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## Numerical Simulation of Proposed

## Surface Diffusion Experiments

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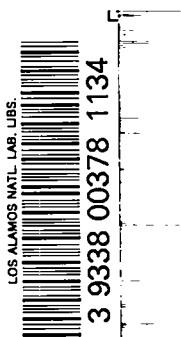
# LOS ALAMOS SCIENTIFIC LABORATORY
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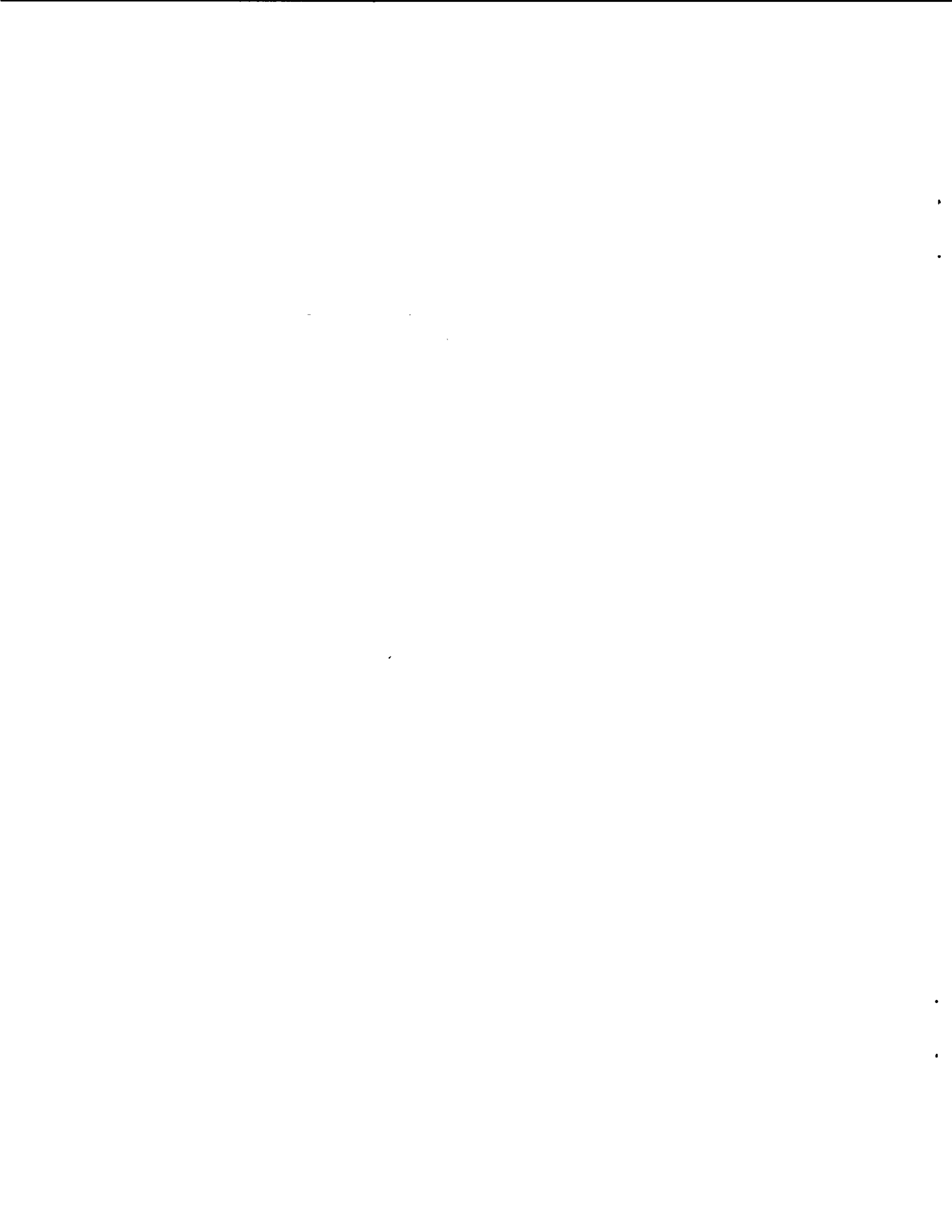### LOS ALAMOS • NEW MEXICO

# Numerical Simulation of Proposed
# Surface Diffusion Experiments

by

John P. Brainard

Bruce Goplen

# NUMERICAL SIMULATION OF PROPOSED SURFACE DIFFUSION EXPERIMENTS

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## ABSTRACT

*This report describes two possible experiments to measure the surface diffusion of sodium on metal substrates. Based on estimated data, numerical calculations were performed to simulate these experiments, and judgments were formed as to their feasibility.*

## INTRODUCTION

### Surface Diffusion of Sodium

Three general mechanisms by which sodium can transfer in sodium loops are: momentum transfer, gas diffusion, and surface diffusion. All transfer mechanisms must be considered when instrumenting a sodium loop; sodium that transfers in an unknown manner can perturb the desired results. Knowledge of all transfer mechanisms is important to safety in the event of fuel-pin or sodium-containment ruptures. Of these three transport mechanisms, surface diffusion is the least known.

