TRANSIENT EVAPORATION OF A SOLUTION FROM A PLANE SURFACE

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The parabolic interpolation for the transient-state approximation is used in analyzing the temperature field and the concentration field of a nonvolatile substance in solution as well as the temperature field and the concentration field of the solvent vapor in the ambient atmosphere, when evaporation is accompanied by a lowering of the liquid level.

Although the solution of problems in transient evaporation with a moving interphase boundary has been the object of many studies [1-9], the nonlinearity of such problems still presents a serious obstacle in the way of completely establishing the interrelations between all quantities involved.

We will attempt here to fill the gap as much as possible. Evaporation of a solution under certain generally reasonable assumptions can be described by the following system of equations:

$$\left.\begin{aligned}\frac{\partial T_1}{\partial \tau} &= \frac{\partial}{\partial x}\left(a_1\frac{\partial T_1}{\partial x}\right)\\ \frac{\partial C}{\partial \tau} &= \frac{\partial}{\partial x}\left(D_1\frac{\partial C}{\partial x}\right)\end{aligned}\right\},\quad \xi < x < h_1, \tag{1}$$

$$\left.\begin{aligned}\frac{\partial T_2}{\partial \tau} &= \frac{\partial}{\partial x}\left(a_2\frac{\partial T_2}{\partial x}\right)\\ \frac{\partial u}{\partial \tau} &= \frac{\partial}{\partial x}\left(D^2\frac{\partial u}{\partial x}\right)\end{aligned}\right\},\quad -h_2 < x < \xi, \tag{2}$$

$$C(\xi,\ \tau) \equiv C_\xi,\ T_1(\xi,\ \tau) \equiv T_\xi \equiv T_2(\xi,\ \tau),\ u(\xi,\ \tau) = u_s(T_\xi,\ C_\xi), \tag{3}$$

$$\left.\begin{aligned}T_1(x,\ 0) &= T_0 = \mathrm{const}\\ C(x,\ 0) &= C_0 = \mathrm{const}\end{aligned}\right\},\ x > 0;\ \xi(0) = 0;\ \left.\begin{aligned}T_2(x,\ 0) &= T_\infty = \mathrm{const}\\ u(x,\ 0) &= u_0 = \mathrm{const}\end{aligned}\right\},\ x<0, \tag{4}$$

$$\left.\frac{\partial T_1}{\partial x}\right|_{x=h_1} = 0,\ \left.\frac{\partial C}{\partial x}\right|_{x=h_1} = 0,\ \left.\frac{\partial T_2}{\partial x}\right|_{x=-h_2} = 0,\ \left.\frac{\partial u}{\partial x}\right|_{x=-h_2} = 0, \tag{5}$$

$$\int_{-h_2}^{\xi}\frac{k_2}{a_2}(T_2 - T_\infty)\,dx + \int_{\xi}^{h_1}\frac{k_1}{a_1}(T_1 - T_0)\,dx + \rho L\xi = \int_0^{\xi}\frac{k_1}{a_1}T_0dx - \int_0^{\xi}\frac{k_2}{a_2}T_\infty dx, \tag{6}$$

$$\int_{\xi}^{h_1} Cdx = \int_0^{h_1} C_0dx, \tag{7}$$

$$\int_{-h_2}^{\xi} udx + \int_{\xi}^{h_1}\rho dx = \int_{-h_2}^{0} u_0dx + \int_0^{h_1}\rho dx. \tag{8}$$

Here the x axis runs into the liquid and the origin of coordinates has been fixed so that the evaporation surface at the initial instant of time coincides with the x = 0 plane. While functions $T_1(x,\ \tau)$, $T_2(x,\ \tau)$, $C(x,\ \tau)$,

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and $u(x, \tau)$ are unknown, u_s is assumed a known function of two variables T_ξ, C_ξ and represents either Raoult's Law when T_ξ is fixed or the Clapeyron–Clausius relation when C_ξ is fixed. Equations (6)-(8) express the conservation of the total heat content of solvent and solute.

We assume further that the thermal conductivities, the thermal diffusivities, and the molecular diffusivities remain constant.

