THE EVAPORATION OF A LIQUID FROM THE FLAT SURFACE OF A SOLUTION

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Inzhenerno-Fizicheskii Zhurnal, Vol. 11, No. 5, pp. 595–600, 1966

UDC 536.823.1

This paper considers the self-similar problem of diffusive evaporation of a liquid from the flat surface of a solution of great depth with due regard to the temperature distribution. An exact solution is given.

The question of the evaporation of a liquid from the surface of a solution is of interest for chemistry and chemical technology, as well as for geophysics. In comparison with the evaporation of a pure liquid the evaporation from the surface of a solution has several significant special features. First, the saturated vapor concentration on the surface of the solution [1] depends not only on the temperature, as in the case of a pure liquid, but also on the concentration of the substance. Second, if the dissolved substance is nonvolatile the vapor-solution phase-transition boundary is impenetrable for it, and as the boundary advances, the substance must move deeper into the solution. Since the vapor concentration on this boundary depends on the concentration of dissolved substance, the transfer of mass of the substance in the solution affects the evaporation process in turn.

Even in the purely diffusive stage the process of evaporation is nonlinear, generally speaking. In actual conditions this process is very often accompanied by convective effects, which make its mathematical description even more complicated. In view of this, it is of great importance to select reasonable limiting cases which can be solved analytically.

In this paper we will consider the limiting case of purely diffusive evaporation into a gaseous medium from the surface of a solution of great ("infinitely great") depth. The concentrations of vapor and dissolved substance and the temperatures of the vapor-gas mixture and solution of the initial instant are assumed constant. The evaporation calculated by this method is obviously the minimum possible for the given conditions.

Let the vapor-air mixture at the initial instant occupy the upper half of the space and the solution the lower half, and let the axis 0x be directed into the solution. We will assume that the dissolved substance is nonvolatile. Then the vapor-solution phase-transition boundary is impenetrable for it, and as the boundary advances, the dissolved substance must diffuse into the depth of the solution. Hence, the considered process is described by a system of equations of diffusion of vapor and substance in the solution and heat-conduction equations (for the vapor-air mixture and solution)

$$\frac{\partial q}{\partial t} = D\,\frac{\partial^2 q}{\partial x^2},\quad \frac{\partial T}{\partial t} = \varkappa\,\frac{\partial^2 T}{\partial x^2},\quad -\infty \leqslant x \leqslant l(t); \tag{1}$$

$$\frac{\partial c}{\partial t} = D_*\frac{\partial^2 c}{\partial x^2},\quad \frac{\partial \theta}{\partial t} = \varkappa_*\,\frac{\partial^2 \theta}{\partial x^2},\quad l(t) \leqslant x \leqslant \infty. \tag{2}$$

The required solutions of these equations must satisfy uniform initial conditions and conditions at infinity

$$q(x,\ 0) = q(-\infty,\ t) = q_0,$$
$$T(x,\ 0) = T(-\infty,\ t) = T_0,$$
$$c(x,\ 0) = c(\infty,\ t) = c_0,$$
$$\theta(x,\ 0) = \theta(\infty,\ t) = \theta_0,\quad l(0) = 0, \tag{3}$$

and also a number of conditions on the moving evaporation boundary $l(t)$.

First, on this boundary the condition of conservation of mass of the solvent, the calorimetric relationship, and the condition of equality of the phase temperatures (see [2], for instance) must be satisfied:

$$\frac{dl}{dt} = \frac{D}{\rho}\,\frac{\partial q}{\partial x}\bigg|_{x=l},$$
$$LD\,\frac{\partial q}{\partial x}\bigg|_{x=l} = \lambda_*\,\frac{\partial \theta}{\partial x}\bigg|_{x=l} - \lambda\,\frac{\partial T}{\partial x}\bigg|_{x=l},$$
$$T(l,\ t) = \theta(l,\ t) = T_s. \tag{4}$$

Second, on the boundary $l(t)$ the vapor concentration must be saturated. For a solution the saturated vapor concentration depends not only on the temperature, as in the case of a pure liquid, but also on the concentration of dissolved substance [1]. At not very high concentrations of dissolved substance this dependence is expressed by the Raoult law [1]:

$$q(l,\ t) = q_s(T_s)\,[1 - kc(l,\ t)]. \tag{5}$$

The dependence of the concentration of saturated vapor of the solvent on the temperature $q_s(T)$ will be approximated by the Clapeyron-Clausius formula [1, 2]:

$$q_s(T) = q_s(T_0)\,\frac{T_0}{T}\,\exp\left[G\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]. \tag{6}$$