Two experimental techniques, one called "flash-wire" and the other "hot-point," have been considered for determining surface diffusion rates. Both involve placing sodium on a wire and measuring its evaporation from that wire.

The "flash-wire" experiment involves placing some unknown, but reproducible, sodium distribution on a wire at a predetermined temperature. A wire rather than a ribbon is used to avoid edge effects. After some time the wire is flashed to high temperature with subsequent desorption of the sodium.[1] A hot ribbon detector some distance from but parallel to the wire interrupts some of the desorbed sodium. This sodium is surface ionized, and the rate of ionization is measured as a current to a collector filament.[2] The hot ribbon detector is designed to have a potential drop of about 30V down its length. By gating a grid between the ribbon detector and the collector, the collector current can be associated with sodium desorption at a particular position on the wire, and the sodium density distribution along the wire can be measured. Measuring the distribution at two different times gives enough information to determine the surface diffusion rate.

The "hot-point" experiment involves depositing sodium continuously at some known rate on a region of the wire which is small compared to its total length. The wire is at some predetermined temperature. At each extremity of the wire is a hot point. As sodium arrives at these points, it is removed by desorption. The desorbed sodium is ionized and collected. The current measured eventually builds up to a maximum when the rate of desorption equals the rate of sodium deposition. The surface diffusion rate can be obtained by observing the buildup in current with time.

To allow comparison of experimental techniques, a computer program was required to simulate each of the methods using estimated data. The resulting effort is the subject of this report.

### SUMMARY

A computer code named SWEETBRIAR has been written in FORTRAN IV for the IBM 7030 to solve the

surface diffusion equation with evaporation term in one dimension,

$$D \frac{\partial^2 n}{\partial x^2} - Rn = \frac{\partial n}{\partial t} . \qquad (1)$$

The calculation is in finite difference, and the extrapolated Liebmann technique is used to speed convergence. The code has been checked against two analytic solutions: the Dirac delta and a Fourier square wave.

Three types of problems may be considered. The first is the straightforward case in which diffusion rate, evaporation rate, and initial concentration distribution are all known or assumed. The second case, of more interest experimentally, is the "flash-wire" in which the concentration distribution is known (measured) at two different times. Given this information, the program calculates diffusion and evaporation coefficients. The third case, also of experimental usefulness, is the "hot-point" problem in which mass deposited at a constant rate on one point of an initially bare wire is evaporated at two hot points, and a characteristic time of equilibrium (mass deposition rate = evaporation rate) is measured.

Examples of the three solution techniques and several cases involving experimental data are included below, along with a code input.

CONCLUSION

This study has shown that the "flash-wire" experiment does not appear to be the most practical method of obtaining surface diffusion coefficients. The measurement of sodium distribution must be done within a few minutes of the time of initial distribution at room temperature to within a few milliseconds at 500°C. Also, the flashing of the wire must be very fast to prevent change of the sodium distribution during the measurement. The flashing has to raise the wire temperature well over 1000°C in a few microseconds. Further, the "flash-wire" experiment requires two runs with reproducible initial distribution, and this may be very difficult to obtain.

The "hot-point" experiment, on the other hand, looks more promising. Much longer times can be taken for measurement. Also, enough data can be obtained from a single run to determine the diffusion coefficient. Since surface diffusion is strongly

influenced by temperature, it is well to keep temperatures fixed during the experiment. This can be accomplished in the "hot-point" method.

