

Modeling evaporation using a nonlinear diffusion equation

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A nonlinear model of the evaporation of a pure volatile liquid is presented in which the moving liquid–vapour interface appears very naturally. The model gives the same results as an earlier linear formulation for the Stefan diffusion problem, but far more simply.

KEY WORDS: mathematical modeling, diffusion, evaporation, interface, Stefan problem, nonlinear model

1. Introduction

Modeling the evaporation of a volatile liquid from a partially filled open container has to confront certain problems with the moving liquid–vapor interface. Using the linear Fick equation with suitable initial boundary conditions gives a poor description of the real process. The speed of propagation of the vapor, for instance, would be infinite. One can overcome this problem by assuming the existence of a moving interface between the liquid and vapor phases. Now, additional conditions for the solution at the interface must be given. Such a description is often referred to as the Stefan diffusion problem [1,2]. Recently, Slattery and Mhetar [3] and Mhetar and Slattery [4] have used this formulation to find the moving liquid–vapor interface. We do not want to repeat the mathematical considerations of Slattery and Mhetar, but we would like to present a nonlinear model to describe this same phenomenon. This model has been used recently with great success to describe different gas and fluid diffusion phenomena, one example being dopant diffusion through a semiconductor [5–8]. In this model, we do not need to postulate the existence of the moving interface, because it appears naturally as a result of this new description. The main difference between the linear Fick equation and this nonlinear one is that without assuming the existence of the interface, in the Fick model the speed of propagation of the vapor is infinite, whereas in the nonlinear one it is finite. This latter fact by itself implies the existence of the interface. Using this model, we get the

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numerical calculation of the solutions, determining directly the difference between the position of the liquid–gas interface at any time. We obtain the same results concerning the interface as those obtained by Slattery and Mhetar [3] and Mhetar and Slattery [4].

2. Presentation of the phenomenon and its nonlinear description

We consider a very long tube that is fixed in laboratory frame of reference. This tube is partially filled with a pure liquid A . The liquid is isolated from the remainder of the tube, which is filled with a gas mixture of A and B , by a closed diaphragm. The entire system is maintained at a constant temperature and pressure. We assume that A and B form an ideal-gas mixture and that B is insoluble in liquid A . At time $t = 0$, the diaphragm is carefully opened and the evaporation of A commences. We wish to determine the concentration of A in the gas phase as well as the position of the liquid–gas interface as functions of time.

To compare results, we shall use the notation of Slattery and Mhetar.

For simplicity, we replace the finite gas phase with a semi-infinite gas that occupies all space corresponding to $z > 0$. At all times, the position $z = 0$ refers to the liquid–gas interface. At $t = 0$, this position also denotes the diaphragm.

Let $x_{(A)}(t, z)$ be the mole fraction of species A in the AB gas mixture at point $z \geq 0$ and time $t > 0$. Also assume that

$$x_{(A)}(0, z) = x_{(A)0} \quad \text{for } z > 0 \quad (1)$$

and

$$x_{(A)}(t, 0) = x_{(A)\text{eq}} \quad \text{for } t > 0, \quad (2)$$

where $x_{(A)0}$ and $x_{(A)\text{eq}}$ are constants.

We introduce the function

$$\bar{x}_{(A)}(t, z) \triangleq x_{(A)}(t, z) - x_{(A)0} \quad (3)$$

If we use the nonlinear diffusion model described by Okrański and Vila [13], then $\bar{x}_{(A)}$ should satisfy the following equation:

$$\frac{\partial \bar{x}_{(A)}}{\partial t} = \frac{\partial}{\partial z} \left(\bar{x}_{(A)}^m \frac{\partial \bar{x}_{(A)}}{\partial z} \right), \quad z > 0, \quad t > 0, \quad (4)$$

where m is a positive parameter, with the following conditions:

$$\bar{x}_{(A)}(0, z) = 0 \quad \text{for } z > 0 \quad (1')$$

and

$$\bar{x}_{(A)}(t, 0) = x_{(A)\text{eq}} - x_{(A)0} \quad \text{for } t > 0. \quad (2')$$

Let us note that thanks to an easy scaling (see, for example, [9,10]) the right-hand side of equation (4) is multiplied by the coefficient having the numerical value equal to one. It has not any influence in the considerations concerning the interface. The comprehensive

information about the mathematical literature devoted to (4) and related equations can be found in [12].

