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Manuscript received May 24, 1963; revision received September 25, 1964; paper accepted September 28, 1964. Paper presented at A.I.Ch.E. Atlanta meeting.

Analysis of Phase Boundary Motion in Diffusion-Controlled Processes: Part II. Application to Evaporation from a Flat Surface

J. R. GRIFFIN and D. R. COUGHANOWR

Purdue University, Lafayette, Indiana

In an earlier paper (*1*), three general methods of approaching the moving-boundary problems were developed. In the present work, these three methods are applied in detail to the solution of the problem of evaporation from a flat surface into a vapor phase of infinite depth. While this particular problem has been solved before (*2,3*), it has been chosen as an example here because all three methods apply directly.

DESCRIPTION OF PROBLEM

A liquid evaporates from a large, flat surface into a vapor region which may be considered to extend an infinite distance above the interface. The vapor consists of the diffusant and a gas, such as air, which is insoluble in the liquid. The process is assumed to be controlled by mass diffusion of the evaporated species through the vapor. The evaporating species is the only transferred matter, and the initial concentration in the gas is uniform. The concentration levels and phase density difference are such that the motion of the vapor phase away from the surface cannot be ignored. It is desired to find an equation for the phase boundary motion.

The differential equation accounting for the bulk motion is given by Equation (I.38):*

$$D\frac{\partial^2 w}{\partial x^2} - \epsilon \dot{X}\frac{\partial w}{\partial x} = \frac{\partial w}{\partial \theta} \tag{1}$$

The initial conditions are

$$w = w_o \qquad X = X_o \qquad \theta = 0 \tag{2}$$

J. R. Griffin is with the Humble Oil and Refining Company, Baytown, Texas.

* The Roman numeral preceding an equation number refers to an equation in Part I of this series of papers (*1*). The form taken by Equation (1) involves a number of assumptions, such as constant phase densities and diffusivity.

From the initial conditions, it follows that

$$w = w_o \qquad x \to \infty \tag{3}$$

For the present, the interface composition may be permitted to vary:

$$w = w_X(\theta) \qquad x = X(\theta) \tag{4}$$

Since it has been assumed that air does not cross the moving boundary, an air balance and a total material balance at the moving phase boundary may be combined to produce the following:

$$D\left(\frac{\partial w}{\partial x}\right)_x = [(1-\epsilon)(1-w_X)]\,\dot{X} \tag{5}$$

THE INTEGRAL EQUATION SOLUTION

The integral equation method discussed in Part I (*1*) is applicable to all linear flow problems, including those involving motion of the phase. The problem considered here may be put into a suitable form by defining the following new variables:

$$u = w - w_o \tag{6}$$

$$s = x - \epsilon X(\theta) \tag{7}$$

$$B(\theta) = (1-\epsilon)\,X(\theta) \tag{8}$$

The resulting problem is as follows:

$$D\frac{\partial^2 u}{\partial s^2} = \frac{\partial u}{\partial \theta} \tag{9}$$

$$u(s, 0) = 0 \tag{10}$$

$$B(0) = (1-\epsilon)\,X_o \tag{11}$$

$$u(\infty, \theta) = 0 \tag{12}$$

$$u(B, \theta) = (w_X - w_o) \tag{13}$$

$$\frac{\partial u}{\partial s}(B, \theta) = \frac{1-w_X}{D}\dot{B} \tag{14}$$

The auxiliary problem [Equations (I.19) to (I.24)] may be written as

$$D\frac{\partial^2 v}{\partial s'^2} = \frac{\partial v}{\partial t}, \quad (t \equiv \theta - \theta') \tag{15}$$

$$v(s', 0) = 0, \quad s' \neq s \tag{16}$$

$$v(s, 0) = \infty \tag{17}$$

$$\lim_{\epsilon \to 0}\int_{s-\epsilon}^{s+\epsilon} v(s', 0)\, ds' = 1 \tag{18}$$

$$v(\infty, \theta) = 0 \tag{19}$$

Solution of this auxiliary problem by means of a Laplace transformation with respect to t yields the following auxiliary function:

$$v = \frac{1}{\sqrt{4\pi D(\theta-\theta')}}\exp - \left[\frac{(s-s')^2}{4D(\theta-\theta')}\right] \tag{20}$$

The boundary equations for the problem, corresponding to Equations (I.7) and (I.13), are as follows:

$$(w'_X - w_o) - F_{B'}\frac{(1-w'_X)}{D}\dot{B}' = G_{B'} \tag{21}$$

$$\frac{v_{B'}}{F_{B'}} = \left(\frac{\partial v}{\partial s'}\right)_{B'} - \frac{v_{B'}}{D}\dot{B}' \tag{22}$$