Differentiating (6)-(8) with respect to time, we obtain

$$-k_2 \frac{\partial T_2}{\partial x}\bigg|_{x=\xi} + k_1 \frac{\partial T_1}{dx}\bigg|_{x=\xi} = \left[\rho L + \left(\frac{k_2}{a_2} - \frac{k_1}{a_1}\right) T_\xi\right] \frac{d\xi}{d\tau}, \tag{9}$$

$$-D_1 \frac{\partial C}{\partial x}\bigg|_{x=\xi} = C_\xi \frac{d\xi}{d\tau}, \tag{10}$$

$$D_2 \frac{\partial u}{\partial x}\bigg|_{x=\xi} = (\rho - u_s) \frac{d\xi}{d\tau}. \tag{11}$$

The unknowns will be sought in the transient-state parabolic approximation

$$\begin{aligned}
C(x, \tau) &= \begin{cases} C_\delta + \dfrac{(C_\xi - C_\delta)}{\delta_1^2}[x - (\xi + \delta_1)]^2, & \xi \leqslant x \leqslant \xi + \delta_1, \\ C_\delta, & \xi + \delta_1 \leqslant x, \end{cases} \\
u(x, \tau) &= \begin{cases} u_\delta + \dfrac{(u_s - u_\delta)}{\delta_2^2}[x - (\xi - \delta_2)]^2, & \xi - \delta_2 \leqslant x \leqslant \xi, \\ u_\delta, & x \leqslant \xi - \delta_2, \end{cases} \\
T_1(x, \tau) &= \begin{cases} T_{1\delta} + \dfrac{(T_\xi - T_{1\delta})}{\delta_3^2}[x - (\xi + \delta_3)]^2, & \xi \leqslant x \leqslant \xi + \delta_3, \\ T_{1\delta}, & \xi + \delta_3 \leqslant x, \end{cases} \\
T_2(x, \tau) &= \begin{cases} T_{2\delta} - \dfrac{(T_{2\delta} - T_\xi)}{\delta_4^2}[x - (\xi - \delta_4)]^2, & \xi - \delta_4 \leqslant x \leqslant \xi, \\ T_{2\delta}, & x \leqslant \xi - \delta_4. \end{cases}
\end{aligned} \tag{12}$$

Here the four symbols with the subscript δ represent the values of the sought functions at the respective "depths of penetration" δ (particular for each function) [1] measured from the moving interphase boundary ξ. Both ξ and δ are functions of time or of quantities uniquely related to time, namely:

$$C(x, \tau)\bigg|_{x=\xi+\delta_1} = C_\delta, \quad \frac{\partial C}{\partial x}\bigg|_{x=\xi+\delta_1} = 0 \tag{13}$$

and analogously for the other unknowns.

Inserting (12) into (6)-(8) and then integrating, we obtain

$$\frac{k_2}{a_2}\left[(T_{2\delta} - T_\infty)(h_2 + \xi) - (T_{2\delta} - T_\xi)\frac{\delta_4}{3}\right] + \frac{k_1}{a_1}\left[(T_{1\delta} - T_0)(h_1 - \xi) + (T_\xi - T_{1\delta})\frac{\delta_3}{3}\right] + \left(\rho L + \frac{k_2}{a_2}T_\infty - \frac{k_1}{a_1}T_0\right)\xi = 0, \tag{14}$$

$$C_\delta(h_1 - \xi + \delta_1) + C_\delta\delta_1 + (C_\xi - C_\delta)\frac{\delta_1}{3} = C_0 h_1, \tag{15}$$

$$(u_\delta - u_0)(\xi - \delta_2 + h_2) + (u_\delta - u_0)\delta_2 + (u_s - u_\delta)\frac{\delta_2}{3} = (\rho - u_0)\xi. \tag{16}$$

Inserting (12) into (9)-(11) yields

$$\frac{k_2(T_{2\delta} - T_\xi)}{\delta_4} - \frac{k_1(T_\xi - T_{1\delta})}{\delta_3} = \frac{1}{2}\left[\rho L + \left(\frac{k_2}{a_2} - \frac{k_1}{a_1}\right)T_\xi\right]\frac{d\xi}{d\tau}, \tag{17}$$

$$C_\xi \frac{d\xi}{d\tau} = \frac{2D_1(C_\xi - C_\delta)}{\delta_1}, \tag{18}$$

$$(\rho - u_s)\frac{d\xi}{d\tau} = \frac{2D_2(u_s - u_\delta)}{\delta_2}. \tag{19}$$

Instead of (1) and (2) we will solve the equations of "heat balance" [1]

$$\int_{\xi}^{\xi+\delta_3} \frac{\partial T_1}{\partial \tau} dx = \int_{\xi}^{\xi+\delta_3} \frac{\partial}{\partial x}\left(a_1 \frac{\partial T_1}{\partial x}\right) dx, \tag{20}$$

$$\int_{\xi-\delta_4}^{\xi} \frac{\partial T_2}{\partial \tau} dx = \int_{\xi-\delta_4}^{\xi} \frac{\partial}{\partial x}\left(a_2 \frac{\partial T_2}{\partial x}\right) dx. \tag{21}$$

