DIFFUSION AND THERMAL RELAXATION AT THE PLANE SURFACE OF AN EVAPORATING LIQUID

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Nonstationary evaporation and diffusion of vapor is considered in conjunction with the associated heat conduction processes. An exact solution of the problem for a plane evaporation surface is obtained with allowance for temperature and concentration discontinuities.

The successful solution of a number of practical problems requires a combined theoretical treatment of the diffusion and thermal processes associated with the evaporation of a liquid in a gaseous medium. It is usually assumed that all these processes are quasi-stationary, and their relaxation is considered separately [1, 2]. This assumption often leads to gross errors: for instance, the relationships characterizing evaporation turn out to be independent of the thermophysical characteristics of the liquid, a situation which is unacceptable from the physical viewpoint. An attempt to consider the problem in general form for a drop was made in [3, 4]. Using the Duhamel transformation, the authors managed to reduce the problem of determining the temperature at the surface of the drop to the solution of a nonlinear integral equation. In [3, 4] this equation was linearized and an approximate solution was obtained for the particular case of small undersaturations.

The main difficulty is due to the complex relationship between the parameters of the problem and the temperature. Yet in many technical applications most of these parameters can be regarded as constant over a fairly wide temperature range. This assumption was made, in particular, in [3, 4] and is justified if the liquid is not volatile in the temperature range in question.

In this paper attention is concentrated on fundamentals and, hence, it is sufficient to examine only the very simple case of evaporation from a plane surface, a case which is, of course, of independent interest. The extension of the results to more complex cases will be considered later.

We will consider the one-dimensional problem, assuming for simplicity that the liquid is infinitely deep and no restrictions are imposed on the upward diffusion of its vapor. The vapor concentration $q(t, x)$ and the temperatures of the liquid $u_1(t, x)$ $(x \leq 0)$ and vapor-gas medium $u_{2(t,\ x)}$ $(x > 0)$ satisfy the equations

$$\frac{\partial q}{\partial t} = D\ \frac{\partial^2 q}{\partial x^2},\quad \frac{\partial u_i}{\partial t} = a_i^2\ \frac{\partial^2 u_i}{\partial x^2}\quad (i = 1,\ 2). \tag{1}$$

In accordance with our assumptions, we take

$$\lim_{x\to-\infty} u_1 = T_0,\quad \lim_{x\to\infty} u_2 = T_\infty,\quad \lim_{x\to\infty} q = q_\infty. \tag{2}$$

We write the initial conditions in the form

$$q_{(0,x)} = q_\infty,\quad u_{1\,(0,x)} = T_0,\quad u_{2(0,x)} = T_\infty. \tag{3}$$

It is usual to assume continuity of temperature and equality of $q_{(t,\ x)}$ and the saturated vapor concentration $q_{s(t)}$ at the evaporation surface. This obviously leaves out of account the surface layer in which $u_{2(t,\ x)}$ and $q_{(t,\ x)}$ undergo an abrupt change not predicted by Eqs. (1) [1, 5, 6]. The existence of this layer is due to the face that in the immediate vicinity of the liquid surface heat and mass transfer occur by molecular-kinetic mechanisms, lying outside the range of the macroprocesses for which Eqs. (1), averaged over a large number of particles, are valid. The presence of such a layer is of particular significance during the initial instants, when, roughly speaking, the escape of vapor molecules into the gaseous phase is similar to evaporation into a vacuum, and the diffusion processes proper play a secondary role. Hence, it is obvious a priori that the relationships obtained on the basis of the above conditions can be valid, at best, only for the steady phase and are unsuitable for the investigation of the unsteady state, particularly for the investigation of relaxation.