CALCULATIONAL TECHNIQUE

The general one-dimensional diffusion equation with evaporation term,

$$D \frac{\partial^2 n}{\partial x^2} - Rn = \frac{\partial n}{\partial t} , \qquad (1)$$

(see Nomenclature list at end of report) can be expressed in finite difference as follows:

$$n_J(t+\Delta t) = \frac{n_J(t) + \frac{D\Delta t}{(\Delta x)^2} \cdot \left[ n_{J-1}(t+\Delta t) + n_{J+1}(t+\Delta t) \right]}{1 + R\Delta t + 2 \frac{D\Delta t}{(\Delta x)^2}} . \qquad (2)$$

Values of $n_{J-1}$ and $n_{J+1}$ are taken at $t+\Delta t$ to help convergence. To allow use of a sizable time step, an iterative scheme is used:

$$n_J^I(t+\Delta t) = \frac{n_J(t) + \frac{D\Delta t}{(\Delta x)^2} \left[ n_{J-1}^I(t+\Delta t) + n_{J+1}^{I-1}(t+\Delta t) \right]}{1 + R\Delta t + 2 \frac{D\Delta t}{(\Delta x)^2}} . \qquad (3)$$

Concentrations without superscripts represent converged values, and the first iteration (I=1) requires that $n_{J+1}(t)$ be used instead of $n_{J+1}^{I-1}(t+\Delta t)$. Convergence implies that all nodes have satisfied the following criterion:

$$\left| n_J^I(t+\Delta t) - n_J^{I-1}(t+\Delta t) \right| < \varepsilon_1 . \qquad (4)$$

Finally, to speed convergence, an extrapolation technique is used, in this case the Liebmann method. There is no physical significance involved; rather it is simply a means of extrapolating from the previous iteration to achieve faster convergence. The final form of the diffusion equation solved in the program is then

$$n_J^I(t+\Delta t) = (1-\beta) \, n_J^{I-1}(t+\Delta t)$$

$$+ \beta \left\{ \frac{n_J(t) + \frac{D\Delta t}{(\Delta x)^2} \left[ n_{J-1}^I(t+\Delta t) + n_{J-1}^{I-1}(t+\Delta t) \right]}{1 + R\Delta t + 2 \frac{D\Delta t}{(\Delta x)^2}} \right\} , \qquad (5)$$

where possible values of the Liebmann parameter, $\beta$, are from 1.0 to 2.0.

Some remarks regarding various parameters in

Eq. 5 are in order. First, from a consideration of the case in which only evaporation takes place, it is clear that the denominator of the second term must remain linear. That is, from the analytic solution of Eq. 1 for D=0,

$$\frac{n}{n_o} = e^{-R\Delta t} = 1 - R\Delta t + \frac{(R\Delta t)^2}{2!} + \cdots \quad (6)$$

$$\simeq \frac{1}{1 + R\Delta t} , \quad (7)$$

only if

$$R\Delta t < \epsilon_6 \ll 1 . \quad (8)$$

Second, we tried to maximize the dimensionless quantity $D\Delta t/(\Delta x)^2$ to increase the size of the time step. Results of many calculations indicate a convergent solution if

$$\frac{D\Delta t}{(\Delta x)^2} \leq 20. \quad (9)$$

Similarly, an attempt was made to minimize the number of iterations required by varying the Liebmann parameter, $\beta$. Acceptable values were found between $\beta = 1.0$ and 1.8, whereas the case $\beta = 2$ was always divergent. Note that the case $\beta = 1.0$ corresponds exactly to Eq. 3. Minimum machine time was generally obtained at about $\beta = 1.6$, and all subsequent cases were run using this value. The time saving over use of Eq. 3 is roughly a factor of three.

The calculation has been checked against two analytic solutions, the first of which is the Dirac delta function. Its properties are

$$\delta(x) = 0 \qquad x \neq 0$$

$$\int_{-a}^{b} \delta(x)dx = 1 \qquad a,b > 0 . \quad (10)$$

Identifying the delta function with initial concentration distribution corresponds physically to normalized mass deposited at a point at time equals zero. Beginning with Eq. 1, the substitution

$$u(x,t) = n(x,t)e^{+Rt} \quad (11)$$

eliminates the evaporation term, yielding

$$D \frac{\partial^2 u(x,t)}{\partial x^2} = \frac{\partial u(x,t)}{\partial t} , \quad (12)$$

which is easily solved using the method of Green's functions. That is

$$u(x,t) = \int G(x,x',t) u(x',o)dx, \quad (13)$$

with the condition

$$u(x',o) = n(x',o) = \delta(x') \quad (14)$$

and the Green's function[3] obtained by Fourier transforming the x variable,

$$G(x,x',t) = \frac{1}{2\sqrt{\pi Dt}} e^{-\frac{(x-x')^2}{4Dt}} , \quad (15)$$

yields

$$u(x,t) = \frac{1}{2\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} , \quad (16)$$

and finally

$$n(x,t) = \frac{1}{2\sqrt{\pi Dt}} e^{-\left(\frac{x^2}{4Dt} + Rt\right)} . \quad (17)$$

