - \frac{\kappa'_0 \left(\frac{R_0}{R} \right)^3}{\rho} \right] - C_\infty \right\} \quad (13)$$

The ratio between the rates of evaporation of a drop of solution and of a drop of solvent is:

$$\frac{I_l}{I} = 1 - \frac{\kappa'_0 \left(\frac{R_0}{R}\right)^3}{\rho \left(1 - \frac{C_\infty}{C_s}\right)}$$

Evaporation would stop when $I_l = 0$, i.e., when

$$\rho - \kappa'_0 \left(\frac{R_0}{R}\right)^3 = \rho \frac{C_\infty}{C_s},$$

so that the minimum radius of a evaporating drop of solution is

$$R_{\min} = R_0 \sqrt[3]{\frac{\kappa'_0}{\rho \left(1 - \frac{C_\infty}{C_s}\right)}} \quad (14)$$

We find a relation which determines the time change in the radius of a drop of solution. From the condition for material balance

$$I_l d\tau = 4\pi R D_a \left\{ C_s \left[1 - \frac{\kappa'_0}{\rho} \left(\frac{R_0}{R}\right)^3 \right] - C_\infty \right\} d\tau = -4\pi R^2 \rho dR$$

or,

$$\frac{D_a}{\rho} d\tau = - \frac{R dR}{C_s \left[1 - \frac{\kappa'_0}{\rho} \left(\frac{R_0}{R}\right)^3 \right] - C_\infty}$$

After integration using the condition $R = R_0$ when $\tau = 0$, we have

$$\tau = \tau_l + \frac{\rho R_{\min}^2}{3D_a(C_s - C_\infty)} \left\{ \frac{1}{2} \ln \frac{(R^2 + RR_{\min} + R_{\min}^2)(R_0 - R_{\min})^2}{(R_0^2 + R_0 R_{\min} + R_{\min}^2)(R - R_{\min})^2} + \right. \\ \left. + \sqrt{3} \left(\operatorname{arctg} \frac{\sqrt{3}}{1 + \frac{2R_{\min}}{R_0}} - \operatorname{arctg} \frac{\sqrt{3}}{1 + \frac{2R_{\min}}{R}} \right) \right\}, \quad (15)$$

where $\tau_l = (R_0^2 - R_{\min}^2)/2(C_s - C_\infty)D_a$ is the time it takes for the radius to change from R_0 to R during evaporation of a drop of solvent. According to Eq. (15), $\tau \rightarrow \infty$ when $R \rightarrow R_{\min}$.

We turn to a comparison of these results with experiment. For this purpose, we use both our own experimental data and the results of others.

In our experiments, a drop of distilled water of roughly spherical shape was suspended at the end of a thin vertical glass rod covered by a thin layer of silicone. Nearby (at a distance of ~ 1 m) a drop of 2% solution of NaCl in distilled water was suspended on the same kind of rod. The initial diameters of both drops were roughly the same. At set time intervals, the diameters of both drops were measured with two microscopes as well as the temperature t and the humidity w of the air in the room; the values of t and w were unchanged during the course of an experiment, which lasted about an hour. Experimental conditions for experiments (1)-(3) are shown in Table 1.

The experimental results are presented in Fig. 1 in the dimensionless coordinates $(R/R_0)^2 = f(\tau/\tau_l)$.

The figure makes it clear that the evaporation of a water drop is well described by Eq. (2); i.e., the relation $(R/R_0)^2 = f(\tau/\tau_l)$ is linear for water. The evaporation of a drop of solution followed Eq. (15) [the differences between the evaporation of drops of water and solution were insignificant down to the value $(R/R_0)^2 \approx 0.125$].

Evaporation of a drop of solution stopped at a value of the radius close to that calculated from Eq. (14).

Thus, our hypothesis was confirmed; with slow evaporation, the solvent concentration gradients within a drop were insignificant and evaporation took place in accordance with Eq. (15), which was derived without consideration of such gradients. According to Eq. (11), $B_0 = 0.0905$ ($C_\infty = 4.2 \cdot 10^{-6}$ g/cm³, $C'_s = 9.2 \cdot 10^{-6}$ g/cm³, $\kappa_0 = 0.98$ g/cm³, $D_a = 0.24$ cm²/sec [2], $D_1 = 1.24 \cdot 10^{-5}$ cm²/sec [3]).

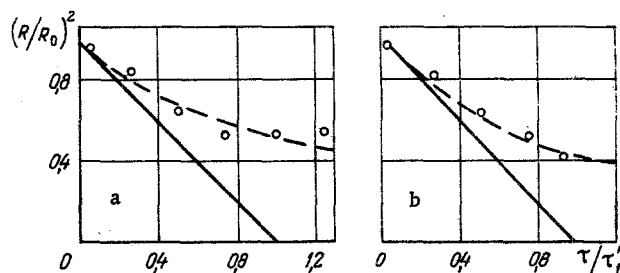


Fig. 2. Dynamics of drop evaporation in stationary air [a) drop of aqueous solution of NH_4NO_3 ; b) drop of aqueous solution of NaCl ; points are experimental data; dashed curve calculated from Eq. (15)].