The rate of evaporation into a vacuum from unit surface of a liquid can be expressed in the form $\nu\alpha q_{s(t)}$, and the rate of back condensation in the form $\nu\alpha q_{(t,\ \Delta)}$ [1]. Equating the difference of these values to the diffusion flow of vapor and neglecting the thickness Δ of the layer, for $q_{(t,\,x)}$ we obtain

$$q_{(t,0)}-\frac{D}{\nu\alpha}\left.\frac{\partial q}{\partial x}\right|_{x=0}=q_{s(t)}. \tag{4}$$

In exactly the same way, taking into account the temperature discontinuity, we have

$$u_{2(t,0)}-\frac{\lambda_2}{\nu\delta}\left.\frac{\partial u_2}{\partial x}\right|_{x=0}=u_{1(t,0)}. \tag{5}$$

Furthermore, to the system of boundary conditions we add the condition of heat balance at a free surface

$$LD\left.\frac{\partial q}{\partial x}\right|_{x=0}=\lambda_1\left.\frac{\partial u_1}{\partial x}\right|_{x=0}-\lambda_2\left.\frac{\partial u_2}{\partial x}\right|_{x=0}. \tag{6}$$

The quantity $q_{s(t)}$ in (4) is a function of the temperature $T_{s(t)}$ at the evaporation surface. The theoretical form of this function is determined from the Clapeyron-Clausius equation, although for practical applications numerous semiempirical formulas for q_s have been proposed. These still continue to appear [7, 8] and sometimes differ significantly from the theoretical formulas. For the sake of generality, we propose to represent q_s in the form of a Taylor expansion correct to the first power of the difference $T_{s(t)}-T_0$,

$$q_{s(t)}=q_0+\beta\left[T_{s(t)}-T_0\right], \tag{7}$$

where q_0 represents the saturated vapor concentration at temperature T_0. For the majority of important practical problems this is quite adequate. The method of calculation for cases where the error of Eq. (7) is high will be considered below.

Applying the Laplace transformation to Eqs. (1) and solving the transformed equations for the above conditions, after simple calculations we obtain for the transforms of the required functions

$$\begin{gathered}\bar{u}_1=\frac{d\sqrt{p}+e}{p\left(p+2b\sqrt{p}+c\right)},\ \bar{u}_2=\left(\frac{T_0-T_\infty}{p}+\bar{u}_1\right)\left(1+\frac{\lambda_2}{\nu\delta\,a_2}\sqrt{p}\right)^{-1},\\ \bar{q}=\left(\frac{q_0-q_\infty}{p}+\beta\bar{u}_1\right)\left(1+\frac{\sqrt{D}}{\nu\alpha}\sqrt{p}\right)^{-1},\end{gathered} \tag{8}$$

where

$$\begin{gathered}b=\frac{a_1a_2\nu\alpha\delta}{2\sqrt{D}\lambda_1\lambda_2}\left[\frac{\lambda_1\lambda_2}{\delta\,a_1a_2}+\frac{\sqrt{D}}{\alpha}\left(\frac{\lambda_1}{a_1}+\frac{\lambda_2}{a_2}\right)+\frac{\beta L\sqrt{D}\lambda_2}{\delta\,a_2}\right],\\ c=\frac{a_1a_2\nu\alpha\delta}{\sqrt{D}\lambda_1\lambda_2}\left[\frac{\lambda_1}{a_1}+\frac{\lambda_2}{a_2}+\beta L\sqrt{D}\right],\\ d=-\frac{a_1\nu\alpha\delta}{\lambda_1}\left[\frac{L}{\delta}\left(q_0-q_\infty\right)+\frac{1}{\alpha}\left(T_0-T_\infty\right)\right],\\ e=-\frac{a_1a_2\nu^2\alpha\delta}{\sqrt{D}\lambda_1\lambda_2}\left[L\sqrt{D}\left(q_0-q_\infty\right)+\frac{\lambda_2}{a_2}\left(T_0-T_\infty\right)\right].\end{gathered} \tag{9}$$