This initial distribution was simulated in the finite difference calculation with a very narrow, normalized square wave. A comparison of this result with Eq. 17 is shown in Fig. 1. Only the right side of the symmetric distribution is shown.
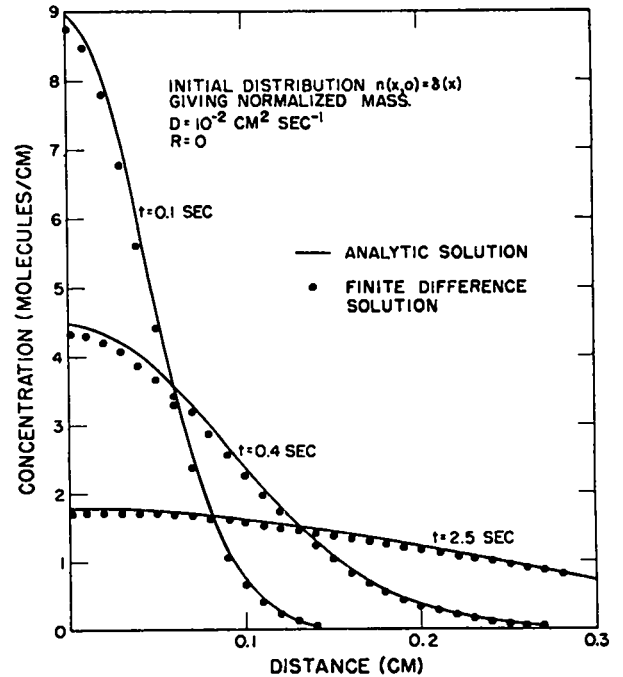


Fig. 1. The Dirac delta solution.

The second analytic solution used in checking the finite difference calculation was the Fourier square wave. Beginning from Eq. 12,

$$D \frac{\partial^2 u}{\partial x^2} = \frac{\partial u}{\partial t} , \tag{12}$$

and assuming the solution $u(x,t)$ to be separable,

$$u(x,t) = X(x)T(t)$$

gives

$$DT(t) \frac{d^2 X(x)}{dx^2} = X(x) \frac{dT(t)}{dt}$$

or

$$\frac{D}{X(x)} \frac{d^2 X(x)}{dx^2} = \frac{1}{T(t)} \frac{dT(t)}{dt} . \tag{18}$$

But since t and x are independent variables, Eq. 18 must equal some constant, k. The resulting two equations are,

$$\frac{d^2 X(x)}{dx^2} - \frac{k}{D} X(x) = 0 \tag{19}$$

and

$$\frac{dT(t)}{dt} - kT(t) = 0. \tag{20}$$

Now a particular solution that fits the boundary condition is found using Fourier analysis,

$$n(x,0) = \begin{cases} \frac{1}{a}, & -\frac{a}{2} < x < \frac{a}{2} \\ 0, & \text{otherwise} \end{cases} . \tag{21}$$

This solution is actually periodic, but the period is chosen large enough to approximate the boundary conditions (21). The even Fourier cosine series,

$$X(x) = a_0 + \sum_{m=1}^{\infty} a_m \cos \frac{\pi m x}{\ell}, \tag{22}$$

where $\ell$ equals one-half the period, satisfies Eq. 19 and has coefficients, $a_m$, determined by integration of an orthonormal set over the period $2\ell$, giving,

$$a_0 = \frac{1}{2\ell} ,$$

$$a_m = \frac{2}{a m \pi} \sin \frac{m \pi a}{2\ell} . \tag{23}$$

Substituting Eq. 22 in Eq. 19 gives,

$$k = - \frac{m^2 \pi^2}{\ell^2},$$

from which Eq. 20 yields,

$$T(t) = e^{-\frac{m^2 \pi^2 D t}{\ell^2}} . \tag{24}$$

Combining Eqs. 11, 22, 23, and 24 gives the complete solution,

$$n(x,t) = \frac{1}{2\ell} e^{-Rt}$$
$$+ \sum_{m=1}^{\infty} \frac{2}{m \pi a} \sin \frac{m \pi a}{2\ell} \cos \frac{m \pi x}{\ell} e^{-\left(\frac{m^2 \pi^2 D}{\ell^2} + R\right) t} . \tag{25}$$