In addition to the relationships (4) and (5) on the phase-transition surface one other specific condition must be satisfied in the case of a solution—the condition of balance of mass of the dissolved substance. It can be obtained, for example, in the following way. We consider the change in mass of the dissolved substance m (per unit area) enclosed between sections $x = x_0 = \text{const}$ and $x = l(t)$ $[x_0 > l(t)]$. Since the phase-transition boundary is impenetrable for the dissolved substance, the change in its mass must be due to entry of dissolved substance through the section $x = x_0$:

$$\frac{dm}{dt} = D_*\,\frac{\partial c}{\partial x}\bigg|_{x=x_0}.$$

On the other hand, by using the first equation of (2), we find

$$\frac{dm}{dt}=\frac{d}{dt}\int\limits_{l(t)}^{x_0} c(x,\ t)\,dx=\int\limits_{l(t)}^{x_0}\frac{\partial c}{\partial t}\,dx-c(l,\ t)\,\frac{dl}{dt}=$$

$$=D_*\left.\frac{\partial c}{\partial x}\right|_{x=x_0}-D_*\left.\frac{\partial c}{\partial x}\right|_{x=l}-c(l,\ t)\,\frac{dl}{dt}.$$

If we equate these relationships we obtain the following condition of balance of mass of the dissolved substance:

$$\frac{dl}{dt}=-\frac{D_*}{c(l,\ t)}\left.\frac{\partial c}{\partial x}\right|_{x=l(t)} \tag{7}$$

It is obvious that the above equations and boundary conditions also describe the condensation of liquid on the surface of a solution. This process occurs when $q(l,t) < q_0$.

We find the solution of the posed problem. On dimensional analysis of the characteristic parameters of the problem in accordance with [3], we come to the conclusion that it is self-similar. Its solution has the form

$$\begin{gathered}q(x,\ t)=A_1+B_1\operatorname{erfc}(-x/2\sqrt{Dt}),\\ c(x,\ t)=A_2+B_2\operatorname{erfc}(x/2\sqrt{D_*t}),\\ T(x,\ t)=F_1+E_1\operatorname{erfc}(-x/2\sqrt{\varkappa t}),\\ \theta(x,\ t)=F_2+E_2\operatorname{erfc}(x/2\sqrt{\varkappa_* t}),\\ l(t)=2\sqrt{\alpha t}.\end{gathered} \tag{8}$$

The constant coefficients in (8) are found from conditions (3), (4), and (7):

$$A_1=q_0,\quad A_2=c_0,\quad B_1=\rho\sqrt{\pi\alpha/D}\exp(\alpha/D),$$

$$B_2=c_0\sqrt{\pi\alpha/D_*}/[\exp(-\alpha/D_*)-$$

$$-\sqrt{\pi\alpha/D_*}\operatorname{erfc}(\sqrt{\alpha/D_*})],\ \ F_1=T_0,$$

$$E_1=[(\theta_0-T_0)+$$

$$+E_2\operatorname{erfc}(\sqrt{\alpha/\varkappa_*})]/[1+\operatorname{erf}(\sqrt{\alpha/\varkappa})],\quad F_2=\theta_0,$$

$$E_2=-\left\{\rho\sqrt{\pi\alpha}\,L\left[1+\operatorname{erf}\left(\sqrt{\frac{\alpha}{\varkappa}}\right)\right]+\right.$$

$$\left.+\lambda\varkappa^{-\frac{1}{2}}(\theta_0-T_0)\exp\left(-\frac{\alpha}{\varkappa}\right)\right\}\times$$

$$\times\left\{\lambda_*\varkappa_*^{-\frac{1}{2}}\exp\left(-\frac{\alpha}{\varkappa_*}\right)\left[1+\operatorname{erf}\left(\sqrt{\frac{\alpha}{\varkappa}}\right)\right]+\right.$$

$$\left.+\lambda\varkappa^{-\frac{1}{2}}\exp\left(-\frac{\alpha}{\varkappa}\right)\operatorname{erfc}\left(\sqrt{\frac{\alpha}{\varkappa_*}}\right)\right\}^{-1}. \tag{9}$$

To obtain the equation to determine the parameter α we must use formula (5) in conjunction with (6) and substitute in it the expressions for $c_s = c(l,t)$, $q_s = q(l,t)$, $T_s = T(l,t)$ from (8) and (9). It has the form

$$q_0+\rho\sqrt{\frac{\pi\alpha}{D}}\exp\left(\frac{\alpha}{D}\right)\left[1+\operatorname{erf}\left(\sqrt{\frac{\alpha}{D}}\right)\right]=$$

$$=q_s(T_s)\left\{1-kc_0-\right.$$

$$-kc_0\sqrt{\frac{\pi\alpha}{D_*}}\operatorname{erfc}\left(\sqrt{\frac{\alpha}{D_*}}\right)\Big/\left[\exp\left(-\frac{\alpha}{D_*}\right)-\right.$$

$$\left.\left.-\sqrt{\frac{\pi\alpha}{D_*}}\operatorname{erfc}\left(\sqrt{\frac{\alpha}{D_*}}\right)\right]\right\}. \tag{10}$$