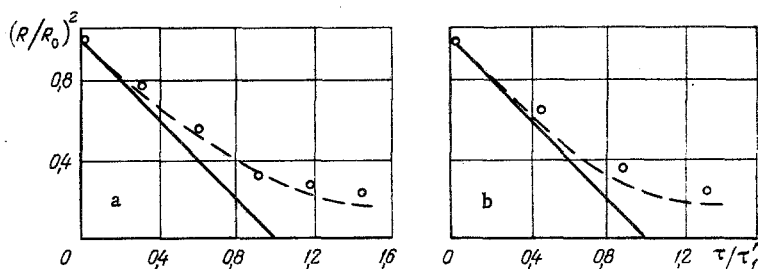


Fig. 3. Dynamics of drop evaporation for an aqueous solution suspended in an air flow [a) $U = 39$ cm/sec; b) $U = 157$ cm/sec; points are experimental data; dashed curve calculated from Eq. (15)].

Data were given in [4] for evaporation of a drop of aqueous solution of NH_4NO_3 . The drop was suspended from the junction of a thermocouple in dry stationary air. The initial drop radius was $R_0 = 0.055$ cm, $C_\infty = 0$, $C'_S = 7.8 \cdot 10^{-6}$ g/cm³, $\kappa_0 = 0.702$ g/cm³, $D_a = 0.245$ cm²/sec. Experimental results and calculations based on Eqs. (2) and (15) are shown in Fig. 2a. The evaporation of a drop of solution took place in accordance with Eq. (15). According to Eq. (12), $B_0 = 0.262$ ($D_l = 0.90 \cdot 10^{-5}$ cm²/sec [3]).

The same paper presented data on the evaporation of a drop of aqueous solution of NaCl ($R_0 = 0.057$ cm, $C_\infty = 0$, $C'_S = 8.2 \cdot 10^{-6}$ g/cm³, $D_a = 0.246$ cm²/sec, $\kappa_0 = 0.805$ g/cm³). The results are shown in Fig. 2b. There is good agreement between the experimental data and the calculations based on Eq. (15). According to Eq. (12), $B_0 = 0.182$ ($D_l = 1.24 \cdot 10^{-5}$ cm²/sec).

Data were presented in [5] for evaporation of a drop of aqueous solution of Na_2SO_4 . The drop was suspended at the end of a rod fastened to the elastic shaft of a microbalance in a flow of dry air (air velocities relative to the drop were 39 and 157 cm/sec). The air temperature was 34.4°C. The change in drop weight with time was determined. The initial drop radius was $R_0 = 0.078$ cm, $C_\infty = 0$, $C'_S = 1.45 \cdot 10^{-5}$ g/cm³, $\kappa_0 = 0.92$ g/cm³, $D_a = 0.26$ cm²/sec. In calculations using Eqs. (2) and (15), the quantity D_a was multiplied by a "wind factor" [1] $(1 + 0.3 \text{Re}^{1/2} \text{Sc}^{1/3})$, where $\text{Re} = 2UR/\nu$ and $\text{Sc} = \nu/D_a$, to allow for acceleration of evaporation resulting from air motion relative to the drop. The results are shown in Fig. 3a ($U = 39$ cm/sec) and Fig. 3b ($U = 157$ cm/sec). The agreement between experimental data and calculations based on Eq. (15) is good. According to Eq. (12), $B_0 = 0.77$ when $U = 39$ cm/sec and $B_0 = 0.97$ when $U = 157$ cm/sec [$D_l = 7.64 \cdot 10^{-6}$ cm²/sec [3], $D_a = 0.261 (1 + 0.3 \text{Re}^{1/2} \text{Sc}^{1/3})$].

On the whole, one can conclude from comparison of experimental data and calculations based in Eq. (15) that for rough calculations of the evaporation of a drop of nonvolatible material in water one need not take into consideration solvent concentration gradients within a drop and that Eq. (15) can be used in the region $B_0 \leq 0.26$ for a drop which is stationary relative to air and in the region $B_0 \leq 1$ for a drop moving at a moderate velocity ($\text{Re} \leq 150$) relative to air.*

*Motion of a drop relative to air produces motion of the solution within the drop, facilitating equalization of concentration.

NOTATION

I	is the rate of evaporation of drop of solvent;
I_l	is the rate of evaporation of a drop of solution;
R	is the drop radius;
R_0	is the initial drop radius;
R_{\min}	is the minimum radius of evaporating drop of solution;
D_a	is the vapor diffusion coefficient in air;
D_l	is the solvent diffusion coefficient within drop;
C_s	is the concentration of saturated solvent vapor at the temperature of the surface of the evaporating drop of solution;
C'_s	is the concentration of saturated solvent vapor at the temperature of the surface of the drop of solution at the beginning of evaporation;
C_∞	is the concentration of solvent vapor far from drop;
ρ	is the solvent density;
r	is the distance from center of drop;
κ_0	is the initial solvent concentration in the drop;
$\bar{\kappa}$	is the average solvent concentration in drop;
$\Delta\kappa$	is the solvent concentration difference within drop;
κ_∞	$=C_\infty \kappa(R)/C_s$
κ'_0	is the initial concentration of dissolved nonvolatile material;
B	is the degree of nonuniformity of solvent concentration in drop;
B_0	is the initial degree of nonuniformity of concentration;
N	is the mole fraction of solvent;
τ	is the time ;
τ_1	is the time for complete evaporation of drop;
τ_l	is the time for change of radius from R_0 to R during evaporation of a drop of solvent;
Re	is the Reynolds number;
Sc	is the Schmidt number;
U	is the air velocity;
ν	is the kinematic viscosity of air;
t	is the temperature;
w	is the relative humidity of air.

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