It is illustrated in Fig. 2 along with the corresponding finite difference solution.
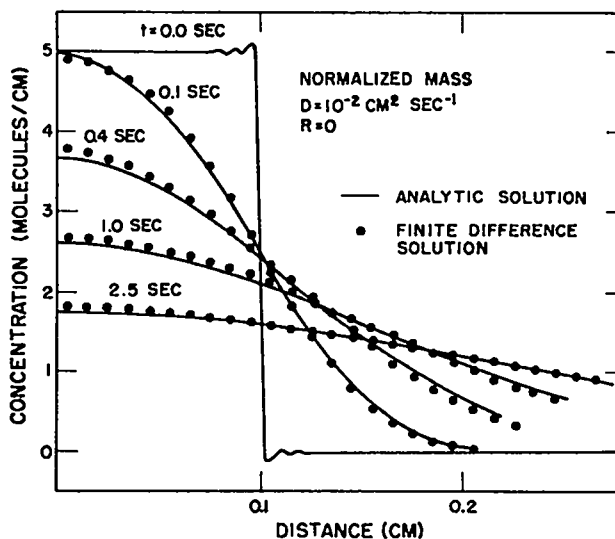


Fig. 2. The Fourier square-wave solution.

Because of sparse data on sodium, we have used surface-diffusion estimates of indium on tantalum[4] and evaporation rates of sodium on gas-covered and atomically clean tungsten.[5] These estimates are shown in Fig. 3. These data are believed to be representative of an alkali metal on a refractory metal. Figure 4 is the result of computer runs for a gas-covered refractory metal at various temperatures. Gas-covered tantalum was chosen because of the higher evaporation rate. A square wave of 500-molecules/cm concentration and 0.2-cm width was assumed as an initial distribution in all cases. (Concentra-

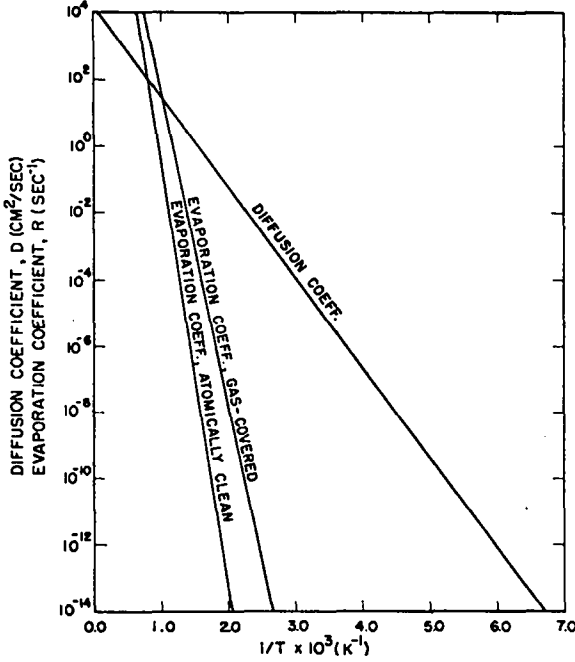tion may be adjusted to any desired level by multiplication.)



Fig. 3. Estimated diffusion characteristics of indium on tantalum.

In practice, it would not be possible to start from an initial square wave distribution, but it may be possible to determine distributions at two different times during the diffusion process, and from this information the evaporation and diffusion coefficients can be obtained. This "flash-wire" experiment is the second type of case solved by SWEET-BRIAR. Given two concentration distributions at times 0 and $t'$, the solution for evaporation coefficient becomes analytic. That is,

$$-RN = \frac{\partial N}{\partial t}$$

gives

$$N_t = N_0 e^{-Rt},$$

or, in finite difference,

$$R = \frac{1}{t'} \ln \left[ \frac{\sum_{J=1}^{JMAX} n(J)_{t=0}}{\sum_{J=1}^{JMAX} n(J)_{t=t'}} \right]. \tag{26}$$

Determining the diffusion coefficient is more difficult and requires a trial-and-error solution beginning with an assumed value for D, and a means of convergence. A general solution to the mass diffusion equation (1) is the Fourier solution in which generality is provided by specifying the initial distribution through the coefficients, $a_m$. That is,

$$n(x,t)$$

$$= a_0 e^{-Rt} + \sum_{m=1}^{\infty} a_m \cos \frac{m\pi x}{\ell} e^{-\left(\frac{m^2\pi^2 D}{\ell^2} + R\right)t}. \tag{27}$$

Then the following relationships are determined:

$$\frac{\partial n(x,t,D)}{\partial t}$$

$$= -a_0 R e^{-Rt} - \sum \left(\frac{m^2\pi^2 D}{\ell^2} + R\right) a \cos \frac{m\pi x}{\ell} e^{-\left(\frac{m^2\pi^2 D}{\ell^2}\right)t}, \tag{28}$$

and

$$\frac{\partial n(x,t,D)}{\partial D}$$

$$= 0 - \sum \frac{m^2\pi^2 t}{\ell^2} a_m \cos \frac{m\pi x}{\ell} e^{-\left(\frac{m^2\pi^2 D}{\ell^2} + R\right)t}. \tag{29}$$