3. Mathematical analysis of the proposed model

If we substitute $\bar{x}_{(A)}/(x_{(A)\text{eq}} - x_{(A)0})$ for $\bar{x}_{(A)}$ and $(x_{(A)\text{eq}} - x_{(A)0})^m t$ for t , then the condition (2') can be reduced to

$$\bar{x}_{(A)}(t, 0) = 1 \quad \text{for } t > 0. \tag{2''}$$

The problem (4), (4'), (2'') has been considered by Okrański and Vila [11], who show that the unique solution of (4), (1'), (2'') has the form

$$\bar{x}_{(A)}(t, z) = \begin{cases} \bar{x}_{(A)}\left(\frac{z}{\sqrt{t}}\right) & \text{for } \frac{z}{\sqrt{t}} \leq \eta_0(m), \\ 0 & \text{for } \frac{z}{\sqrt{t}} > \eta_0(m), \end{cases} \tag{5}$$

where $\eta_0(m)$ is a constant depending on m .

As in [13], it can be proved that

$$\bar{x}_{(A)}^m\left(\frac{z}{\sqrt{t}}\right) = \eta_0^2(m) m v \left(1 - \frac{z}{\eta_0(m)\sqrt{t}}\right), \tag{6}$$

where

$$v(s) = \frac{s}{2} + \sum_{k=2}^{\infty} a_k(m) s^k. \tag{7}$$

The coefficients $a_k(m)$ are given by the formulae

$$\begin{aligned} a_2(m) &= -\frac{1}{4(m+1)}, \\ a_3(m) &= \frac{m}{12(2m+1)(m+1)^2}, \\ a_4(m) &= \frac{m}{48(3m+1)(2m+1)(m+1)^2}, \\ (n+1)(mn+1)a_{n+1}(m) &= \frac{2n+m(n^2-3n+2)}{2(m+1)} a_n(m) \\ &\quad - 2 \sum_{p=2}^{n-2} (p+1)(n+1+p(m-1)) a_{p+1}(m) a_{n-p+1}(m). \end{aligned} \tag{8}$$

The constant $\eta_0(m)$ can be calculated by the formula

$$\eta_0(m) = \frac{1}{\sqrt{mv(1)}}. \tag{9}$$

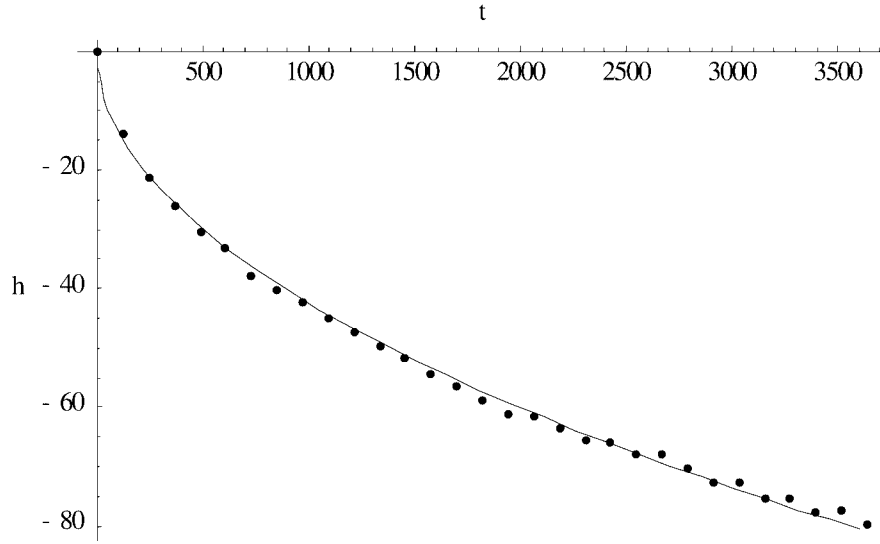


Figure 1. Points denote measured positions of the phase interface h (μm) as a function of t (s) for the evaporation of methanol into air at 25.4°C and $P = 1.006 \times 10^5$ Pa. The solid curve is the result of the least square fit of these data with equation (11).