Expressing the left-hand sides in terms of the derivatives of the integral with respect to time τ, and using the approximations (12), we obtain instead of (20) and (21):

$$d\ln[(T_\xi - T_{1\delta})v] + \left(1 + \frac{3}{v} - \frac{9a_1}{\beta v^2}\right) d\ln\xi = -\frac{3dT_{1\delta}}{(T_\xi - T_{1\delta})}, \tag{22}$$

$$d\ln[(T_{2\delta} - T_\xi)w] + \left(1 - \frac{3}{w} - \frac{9a_2}{\beta w^2}\right) d\ln\xi = \frac{3dT_{2\delta}}{(T_{2\delta} - T_\xi)}, \tag{23}$$

where, in order to simplify the notation, we introduce

$$\frac{d\xi^2}{d\tau} = \frac{4}{3}\beta,\ v = \frac{\delta_3}{\xi},\ w = \frac{\delta_4}{\xi}. \tag{23a}$$

and

$$p = \frac{\delta_1}{\xi},\ s = \frac{\delta_2}{\xi}. \tag{23b}$$

In this case Eq. (14) becomes an identity and can be used either for verification or as an auxiliary equation.

It should be noted (and remembered later on) that $T_{1\delta}$ and δ_1 are directly related for each of the unknown functions. By virtue of the limitation $\xi + \delta_3 \leq h_1$, indeed, $T_{1\delta}$ is equal to T_0 if $\xi + \delta_3 < h_1$ but remains unknown if $\xi + \delta_3 = h_1$, i.e., if δ_3 can be expressed in terms of ξ. As a consequence, we have four characteristic instants of time corresponding to the roots of the equations

$$\begin{gathered} \xi(\tau) + \delta_1(\tau) = h_1, \\ \xi(\tau) + \delta_3(\tau) = h_1, \\ \xi(\tau) - \delta_2(\tau) = -h_2, \\ \xi(\tau) - \delta_4(\tau) = -h_2. \end{gathered} \tag{24}$$

Relations (15)-(19), (22), (23) are sufficient for determining ξ, T_ξ, C_ξ, and the four (by virtue of the earlier observation) unknowns for the sought functions. In this case the "heat balance" equations for $C(x, \tau)$ and $u(x, \tau)$ become identities.

From (15) and (18) we have (remembering the earlier observation)

$$\frac{d\xi^2}{d\tau} = \frac{4}{3} D_1 \frac{(C_\xi - C_0)^2}{C_0 C_\xi}, \quad \text{if} \quad \xi + \delta_1 \leqslant h_1, \tag{25}$$

$$\frac{d\xi^2}{d\tau} = 6D_1\left[\left(1 - \frac{C_0}{C_\xi}\right)\left(\frac{\xi}{h_1 - \xi}\right) - \frac{C_0}{C_\xi}\left(\frac{\xi}{h_1 - \xi}\right)^2\right], \quad \text{if} \quad \xi + \delta_1 = h_1. \tag{26}$$

or, which is equivalent,

$$\frac{d(h_1 - \xi)^2}{d\tau} = -6D_1\left[1 - \frac{C_0}{C_\xi}\left(\frac{h_1}{h_1 - \xi}\right)\right], \quad \text{if} \quad \xi + \delta_1 = h_1, \tag{26a}$$

and from (16) and (19) we have

$$\frac{d\xi^2}{d\tau} = \frac{4}{3} D_2 \frac{(u_s - u_0)^2}{(\rho - u_s)(\rho - u_0)}, \quad \text{if} \quad \xi - \delta_2 \geqslant -h_2, \tag{27}$$

$$\frac{d\xi^2}{d\tau} = 6D_2\left[\left(\frac{u_s - u_0}{\rho - u_s}\right) \cdot \frac{h_2 \xi}{(h_2 + \xi)^2} - \left(\frac{\xi}{h_2 + \xi}\right)^2\right], \quad \text{if} \quad \xi - \delta_2 = -h_2, \tag{28}$$

or, which is equivalent,

$$\frac{d(h_2 + \xi)^2}{d\tau} = 6D_2\left[\left(\frac{\rho - u_0}{\rho - u_s}\right)\left(\frac{h_2}{h_2 + \xi}\right) - 1\right], \quad \text{if} \quad \xi - \delta_2 = -h_2. \tag{28a}$$