Multiplying Eq. 29 by $\frac{D}{t}$ and subtracting Eq. 28 gives,

$$\frac{D}{t'} \left(\frac{\partial n}{\partial D}\right)_{t,x} - \left(\frac{\partial n}{\partial t}\right)_{D,x} = Rn, \tag{30}$$

or

$$\left(\frac{\partial n}{\partial D}\right) = \frac{t'}{D} \left[Rn + \left(\frac{\partial n}{\partial t}\right)\right],$$
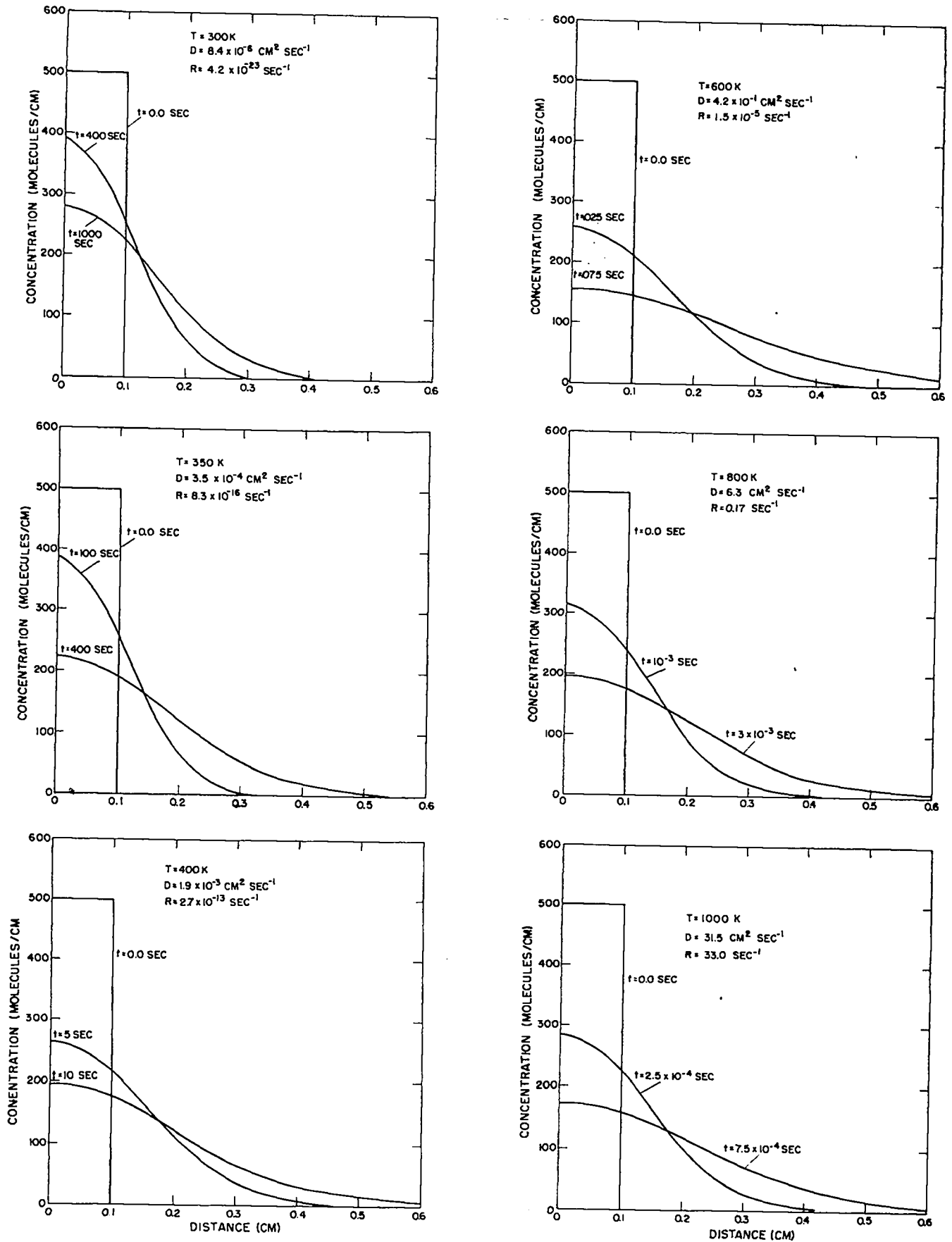
Fig. 4. Indium on gas-covered tantalum at various temperatures.