Therefore

$$\left(\frac{vG}{F}\right)_{B'} = (w'_X - w_o)\left[\left(\frac{\partial v}{\partial s'}\right)_{B'} - \frac{1-w_o}{w'_X - w_o}\frac{v_{B'}}{D}\dot{B}'\right] \tag{23}$$

The solution is then given by Equation (I.14):

$$u = D\int_0^\theta (w'_X - w_o)\left[\frac{(s-B')}{4\sqrt{\pi}\{D(\theta-\theta')\}^{3/2}} - \frac{1}{D}\frac{1-w_o}{w'_X-w_o}\frac{\dot{B}'}{2\sqrt{\pi D(\theta-\theta')}}\right] \times \exp - \left[\frac{(s-B')^2}{4D(\theta-\theta')}\right] d\theta' \tag{24}$$

In terms of the original variables, the weight fraction profile is then as follows:

$$(w - w_o) = D\int_0^\theta (w'_X - w_o)\left[\frac{(x-X)+(1-\epsilon)(X-X')}{4\sqrt{\pi}\{D(\theta-\theta')\}^{3/2}} - \frac{1}{D}\frac{1-w_o}{w'_X-w_o}\frac{(1-\epsilon)\dot{X}'}{2\sqrt{\pi D(\theta-\theta')}}\right] \times \exp - \left[\frac{[(x-X)+(1-\epsilon)(X-X')]^2}{4D(\theta-\theta')}\right] d\theta' \tag{25}$$

An equation for the moving boundary may now be realized by applying either Equation (4) or Equation (5), or some combination of these, to Equation (25). Solution follows in principle as soon as w_X is specified. Formulation of this quantity in terms of the other variables normally involves an energy balance at the phase boundary and consideration of the liquid-vapor equilibrium.

When the procedures shown here are followed, one thus obtains a single equation to be solved, which contains all of the information originally formulated in terms of a partial differential equation and five auxiliary conditions.

It is not suggested that solution of these nonlinear integro-differential equations will be a simple matter, for in general it will not. There are a number of methods of approaching the solution of nonlinear integral equations, including numerical solution by iteration, approximation schemes which may be used to place bounds upon the solution, and, in some simple cases, merely guessing the form of the solution. Thus, in the present case, if w_X is constant, a study of the form of Equation (25) reveals that the solution must be of the form $X \propto \sqrt{\theta}$. Substitution of this guess into Equation (25) reduces the problem to the determination of a constant.

THE INTERMEDIATE-INTEGRAL SOLUTION

The dimensionless transformations

$$z = \frac{x - X_o}{2\sqrt{D\theta}} \qquad y = \frac{X - X_o}{2\sqrt{D\theta}} \tag{26}$$

transform Equation (1) into the following:

$$\bar{r} + 2\left[z - \frac{\epsilon(X-X_o)\dot{X}}{2Dy}\right]p + 2\left[y - \frac{(X-X_o)\dot{X}}{2Dy}\right]q = 0 \tag{27}$$

where, corresponding to Equations (I.41), one has

$$\bar{r} \equiv \frac{\partial^2 w}{\partial z^2} \qquad p \equiv \frac{\partial w}{\partial z} \qquad q \equiv \frac{\partial w}{\partial y} \tag{28}$$

$$\beta_1 = 1; \qquad \beta_2 = \beta_3 = 0 \tag{29}$$

$$\beta_4 = 2\left[z - \frac{\epsilon(X - X_o)\dot{X}}{2Dy}\right]$$

$$\beta_5 = 2\left[y - \frac{(X - X_o)\dot{X}}{2Dy}\right]$$

Equations (I.46) and (I.47) are, respectively

$$F_1 \equiv \frac{G_z}{G_p} - 2\left[z - \frac{\epsilon(X - X_o)\dot{X}}{2Dy}\right]p - 2\left[y - \frac{(X - X_o)\dot{X}}{2Dy}\right]q = 0 \quad (30)$$

and

$$F_2 \equiv G_q = 0 \quad (31)$$

From this, one has

$$(F_1, F_2) \equiv -2\left[y - \frac{(X - X_o)\dot{X}}{2Dy}\right] \quad (32)$$

The functions F_1 and F_2 are therefore consistent if

$$(X - X_o)\dot{X} = 2\,Dy^2 \quad (33)$$

Then

$$F_1 \equiv \frac{G_z}{G_p} - 2(z - \epsilon y)\,p = 0 \quad (34)$$

and

$$F_2 \equiv G_q = 0 \quad (35)$$

The subsidiary equations corresponding to Equations (I.52) are

$$dG_q = dy = dq = 0$$

$$-\frac{dG_z}{2p} = \frac{dG_y}{2\epsilon p} = \frac{-dG_p}{2(z - \epsilon y)} = -G_p\,dz = +\frac{G_p^2}{G_z}dp \quad (36)$$