We calculate the originals of expressions (8). For definiteness we assume that the equation $p^2+2bp+c=0$ has only real negative roots σ_1 and σ_2. The treatment in other cases does not differ fundamentally from that given below. Moreover, using (9), it is easy to show that other cases are hardly ever realized. Reducing the denominators of (8) to their simplest factors and going over to the originals, we finally obtain

$$\begin{gathered}u_{1(t,x)}=T_0+k_1\operatorname{erfc}\left(-\frac{x}{2a_1\sqrt{t}}\right)+k_2\frac{1}{\sqrt{\pi t}}\exp\left(-\frac{x^2}{4a_1^2t}\right)+\\ +k_3\left\{\frac{1}{\sqrt{\pi t}}\exp\left(-\frac{x^2}{4a_1^2t}\right)+\sigma_1\exp\left(\sigma_1^2t-\sigma_1\frac{x}{a_1}\right)\times\right.\end{gathered}$$

$$\times \operatorname{erfc}\left(-\frac{x}{2a_1\sqrt{t}}-\sigma_1\sqrt{t}\right)\Bigg\} + k_4\left\{\frac{1}{\sqrt{\pi t}}\exp\left(-\frac{x^2}{4a_1^2 t}\right)+\right.$$
$$\left.+\sigma_2\exp\left(\sigma_2^2 t-\sigma_2\frac{x}{a_1}\right)\operatorname{erfc}\left(-\frac{x}{2a_1\sqrt{t}}-\sigma_2\sqrt{t}\right)\right\}. \tag{10}$$

$$u_{2(t,x)} = T_\infty + (T_0 - T_\infty + k_1)\operatorname{erfc}\left(\frac{x}{2a_2\sqrt{t}}\right)+$$
$$+\left[\frac{\nu\delta a_2}{\lambda_2}\left(k_2+\frac{k_3}{1+\lambda_2\sigma_1/\nu\delta a_2}+\frac{k_4}{1+\lambda_2\sigma_2/\nu\delta a_2}\right)-\right.$$
$$\left.-(T_0+k_1-T_\infty)\right]\exp\left(\frac{\nu\delta x}{\lambda_2}+\frac{\nu^2\delta^2 a_2^2}{\lambda_2^2}t\right)\times$$
$$\times\operatorname{erfc}\left(\frac{x}{2a_2\sqrt{t}}+\frac{\nu\delta a_2}{\lambda_2}\sqrt{t}\right)+\frac{k_3\sigma_1}{1+\lambda_2\sigma_1/\nu\delta a_2}\times \tag{11}$$
$$\times\exp\left(-\frac{\sigma_1}{a_2}x+\sigma_1^2 t\right)\operatorname{erfc}\left(\frac{x}{2a_2\sqrt{t}}-\sigma_1\sqrt{t}\right)+$$
$$+\frac{k_4\sigma_2}{1+\lambda_2\sigma_2/\nu\delta a_2}\exp\left(-\frac{\sigma_2}{a_2}x+\sigma_2^2 t\right)\operatorname{erfc}\left(\frac{x}{2a_2\sqrt{t}}-\sigma_2\sqrt{t}\right),$$

$$q_{(t,x)} = q_\infty + (q_0 - q_\infty + \beta k_1)\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)+$$
$$+\left[\frac{\nu\alpha\beta}{D}\left(k_2+\frac{k_3}{1+D\sigma_1/\nu\alpha}+\frac{k_4}{1+D\sigma_2/\nu\alpha}\right)-\right.$$
$$\left.-(q_0-q_\infty+\beta k_1)\right]\exp\left(\frac{\nu\alpha x}{\sqrt{D}}+\frac{\nu^2\alpha^2}{D^2}t\right)\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}+\frac{\nu\alpha}{D}\sqrt{t}\right)+$$
$$+\frac{\beta k_3\sigma_1}{1+D\sigma_1/\nu\alpha}\exp(-\sigma_1 x+\sigma_1^2 t)\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}-\sigma_1\sqrt{t}\right)+ \tag{12}$$
$$+\frac{\beta k_4\sigma_2}{1+D\sigma_2/\nu\alpha}\exp(-\sigma_2 x+\sigma_2^2 t)\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}-\sigma_2\sqrt{t}\right);$$
$$k_1=\frac{e}{c},\quad k_2=\frac{d}{c}-\frac{2eb}{c^2},\quad k_3=-\frac{d}{c}+\frac{2eb}{c^2}-\frac{e}{\sigma_2(\sigma_1-\sigma_2)},$$
$$k_4=-\frac{d}{c}+\frac{2eb}{c^2}-\frac{e}{\sigma_1(\sigma_2-\sigma_1)}.$$