and then,

$$\Delta D = \left(\frac{\partial D}{\partial n}\right) \Delta n = \frac{D}{t' \left[Rn + \left(\frac{\partial n}{\partial t}\right)\right]} \Delta n. \qquad (31)$$

Finally, Eq. 31 is weighted by mass, summed over all nodes, and normalized, giving

$$\Delta D = \frac{D \cdot \sum_{J=1}^{JMAX} \frac{n_J \, \Delta n_J}{Rn_J + \left(\frac{\partial n}{\partial t}\right)_J}}{t' \cdot \sum_{J=1}^{JMAX} n_J}, \qquad (32)$$

where the values $\Delta n_J$ are the difference between the desired measured values and the latest calculation trial at $t'$, and the values $(\partial n/\partial t)_J$ are taken from the last time step of the calculation. It is required that

$$\left[Rn_J + \left(\frac{\partial n}{\partial t}\right)_J\right] > \varepsilon_3$$

to prevent divergence. Further, solution requires that,

$$\left|\Delta n_J\right| \leq \varepsilon_2$$

for all nodes. The calculation is redone using better values of D through Eq. 32 until this occurs.

This technique was checked by inputting results (two concentration distributions) from a previous run. The program calculated the evaporation coefficient and converged upon the diffusion coefficient in five cycles to an acceptable degree of accuracy.

The third case solved by the program is the "hot-point" problem. Beginning with a bare wire,

$$n_J = 0 \; ,$$

mass is deposited on a central point of the wire at each time step according to,

$$\Delta n_1 = \frac{r\Delta t}{2\Delta x} \; .$$

Two points at the ends of the wire are then maintained at zero concentration (the last node, or evaporation point),

$$n_{JMAX} = 0.$$

The rate of flow out of each hot point is just,

$$\phi = \frac{D}{\Delta x} \left(n_{JMAX-1} - n_{JMAX}\right) .$$

Figures 5, 6, and 7 show plots of the hot-point evaporation rate versus time for indium on gas-covered tantalum at 350, 400, and 500°K. Indium was deposited at the rate of 500 molecules per second, and evaporated at two points 3 cm from the deposition point. These curves are characteristic of the estimated diffusion coefficients.
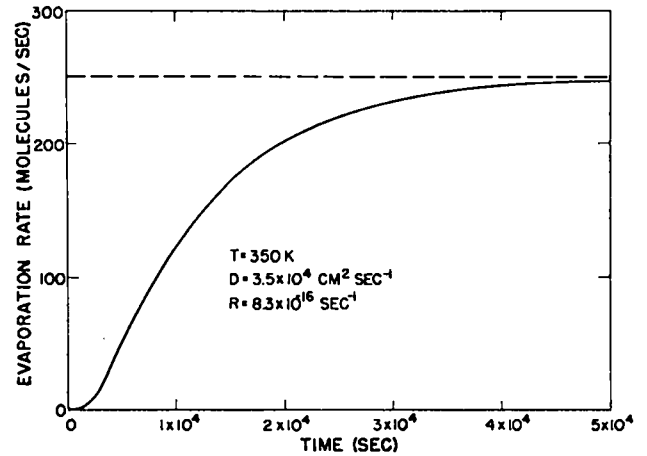


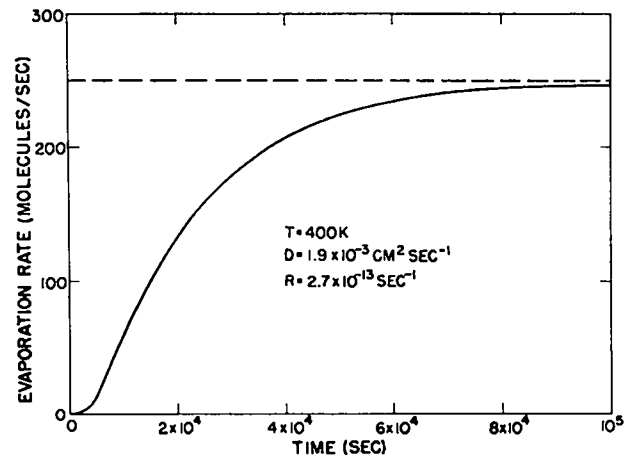Fig. 5. "Hot-Point" problem for indium on tantalum at 350°K.