The earlier observation applies also to Eqs. (22) and (23). For instance, at $\tau \leq \tau_0$ (τ_0 denoting the smallest root of Eq. (24) and with

$$\frac{D_2 (u_s - u_0)^2}{(\rho - u_s)(\rho - u_0)} = \frac{D_1 (C_\xi - C_0)^2}{C_0 C_\xi} = \beta, \tag{29}$$

following from (25) and (27)), we note (since $T_{1\delta} = T_0$ and $T_{2\delta} = T_\infty$) that (22) and (23) are satisfied together with (29) and (17) if v and w are constant and satisfy the equations

$$1 + \frac{3}{v} - \frac{9a_1}{\beta v^2} = 0, \tag{30}$$

$$1 - \frac{3}{w} - \frac{9a_2}{\beta w^2} = 0, \tag{31}$$

i.e., selecting the roots which correspond to evaporation (other roots correspond to other phase transformations) yields

$$v = \frac{3}{2}\left(\sqrt{1 + \frac{4a_1}{\beta}} - 1\right), \tag{32}$$

$$w = \frac{3}{2}\left(\sqrt{1 + \frac{4a_2}{\beta}} + 1\right), \tag{33}$$

and these two expressions inserted into (17) will add to system (29) that lacking equation

$$\frac{k_2}{a_2}(T_\infty - T_\xi)\left(\sqrt{1 + \frac{4a_1}{\beta}} - 1\right) - \frac{k_1}{a_1}(T_\xi - T_0)\left(\sqrt{1 + \frac{4a_1}{\beta}} + 1\right) = 2\left[\rho L + \left(\frac{k_2}{a_2} - \frac{k_1}{a_1}\right)T_\xi\right], \tag{34}$$

or the equivalent

$$\frac{k_2}{a_2}(T_\infty - T_\xi)\left(\sqrt{1 + \frac{4a_2}{\beta}} + 1\right) - \frac{k_1}{a_1}(T_\xi - T_0)\left(\sqrt{1 + \frac{4a_1}{\beta}} - 1\right) = 2\left(\rho L + \frac{k_2}{a_2}T_\infty - \frac{k_1}{a_1}T_0\right). \tag{34a}$$

for determining the quantities β, T_ξ, and C_ξ found to be constant.

In this way, we find that at $0 < \tau \leq \tau_0$ the quantities δ_1, δ_2, δ_3, and δ_4 are proportional to ξ and thus $\xi_0 = \xi(\tau_0)$ can be easily determined from Eqs. (24). Since function ξ yields τ readily, hence τ_0 is determinate.

It becomes obvious now that the solution is self-adjoint at $0 < \tau \leq \tau_0$ and it matches, within the proper approximation, the solution for an unbounded liquid in an unbounded medium. At $\tau > \tau_0$ the solution is also not an explicit function of time, which has to do with the conservation of total energy of the liquid and the ambient medium.

NOTATION

x	is the space coordinate;
τ	is the time;
ξ	is the coordinate of the liquid surface;
a_1, a_2	are the thermal diffusivity of the liquid and the ambient medium respectively;
k_1, k_2	are the thermal conductivity of the liquid and the ambient medium respectively;
D_1	is the molecular diffusivity of solute in the solvent;
D_2	is the molecular diffusivity of solvent vapor in the ambient medium;
ρ	is the density of the solvent;
L	is the heat of evaporation of the solvent;
T_0, T_∞	is the initial temperature of the liquid and the medium respectively;
C_0	is the initial concentration of solute in the solvent;
u_0	is the initial concentration of solvent vapor in the ambient medium;
h_1	is the initial depth of liquid;
h_2	is the initial thickness of vapor-gas layer in the ambient medium;
T_ξ	is the temperature of liquid surface;
C_ξ	is the concentration of solute at the liquid surface;
δ_1	is the "penetration depth" of solute concentration in the solvent;
δ_2	is the "penetration depth" of solvent vapor concentration in the ambient medium;
δ_3	is the "penetration depth" of temperature in the liquid;
δ_4	is the "penetration depth" of temperature in the ambient medium;

C_δ	is the concentration of solute beyond its penetration depth;
u_δ	is the concentration of solvent vapor beyond its penetration depth;
$T_{1\delta}$	is the temperature in the liquid beyond the penetration depth;
$T_{2\delta}$	is the temperature in the ambient medium beyond the penetration depth;
$u_s(T_\xi, C_\xi) = u_s$	is the concentration of saturated solvent vapor (known function of T_ξ and C_ξ, which are unknown functions of time or of a quantity uniquely related to it).

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