Going back to the problem, we have that the unique solution of (4), (1'), (2') is given by

$$\bar{x}_{(A)}(t, z) = \begin{cases} (x_{(A)\text{eq}} - x_{(A)0})\bar{x}_{(A)}\left(\frac{z}{(x_{(A)\text{eq}} - x_{(A)0})^{m/2}\sqrt{t}}\right), & z < (x_{(A)\text{eq}} - x_{(A)0})^{m/2}\eta_0(m)\sqrt{t}, \\ 0, & z > (x_{(A)\text{eq}} - x_{(A)0})^{m/2}\eta_0(m)\sqrt{t}. \end{cases} \quad (10)$$

From this, we can determine directly the difference $h(t)$ between the position of the liquid–gas interface at any time $t > 0$ and $t = 0$:

$$h(t) = -(x_{(A)\text{eq}} - x_{(A)0})^{m/2}\eta_0(m)\sqrt{t}. \quad (11)$$

This same formula in the Stefan diffusion problem is given with the help of the diffusion coefficient.

4. Comparison with experimental data

We use the data presented in [3,4].

For the evaporation of methanol into air at 25.4°C and $P = 1.006 \times 10^5$ Pa, $x_{(A)\text{eq}} = 0.172$, $x_{(A)0} = 0$, a least-squares fit gives $h(t) = -1.34335\sqrt{t}$ (figure 1).

For the evaporation of methyl formate into air at 25.4°C and $P = 1.011 \times 10^5$ Pa, $x_{(A)\text{eq}} = 0.784$, $x_{(A)0} = 0$, a least-squares fit gives $h(t) = -11.8042\sqrt{t}$ (figure 2).

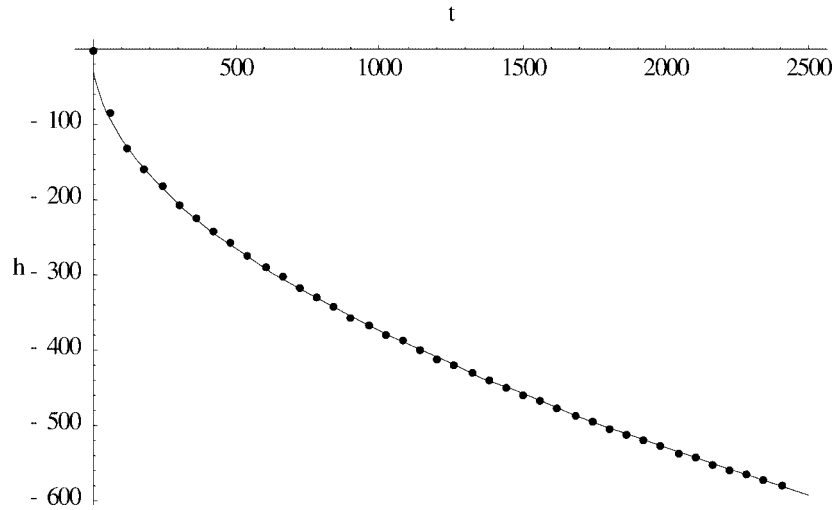


Figure 2. Points denote measured positions of the phase interface h (μm) as a function of t (s) for the evaporation of methyl formate into air at 25.4°C and $P = 1.011 \times 10^5$ Pa. The solid curve is the result of the least square fit of these data with equation (11).

If we can determine m , then formula (10) gives a very good approximation to the mole fraction $\bar{x}_{(A)}$ of suitable species.