A particular integral may be written from the second and fourth members of Equations (36):

$$F_3 \equiv y - a_1 = 0 \qquad (a_1 = \text{constant}) \quad (37)$$

When one eliminates y from the subsidiary equations using Equation (37), another particular integral may be written from the seventh and eighth members:

$$\frac{dG_p}{2(z - \epsilon a_1)} = G_p\,dz \quad (38)$$

so that

$$F_4 \equiv G_p - a_2 \exp\,(z^2 - 2\epsilon a_1 z) = 0 \quad (39)$$

From Equations (34), (35), (37), and (39) one has

$$G_z = 2(z - \epsilon a_1)\,p\,a_2 \exp\,(z^2 - 2\epsilon a_1 z) \quad (40)$$

$$dy = 0 \quad (41)$$

$$G_p = a_2 \exp\,(z^2 - 2\epsilon a_1 z) \quad (42)$$

$$G_q = 0 \quad (43)$$

The differential of G is exact, then

$$dG = G_z dz + G_y dy + G_p dp + G_q dq = 2(z - \epsilon a_1)pa_2 \exp\,(z^2 - 2\epsilon a_1 z)\,dz + a_2 \exp\,(z^2 - 2\epsilon a_1 z)\,dp \quad (44)$$

The intermediate integral is therefore

$$G = a_2 p \exp\,(z^2 - 2\epsilon a_1 z) - a_3 = 0 \quad (45)$$

Solving Equation (45) for p one obtains

$$p \equiv \frac{\partial w}{\partial z} = \frac{a_3}{a_2}\exp -\,(z^2 - 2\epsilon a_1 z) \quad (46)$$

which may be integrated immediately to give

$$(w - w_o) = A\int_z^\infty \exp\,[-(z^2 - 2\epsilon a_1 z)]dz \quad (47)$$

By use of Equation (26), this may be written in terms of the original variables:

$$(w - w_o) = C\,\text{erfc}\left[\frac{x - X_o}{2\sqrt{D\theta}} - \epsilon a_1\right] \quad (48)$$

A and C are arbitrary constants.

From Equations (33) and (37)

$$(X - X_o)\dot{X} = 2Da_1^2 \quad (49)$$

Integrating Equation (49) one obtains

$$X - X_o = 2a_1\sqrt{D\theta} \quad (50)$$

Applying Equation (4) to Equation (48), in view of Equation (50), one has

$$(w_X - w_o) = C\,\text{erfc}\,(1 - \epsilon)a_1 \quad (51)$$

From Equation (51), it is clear that the particular solution is for constant w_X, a condition corresponding to isothermal evaporation of a pure liquid.

Elimination of C from Equation (48) by Equation (51) and application of Equations (5) and (50) give the following equation to be satisfied by the boundary motion constant a_1:

$$(1 - \epsilon)a_1 \exp\,[(1 - \epsilon)a_1]^2\,\text{erfc}\,[(1 - \epsilon)a_1] = -\frac{1}{\sqrt{\pi}}\left[\frac{w_X - w_o}{1 - w_X}\right] \quad (52)$$

While it is clear that the integral equation solution [Equation (25)] is more general than that obtained by the intermediate integral method [Equation (48)], since it permits variable surface concentrations, it is not at all obvious that the results are equivalent for the case of constant w_X. For a detailed demonstration of this equivalence, the interested reader is referred to reference *4*, pp. 80-83.

DIFFERENTIAL ANALYZER SOLUTIONS

The analytical solution of the isothermal evaporation problem which has been given above may be compared with results of the numerical method suggested in (*1*) in order to demonstrate the validity of the numerical approach.

The differential equation under consideration is Equation (1). The boundary conditions for the isothermal problem may be written in the following simple form:

$$w(X, \theta) = \alpha_1 \quad (53)$$

$$D\frac{\partial w}{\partial x}(X, \theta) = \alpha_2\dot{X} \quad (54)$$

$$w(x, 0) = \alpha_3 \quad (55)$$

$$w(\infty, \theta) = \alpha_3 \quad \text{or} \quad \frac{\partial w}{\partial x}(\infty, \theta) = 0 \quad (56)$$

where the α_j are constants.