For the temperature at the evaporation surface we have

$$T_{s(t)} = T_0 + k_1 + (k_2+k_3+k_4)\frac{1}{\sqrt{\pi t}} + \sigma_1 k_3\exp(\sigma_1^2 t)\operatorname{erfc}(-\sigma_1\sqrt{t})+$$
$$+\sigma_2 k_4\exp(\sigma_2^2 t)\operatorname{erfc}(-\sigma_2\sqrt{t}), \tag{13}$$

or when $t \gg \frac{1}{\sigma_1^2}$, $t \gg \frac{1}{\sigma_2^2}$, correct to $\frac{1}{\sqrt{t}}$:

$$T_{s(t)} \simeq T_0 + k_1 + \frac{k_2}{\sqrt{\pi t}} \xrightarrow[t\to\infty]{} T_0 + k_1. \tag{14}$$

It is easy to see that when the temperature and concentration discontinuities are neglected (α, δ → ∞) the expressions for the unknowns have the form

$$u_{1(t,x)} = T_0 + k_1 \operatorname{erfc}\left(-\frac{x}{2a_1\sqrt{t}}\right),$$

$$u_{2(t,x)} = T_\infty + (T_0 - T_\infty + k_1)\operatorname{erfc}\left(\frac{x}{2a_2\sqrt{t}}\right), \tag{15}$$

$$q = q_\infty + (q_0 - q_\infty + \beta k_1)\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right), \quad T_{s(t)} = T_0 + k_1.$$

A comparison of formulas (10)-(14) and (15) shows that a consideration of these discontinuities is absolutely essential in the analysis of relaxation processes and nonstationary evaporation in general. Otherwise many important features of the effects investigated are completely disregarded, because the simplified expressions (15), corresponding to the first boundary problem, describe only some asymptotic stage of the relaxation processes, where, for instance, the temperature at the free surface can be regarded as constant. But even in this last case (15) give only approximate representations of the required fields, since the values $D/\nu\alpha$ and $\lambda_2/\nu\delta\alpha_2$, usually regarded as small, have a very powerful effect on the form of the basic solutions (10)-(12). Hence, any solution of this and similar problems that ignores these features of the temperature and concentration fields close to the evaporation surface (particularly the results of [3, 4]) should be used with great care.

When $t \to \infty$ for any finite x the temperatures of the liquid and vapor-gas medium tend to the same constant value $T_0 + k_1$, i.e., the asymptotic value $T_{s(t)}$ has the sense of some equilibrium temperature of the liquid-gas system, where the entropy of this system is a maximum. The relaxation time for the establishment of a constant free-surface temperature is given by the expression

$$t_s \simeq \frac{1}{\pi}\left(\frac{k_2}{k_1}\right)^2. \tag{16}$$

The thermal processes in the liquid and the vapor-gas medium, and the diffusion process at a distance x from the surface, will be close to quasi-stationary, respectively, when

$$t \gg t_1 \simeq \frac{x^2}{\pi a_1^2}, \quad t \gg t_2 \simeq \frac{x^2}{\pi a_2^2}, \quad t \gg t_3 \simeq \frac{x^2}{\pi D}. \tag{17}$$

For instants satisfying relation (17) it is easy to obtain asymptotic representations of all the unknowns by automatically using this expression for the Kramp function erfc z. To save space these have not been written out.