To find the value of m , we shall use equation (11). In the case of the evaporation of methanol into air, we must solve for m the equation

$$(0.172)^{m/2} \eta_0(m) = 1.34335, \tag{12}$$

and in the case of the evaporation of methyl formate into air

$$(0.784)^{m/2} \eta_0(m) = 11.8042. \tag{13}$$

Let

$$v_n(1) = \frac{1}{2} + \sum_{k=2}^n a_k(m) \tag{14}$$

and

$$\eta_n(m) = \frac{1}{\sqrt{m v_n(1)}}. \tag{15}$$

Then instead of equations (12') and (13'), we used the program *Mathematica* to solve

$$(0.172)^{m/2} \eta_n(m) = 1.34335 \tag{12'}$$

and

$$(0.784)^{m/2} \eta_n(m) = 11.8042 \tag{13'}$$

by changing the summation limit n .

Table 1
Results of our calculations for the evaporation
of methanol into air.

$h(t) = -1.34335\sqrt{t}$	
n	m
3	0.575
4	0.5735
5	0.573365
6	0.573352
7	0.573358
8	0.573361
9	0.573362
10	0.573362
11	0.573362
12	0.573362

We used the following program:

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a[2,m_]=-1/(4(m+1));
a[3,m_]=m/(12(2 m+1)(m+1)^2);
a[4,m_]=m(m+3)/(48(3 m+1)(2 m+1)(m+1)^3);
a[n_Integer,m_]=If[n>=5,
  ((2(n-1)+m((n-1)^2-3(n-1)+2))/(2(m+1)) a[n-1,m]-
  2 Sum[(p+1)((n-1)+1+p(m-1))a[p+1,m] a[(n-1)-p+1,m],
  {p,2,(n-1)-2}])/(((n-1)+1)(m (n-1)+1))];
v[m_,n_,s_]=If[n>=2,s/2+Sum[a[k,m] s^k,{k,2,n}],s/2];
c=Input["Insert c"];
nhu[m_,n_]=Sqrt[c^m/(m v[m,n,1])];
n=Input["Insert n"];
n0=Input["Insert nhu inicial"];
sol=FindRoot[nhu[m,n]==n0, {m,0.027}]

```

Tables 1 and 2 present the results of our calculations.

On the basis of these tables, we infer that $m = 0.573362$ is the suitable parameter for methanol, and $m = 0.02708$ for the case of methyl formate.

The program presented above is faster if the initial guess $m = 0.57$ for methanol or $m = 0.027$ for the case of methyl formate. If we put another initial guess, then result is the same but computer needs more time to calculate it. Since the left-hand sides of equations (12') and (13') are given by strictly monotonous functions, then the solutions m are unique.

5. Conclusion

We have presented an application of a new nonlinear diffusion model to the evaporation of a pure volatile liquid. It seems that this model describes the phenomenon very

Table 2
Results of our calculations for the evaporation
of methyl formate into air.

$h(t) = -11.8042\sqrt{t}$	
n	m
3	0.0275495
4	0.0274071
5	0.027308
6	0.027378
7	0.0271877
8	0.0271522
9	0.0271273
10	0.0271102
11	0.0270988
12	0.0270914
13	0.0270869
14	0.0270843
15	0.0270830
16	0.0270825
17	0.0270825
18	0.0270827
19	0.0270832
20	0.0270835
21	0.0270840
22	0.0270842
23	0.0270843

well because the moving interface appears naturally without any additional assumptions, as was shown by using it to describe the Stefan problem.

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Appendix. Notation

$a_k(m)$	transformed variable as defined in equation (8)
h	height of phase interface
$\eta_0(m)$	constant depending on m (which can be calculated by equation (9))
t	time
$v(s)$	transformed variable as defined in equation (7)

$x_{(A)}$	mole fraction of species A in the gas phase
$x_{(A)0}$	initial mole fraction of species A in the gas phase
$x_{(A)eq}$	equilibrium mole fraction of species A in the gas phase at the liquid–gas phase interface
$\bar{x}_{(A)}$	transformed variable as defined in equation (3)
z	vertical coordinate measured in the opposite direction of gravity

Miscellaneous symbols

∂ partial derivative

Superscripts

1, 2, 3, . . . , m exponents

Subscripts

0 initial condition

eq equilibrium

A, B components

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