Here the relationship $q_s(T_s)$ is given by formula (6), and T_s is expressed in the following way:

$$T_s=\theta_0-\left[\left\{\rho L\sqrt{\pi\alpha}\left[1+\operatorname{erf}\left(\sqrt{\frac{\alpha}{\varkappa}}\right)\right]+\right.\right.$$

$$\left.+\lambda\varkappa^{-\frac{1}{2}}(\theta_0-T_0)\exp\left(-\frac{\alpha}{\varkappa}\right)\right\}\operatorname{erfc}\left.\left(\sqrt{\frac{\alpha}{\varkappa_*}}\right)\right]\times$$

$$\times\left\{\lambda_*\varkappa_*^{-\frac{1}{2}}\exp\left(-\frac{\alpha}{\varkappa_*}\right)\left[1+\operatorname{erf}\left(\sqrt{\frac{\alpha}{\varkappa}}\right)\right]+\right.$$

$$\left.+\lambda\varkappa^{-\frac{1}{2}}\exp\left(-\frac{\alpha}{\varkappa}\right)\operatorname{erfc}\left(\sqrt{\frac{\alpha}{\varkappa_*}}\right)\right\}^{-1}. \tag{11}$$

We note that the considered problem retains its self-similarity when the dependence of the saturated vapor concentration on the temperature and concentration on the phase-transition boundary has a more general form

$$q(l,\ t)=f(T_s,\ c_s), \tag{12}$$

where $f(T_s, c_s)$ is an arbitrary function of T_s and c_s.

As formulas (8) show, the values of $c_s = c(l,t)$, $q(l,t)$, $T_s = T(l,t) = \theta(l,t)$ for the considered process are constant. In the case of evaporation $c(l,t) > c_0$, $q(l,t) < q_s(T_s)(1 - kc_0)$ and in the case of condensation the inequalities are reversed.

We will now consider some special cases following from the previously obtained general relationships.

Let $\theta_0 = T_0$ and the temperature of the evaporation (condensation) surface be kept constant by compensation of the heat absorbed (released) on this surface. Then $F_1 = F_2 = T_0$, $E_1 = E_2 = 0$, and the equation for the determination of α becomes

$$y\left[\exp\left(\frac{y^2}{\pi}\right)\left[1+\operatorname{erf}\left(\frac{y}{\sqrt{\pi}}\right)\right]+q_skc_0\times\right.$$

$$\times\sqrt{\frac{D}{D_*}}\operatorname{erfc}\left(\frac{y}{\sqrt{\pi}}\sqrt{\frac{D}{D_*}}\right)\Big/\left\{\rho\left[\exp\left(-\frac{D}{D_*}\,\frac{y^2}{\pi}\right)-\right.\right.$$

$$\left.\left.\left.-\sqrt{\frac{D}{D_*}}\,y\operatorname{erfc}\left(\sqrt{\frac{D}{\pi D_*}}\,y\right)\right]\right\}\right]=b, \tag{13}$$

where

$$y=\sqrt{\frac{\pi\alpha}{D}};\quad b=\frac{q_s(T_0)(1-kc_0)-q_0}{\rho}.$$

We recall that in the case of evaporation of a pure liquid formula (13) reduces to

$$y_*\exp(y_*^2/\pi)[1+\operatorname{erf}(y_*/\sqrt{\pi})]=b_*,$$

and

$$b_*=[q_s(T_0)-q_0]/\rho,\quad y_*=\sqrt{\pi\alpha_*/D}. \tag{13'}$$

We will now consider another case where $\theta_0 = T_0$, and at T_0 the solvent is fairly involatile. Then it is clear from physical considerations that the temperature of the interface $T(l,t) = T_s$ will not differ greatly from T_0. Hence, the expression for $q_s(T_s)$ can be expanded in a series of powers of $T_s - T_0$ and the first terms of the expansion taken as

$$q_s(T_s) = q_s(T_0) + \gamma(T_s - T_0). \qquad (14)$$

In this case q, c, T, and θ can be found without resorting to the solution of the general equation for α (10), if we use the method of successive approximations. In the zero approximation we assume that the interface is stationary. Then, using (3)–(5) and (12), we obtain