As already pointed out, for volatile liquids (and also for greatly differing temperatures T_∞ and T_0) the error of relation (7) may be considerable. Hence, for several applications the method of increasing the accuracy of the theoretical results is indicated.

Expression (7) and all the subsequent formulas based on its use can be regarded as the zero-order approximation. We will assume that this approximation gives a value $T_{s(t)}^{(0)}$ for the temperature at the liquid surface. It is natural to construct the next approximation on the basis of a new expansion of type (7):

$$q_{s(t)}^{(1)} = q_{s(t)}^{(0)} + \beta^{(1)}[T_{s(t)}^{(1)} - T_{s(t)}^{(0)}]. \tag{18}$$

As distinct from the coefficient $\beta^{(0)}$, referred to the vicinity of point T_0, $\beta^{(1)}$ is a parameter of the expansion at another point $T_{s(t)}^{(0)}$. Expansion (18), and also all the succeeding expansions of the second, third, etc. approximations, have to be determined separately for each instant and, hence, $\beta^{(1)}$, $\beta^{(2)}$, ... are functions of time. For most liquids, however, the change of $T_{s(t)}$ with time is so slow that $\beta^{(i)}$ can be regarded as an adiabatic invariant of the problem, and this greatly simplifies the calculations.

For quasi-stationary conditions, where, according to (15), the temperature at the evaporation surface can be regarded as constant, there is another "finite" method calculation, in addition to that given. Actually, an approximate expression (7) has to be found to correspond with the real relation $q_s = f(T_s)$:

$$q_0 + \beta(T_s - T_0) = f(T_s). \tag{19}$$

This equation gives the value of β at which T_s, also a function of β, represents the exact temperature at the evaporation surface. It is easy to solve Eq. (19) numerically or graphically.

As an illustration, we will consider the evaporation of an almost involatile liquid and volatile benzene. For simplicity, we will assume that the diffusion and heat-transfer constants in the vapor-gas medium are equivalent to the corresponding constants in pure air and take $T_0 = 30°C$, $T_\infty = 0°C$, $q_\infty = 0$. The characteristics of air, water, and benzene required for the calculations are tabulated in [9].

Table

Parameters of Air, Water, and Benzene at a Pressure of $10 \cdot 10^4$ N/m^2 and Temperature 20-30°C

Parameter	Air	Water	Benzene
λ, W/m · deg	$25.6 \cdot 10^{-3}$	$6.3 \cdot 10^{-1}$	$15.5 \cdot 10^{-2}$
c, J/kg · deg	$1 \cdot 10^3$	$4.2 \cdot 10^3$	$0,7 \cdot 10^3$
ρ, kg/m^3	1,2	$1.0 \cdot 10^3$	$0.88 \cdot 10^3$
L, kJ/kg	—	2268	4326
a^2, m^2/sec	$0.212 \cdot 10^{-4}$	$1.45 \cdot 10^{-7}$	$3.21 \cdot 10^{-6}$
λ/a, W · sec$^{1/2}$/m^2 · deg	$55684.44 \cdot 10^{-4}$	$159098,4 \cdot 10^{-2}$	$48148.2 \cdot 10^{-2}$
D, m^2 · sec^{-1}	—	$0.282 \cdot 10^{-4}$	$0.087 \cdot 10^{-4}$

The relationship between the concentration of saturated water vapor and temperature can be expressed by the formula [10]

$$q_s = q_0 \exp\left[\frac{17(T_s - T_0)}{235 + T_s}\right] \simeq q_0 + \frac{17 q_0}{235 + T_0}(T_s - T_0), \tag{20}$$

where q_0 is the concentration of the saturated vapor, equal to 3.13×10^{-5} g/cm^3 at $T_0 = 30°C$. Thus, $\beta^{(0)} = 2 \cdot 10^{-6}$ g/ /cm^3 · deg.