The problem may be transformed in accordance with

$$z = \exp\,(1 - x/X) \quad (57)$$

$$t = \int_0^\theta DX^{-2}\,d\theta \quad (58)$$

$$\phi(t) = X^{-1}\dot{X} \quad (59)$$

into the following:

$$z^2\frac{\partial^2 w}{\partial z^2} + z\frac{\partial w}{\partial z} + z\,[\epsilon - ln(e/z)]\,\phi\frac{\partial w}{\partial z} = \frac{\partial w}{\partial t} \quad (60)$$

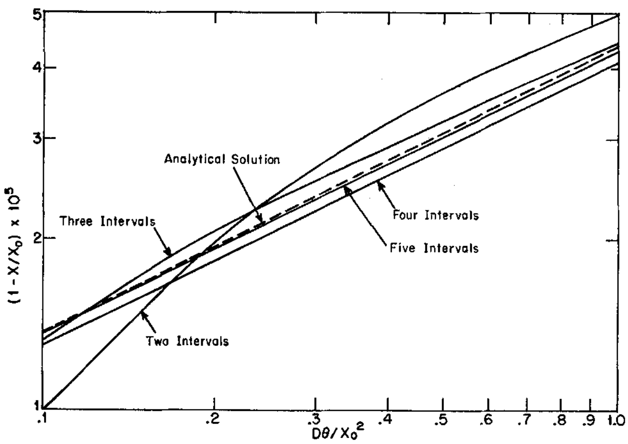

Fig. 1. Comparison of various approximations with analytical solution.

$$w(1,t) = \alpha_1 \tag{61}$$

$$\frac{\partial w}{\partial z}(1,t) = -\alpha_2\,\phi \tag{62}$$

$$w(z,0) = \alpha_3 \tag{63}$$

$$w(0,t) = \alpha_3 \quad \text{or} \quad \frac{\partial w}{\partial z}(0,t) = 0 \tag{64}$$

The transformation given by Equation (57) renders the domain of z finite and independent of t. This particular transformation has a vanishing Jacobian for $z = 0$, which can cause totally incorrect results to be obtained by the present method unless care is exercised. The two boundary conditions noted in Equations (56) and in their transformed versions in Equations (64) are equivalent in this problem involving the infinitely extended domain. These two conditions cannot, however, be satisfied simultaneously with finite-difference approximations of the derivatives except at zero time. In practice, the error realized in using either the initial condition model or the zero gradient model is small for t sufficiently short that conditions at the point $z = 0$ are not significantly affected.

The transformation given by Equation (58) and the function defined by Equation (59) are introduced simply to reduce the number of time function multiplications appearing in the equations to be programed for computer solution.

The problem as stated in Equations (60) through (64) may be reduced to a set of simultaneous ordinary differential equations by replacing the space derivatives with appropriate finite difference approximations. Second-order finite differences were used for two, three, four, and five interval subdivisions of the unit z domain, with results as shown in Figure 1.* The analytical solution shown is derived from Equation (50). For the numerical computations, values were assigned to the parameters as follows: $w(X,\theta) = 0.03$, $w(x,0) = 0$, $\epsilon = -800$.†

The result of the crude approximation employing only two finite difference intervals is considered to be remarkable. This approximation scheme involved but one point, in what corresponds to a semi-infinite interval, which was allowed to vary in concentration. Considerably larger errors were expected for so crude an approximation. It is seen that the five internal scheme gives results which are quite satisfactory for practical purposes.

All of the approximate solutions diverge from the true solution for higher values of $D\theta/X_o^2$, and the reason has already been suggested, following Equation (64). The approximations obtained with the initial value model and the zero gradient model [Equations (64)] diverge in opposite directions, however, and this provides a basis for determining values of $D\theta/X_o^2$ below which the solutions are the approximations desired. When the two approximate solutions diverge from each other, neither is any longer a suitable approximation. It should be noted that the range of validity of the solutions may be extended by using more intervals.

SUMMARY

The three general methods of approaching moving boundary problems have been applied to the problem of evaporation from a flat surface into a vapor phase of semi-infinite extent, to illustrate the application of each method.

In a following and final paper in this series, more challenging problems in cylindrical and spherical coordinates are considered, and the results of the analyses are shown to be of use in interpreting experimental data on the systems considered.

NOTATION

A	=	constant
a_j	=	constant
B	=	boundary position in s coordinate system
C	=	constant
D	=	diffusivity of diffusant in air
e	=	base of natural logarithms
F	=	function symbol
G	=	function symbol
o	=	subscript indicating initial value
s	=	transformed position variable, defined by Equation (7)
t	=	transformed time variable, defined by Equation (58)
v	=	auxiliary function
w	=	weight fraction of diffusant in air
x	=	position coordinate of a point in the gas, measured with respect to a fixed point in the liquid
X	=	boundary position in x coordinate system
$\dot{X}$	=	boundary velocity
y	=	transformed independent variable
z	=	transformed independent variable

Greek Letters

α_j	=	constant
ϵ	=	$\dfrac{\rho_{\text{vapor}} - \rho_{\text{liquid}}}{\rho_{\text{vapor}}}$
θ	=	time
ρ	=	mass density
ϕ	=	function symbol

Primed symbols indicate function of an integrating variable.

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Manuscript received August 30, 1963; revision received August 4, 1964; paper accepted September 17, 1964.

* Computational details and computer circuits may be found in reference 4.

† While these precise values were assigned for convenience, they are of the orders corresponding to the evaporation of water into dry air at room temperature.