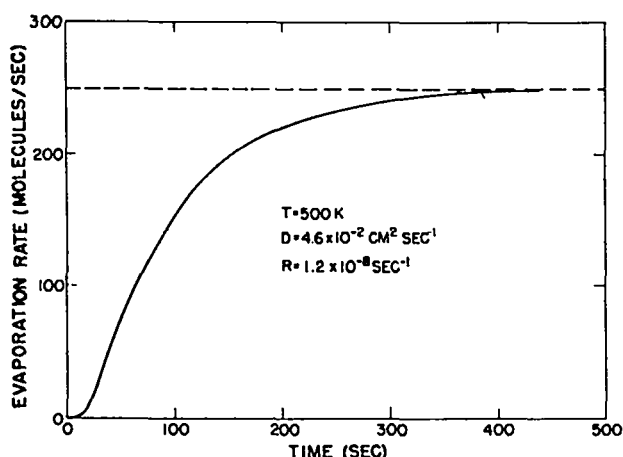Fig. 6. "Hot-Point" problem for indium on tantalum at 400°K.

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Fig. 7. "Hot-Point" problem for indium on tantalum at 500°K.

## CODE INPUT
(Cases of any type may be run back-to-back.)

First Card - format (20A4)

Title card consisting of up to 79 alphanumeric characters preceded by a "1" punch in column 1.

Second Card - format (16I5)

NTYPE   - 0 - gives a diffusion run with all quantities known

1 - gives convergence of diffusion and evaporation coefficients given two concentration distributions

2 - the "hot-point" problem

NMAX   - the maximum number of time steps allowed

NPRINT - the printing frequency in number of time steps

IMAX   - the maximum number of iterations per time step

JMAX   - the initial number of nodes on the wire

JADD   - the number of nodes to be added at the end of each time step, depending upon EPS4. NOTE: if NTYPE = 2, JADD must = 0.

Third Card - format (8E10.3)

D     - diffusion coefficient

R     - evaporation coefficient

DT    - time step

DXI   - node spacing

DELT   - maximum time allowed, or time between input distributions

Fourth Card - format (8E10.3)

B     - Liebmann parameter

EPS1  - iterative concentration convergence criterion

EPS2  - allowable standard deviation of total mass, final-calculated and experimental, for NTYPE = 1

EPS3  - prevents blowup in recalculation of the diffusion rate

EPS4  - concentration criterion determines the JMAX node adjustment   NOTE: EPS4 must be negative for NTYPE = 2.

EPS5  - check on DELT

EPS6  - linearity limit, 1 + R$\Delta$t

Fifth Card - format (8E10.3)

For the case NTYPE = 0, input

X3(J)  - the initial concentration distribution for JMAX nodes
For NTYPE = 1, input (as separate blocks)

X3(J)  - the initial concentration distribution for JMAX nodes, and

X4(J)  - the final distribution
For NTYPE = 2, input

RIN    - rate of mass deposited on the wire

Sixth Card, etc. - format (8E10.3)

Continuation of fifth card if required.

## NOMENCLATURE

a   - Fourier square-wave width

$a_m$  - Fourier series coefficients

D   - Surface mass diffusion coefficient, $cm^2$ $sec^{-1}$

e   - Natural logarithm base

I   - Iteration number

J   - Node number

n   - Linear mass concentration, molecules $cm^{-1}$

N   - Total mass on the wire, molecules

r   - Rate of mass deposited on the wire, molecules $sec^{-1}$

R   - Evaporation coefficient, $sec^{-1}$

t   - Time, sec

t'  - Time interval between measured distributions

u   - Transformation variable

x   - Linear distance, cm

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$\beta$ — Liebmann parameter

$\Delta D$ — Correction to the diffusion coefficient

$\Delta n_J$ — Difference between theoretical and measured concentrations

$\Delta t$ — Time step, sec

$\Delta x$ — Node spacing, cm

$\epsilon_1$ — Concentration convergence criterion

$\epsilon_2$ — Allowable standard deviation of total mass

$\epsilon_3$ — Prevents blowup in diffusion rate

$\epsilon_4$ — Concentration criterion for extending nodes

$\epsilon_5$ — Check on DELT

$\epsilon_6$ — Linearity criterion

$\phi$ — Evaporation rate, molecules $sec^{-1}$

REFERENCES

1. Paul A. Redhead, "Thermal Desorption of Gases," Vacuum, 12, 203 (1962).

2. Norman F. Ramsey, Molecular Beams, Oxford University Press, London, 1956.

3. J. Mathews and R. L. Walker, Mathematical Methods of Physics, W. A. Benjamin, Inc., New York 1965.

4. G. H. Miller, "Interaction of Atoms With Surfaces," p. 549 of Rarified Gas Dynamics, Supplement 3, Vol. 2, of Advances in Applied Mechanics, Academic Press, Inc., New York 1966.

5. Manfred Kaminsky, 4th Annual Surface Physics Symposium, Washington State University, 1966.