The reduction of temperature at the evaporation surface is, as is to be expected, extremely slight: calculation from Eq. (14) gives $T_s - T_0 = 0.36°C$. Sixty-four percent of this reduction is due to heat absorption associated with evaporation and the other 36% to inequality of the initial temperatures of the liquid and gaseous phases. In this case the error of (7) is extremely small and the resultant error in determining T_s, the rate of evaporation, etc., is correspondingly small, so that it is usually unnecessary to use methods for improving the accuracy.

The situation is different in the case of the evaporation of benzene. The relationship between the saturated vapor pressure of benzene and the temperature is satisfactorily represented by the Antoine equation [5]

$$\lg p = 6.897 - \frac{1206.35}{T + 220.24}. \tag{21}$$

Taking the molecular weight of benzene as 78.108 and assuming that benzene vapor is a perfect gas, we obtain for $q_s^{(0)}$ the expansion

$$q_s^{(0)} \simeq q_0 + \frac{2790 q_0}{(T_0 + 220.24)^2}(T_s - T_0), \tag{22}$$

where $q_0 = 4.83 \cdot 10^{-2}$ g/cm^3; hence, $\beta^{(0)} = 2.16 \cdot 10^{-3}$ g/cm^3 · deg. We calculate the change in free-surface temperature: $\Delta T^{(0)} = T_s^{(0)} - T_0 = -19°C$, the overwhelming part of this reduction (99.7%) being due to absorption of heat during evaporation. We now consider the next (first approximation. Instead of q_0 we take a value $q_s^{(0)}$ equal to $2.1 \cdot 10^{-2}$ g/cm^3, as can easily be calculated from the Antoine equation (21). Accordingly, $\beta^{(1)} = 1.09 \cdot 10^{-3}$. Then we easily obtain $\Delta T^{(1)} = -14.2°C$. We construct the second approximation: $q_s^{(1)} = 2.59 \cdot 10^{-2}$ g/cm^3, $\beta^{(2)} = 1.29 \cdot 10^{-3}$, and, finally, $\Delta T^{(2)} = -15.5°C$.

In a similar way we can easily construct all the subsequent approximations. The essential feature is that the values $T_s^{(i)} = T_0 + \Delta T^{(i)}$ give a more and more accurate value of the temperature of the liquid surface, approaching it alternately from above and below with increase in i. (It is easy to demonstrate this for the general case by using the monotonicity of function p from (21) and its first derivative). The actual value thus lies in the "fork" formed by each pair of numbers $T_s^{(i)}$ and $T_s^{(i+1)}$, and the size of this "fork" decreases with increase in i, thus reducing the possible error of the calculation. For instance, in our case we can state that the true temperature at the surface of the evaporating benzene lies between 14.5 and 15.8°C. Hence, the error in determining this temperature does not exceed ± 1.3°C. To attain greater accuracy we must continue the calculation by working out $\Delta T^{(3)}$, $\Delta T^{(4)}$, and so on.

All that has been said regarding the calculation of the temperature T_s can be extended with hardly any change to the calculation of the evaporation rate and other quantities characterizing heat and mass transfer.

NOTATION

D – coefficient of molecular diffusion of vapor in vapor-gas medium; a_1^2 and a_2^2 – thermal diffusivities in liquid and vapor-gas medium, respectively; λ_1 and λ_2 – thermal conductivities in liquid and vapor-gas medium; L – specific heat of vaporization of liquid; T_0, T_∞, q_∞ – limiting values of temperature and vapor concentration at infinity; T_s – temperature of evaporation surface; q_s – density of saturated vapor; ν – fourth part of mean absolute velocity of vapor molecules; α – evaporation coefficient; δ – accomodation coefficient; Δ – thickness of layer of concentration and temperature discontinuity at evaporation surface.

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