$$q(x, t) = q_0 + \rho h \operatorname{erfc}\left(-\frac{x}{2\sqrt{Dt}}\right),$$

$$T(x, t) = T_0 - \frac{\rho L h \sqrt{D\varkappa\varkappa_*}}{\lambda\sqrt{\varkappa_*} + \lambda_*\sqrt{\varkappa}} \operatorname{erfc}\left(-\frac{x}{2\sqrt{Dt}}\right),$$

$$\theta(x, t) = T_0 - \frac{\rho L h \sqrt{D\varkappa\varkappa_*}}{\lambda\sqrt{\varkappa_*} + \lambda_*\sqrt{\varkappa}} \operatorname{erfc}\left(\frac{x}{2\sqrt{\varkappa_* t}}\right),$$

$$h = \frac{(\lambda\sqrt{\varkappa_*} + \lambda_*\sqrt{\varkappa})\, b}{\lambda\sqrt{\varkappa_*} + \lambda_*\sqrt{\varkappa} + \gamma L\sqrt{D\varkappa\varkappa_*}\,(1 - kc_0)}. \qquad (15)$$

Substituting in the first condition (4) the expression for q from (15) we have in the first approximation

$$\sqrt{\pi\alpha/D} = h. \qquad (16)$$

Hence, for c(x, t) and c(l, t) we obtain in the same approximation

$$c(x, t) \approx c_0\,[1 + \sqrt{D/D_*}\, h \operatorname{erfc}(x/2\sqrt{Dt})],$$

$$c(l, t) \approx c_0\,[1 + \sqrt{D/D_*}\,h]. \qquad (17)$$

Expressions (16) and (17) are obviously applicable in the case where the condition $\sqrt{D/D_*}h \ll 1$ is satisfied.

Since for the diffusion of vapor in air $D \approx 10^{-1}$ cm^2/sec and for a substance dissolved in a liquid $D_* \approx 10^{-5}$ cm^2/sec, then $\sqrt{D/D_*} \approx 10^2$, and if the expressions are to be applicable h must be $\ll 10^{-2}$.

In the case of evaporation of a pure liquid the condition of applicability of the linear formula of the form (16) is the satisfaction of a much stricter inequality $h|_{c_0=0} \ll 1$. The value of h~ b and when $q_s \gg q_0$, $b \approx (1 - kc_0)q_s/\rho$.

Thus, in the case of evaporation of a liquid from the surface of a solution the nonlinearity of the process is manifested in the much smaller values of q_s/ρ than in the case of evaporation of a pure liquid. This is illustrated by the dependences of y and y_* on $b_* = q_s/\rho$, shown in the table. These dependences were obtained for the case of isothermic evaporation [from formulas (13) and (13')]. It was assumed in this case that $q_0 = 0$, and the parameter kc_0 in formula (13) is 0.1.

Dependence of y and y_* on b_*, Calculated from Eqs. (13) and (13') with $q_0 = 0$, $kc_0 = 0.1$

$b_* = q_s/\rho$	y_*	y
10^{-3}	10^{-3}	$0.9\cdot10^{-3}$
$2\cdot10^{-2}$	$2\cdot10^{-2}$	$1.4\cdot10^{-2}$
$3\cdot10^{-2}$	$3\cdot10^{-2}$	$1.7\cdot10^{-2}$
$4\cdot10^{-2}$	$3.9\cdot10^{-2}$	$1.9\cdot10^{-2}$
$5\cdot10^{-2}$	$4.9\cdot10^{-2}$	$2.0\cdot10^{-2}$

NOTATION

q(x, t) is the vapor concentration; c(x, t) is the concentration of dissolved substance (mass/volume); T(x, t), θ(x, t) is the temperatures of vapor-gas mixture and solution; D is the diffusion coefficient in vapor-gas mixture; D_* is the diffusion coefficient in liquid; x, x_* are the thermal diffusivities in vapor-gas medium and liquid; λ, λ_* are the thermal conductivities in vapor-gas medium and liquid; ρ is the density of liquid solvent; L is the specific heat of evaporation of liquid; $x = l(t)$ is the coordinate of evaporation (condensation) boundary; $q_s(T)$ is the concentration of saturated vapor of solvent at temperature T; q_0, c_0 is the concentration of vapor and dissolved substance at infinity; T_0, θ_0 are the temperatures of vapor-gas medium and solution at infinity; M_s and M_d are the molecular weights of solvent and dissolved substance; M is the molecular weight of solvent and dissolved substance; M is the molecular weight of vapor; R is the gas constant; $K = M_s/\rho M_d$; $G = LM/R$.

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23 May 1966

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