RM-558

NORMAL EVAPORATION OF
BINARY ALLOYS

November 1972
NORMAL EVAPORATION OF BINARY ALLOYS

by

C. H. Li

Materials and Structural Mechanics

November 1972

Approved by: Charles E. Mack, Jr.
Director of Research
ACKNOWLEDGMENT

The author wants to thank Prof. F. F. Y. Wang, Dr. J. L. Mukherjee, and Mr. K. P. Gupta, all of State University of New York, Stony Brook, our associate team members under NASA Contract NAS 8-27891, for stimulating discussions and help in data analyses.
ABSTRACT

In the study of normal evaporation, it is assumed that the evaporating alloy is homogeneous, that the vapor is instantly removed, and that the alloy follows Raoult's law. The differential equation of normal evaporation relating the evaporating time to the final solute concentration is given and solved for several important special cases. Uses of the derived equations are exemplified with a Ni-Al alloy and some binary iron alloys. The accuracy of the predicted results are checked by analyses of actual experimental data on Fe-Ni and Ni-Cr alloys evaporated at 1600°C, and also on the vacuum purification of beryllium. These analyses suggest that the normal evaporation equations presented here give satisfactory results that are accurate to within an order of magnitude of the correct values, even for some highly concentrated solutions. Limited diffusion and the resultant surface solute depletion or enrichment appear important in the extension of this normal evaporation approach.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Item</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Differential Equation of Normal Evaporation</td>
<td>2</td>
</tr>
<tr>
<td>Special Case Solutions of the Normal Evaporation Equation</td>
<td>4</td>
</tr>
<tr>
<td>Examples of Computation</td>
<td>8</td>
</tr>
<tr>
<td>Accuracy of Predicted Results</td>
<td>18</td>
</tr>
<tr>
<td>Discussion and Conclusion</td>
<td>22</td>
</tr>
<tr>
<td>References</td>
<td>23</td>
</tr>
</tbody>
</table>
INTRODUCTION

In normal evaporation, we assume that the evaporating alloy is always homogeneous in composition, that the vapor is instantly removed, and that the alloy follows the Raoult's law (Ref. 1). Such conditions exist or are approached in an induction-stirred, melt-in-vacuum or liquid drop-in-space.

This memorandum deals with the normal evaporation of binary alloys. In particular, we study the evaporative segregation patterns, i.e., the type and degree of enrichment or depletion of solute in the evaporating source, at different evaporation temperatures and times.
DIFFERENTIAL EQUATION OF NORMAL EVAPORATION

The appendix of Ref. 2 gives the exact solution for the normal evaporation of binary alloys. This equation relates the concentration of the solute, m, at a time, t, when the mole fraction of the alloy remaining is F, as follows:

\[
F = \frac{N}{N_0} = \left(\frac{m}{m_0}\right) \frac{V}{U-V} \frac{U}{U-V} \left(\frac{1 - m}{1 - m_0}\right)
\]  

(1)

where \( N \) and \( N_0 \) are, respectively, the number of moles of both solvent and solute at evaporating times \( t = t \) and \( t = 0 \); \( m_0 \) is the initial molar concentration of the alloy; and \( U \) and \( V \) are, respectively, the evaporation rates of pure solute and solvent.

For pure solute and solvent, respectively, these evaporation rates in \( \text{mol/cm}^2/\text{sec} \) are

\[
U = K 10^{\frac{A_u - B_u}{T}} \left(\frac{M_u T}{10^6}\right)^{-\frac{1}{2}}
\]

(2)

and

\[
V = K 10^{\frac{A_v - B_v}{T}} \left(\frac{M_v T}{10^6}\right)^{-\frac{1}{2}}
\]

(3)

where \( K = 5.833 \times 10^{-5} \) \( \alpha \), \( \alpha = 1 \) for most metals (Ref. 1); \( M_u \) and \( M_v \) are, respectively, the molecular weights of the solute and solvent atoms; \( T \) is the evaporating temperature in degrees Kelvin; and \( A_u \) and \( B_u \) or \( A_v \) and \( B_v \) are evaporating constants for the solute or solvent given, for example, by Ref. 1.
Differentiating Eq. (1) yields

\[ dm = \frac{(U - V)m(1 - m)}{[mU + (1 - m)V]N} \ dN \]  

(4)

but

\[ dN = - [mU + (1 - m)V]A \ dt \]  

(5)

where \( A \) is the evaporating area of the alloy, assumed constant here.

Substituting Eq. (5) into Eq. (4) results in

\[ dt = Gm^\alpha (1 - m)^\beta dm \]  

(6)

where

\[ G = - \frac{N_0 (1 - m)^{\alpha+2}}{A(U - V)^{\alpha+1}} \]  

(7)

\[ \alpha = (2V - U)/(U - V) \]  

(8)

\[ \beta = (V - 2U)/(U - V) \]  

(9)
SPECIAL CASE SOLUTIONS OF THE
NORMAL EVAPORATION EQUATION

Equations (6)-(9) allow us to determine the evaporating time, $t$, for an alloy to reach a specific solute concentration, $m$. Unfortunately, these equations are not exactly solvable in the general case. All of the following special and important cases, (except Case V), however, are solvable in closed forms.

Case I: The solute is much more evaporative than the solvent, i.e., $U \gg V$; or $\alpha = -1$ and $\beta = -2$. In this case

$$\frac{dt_1}{dm} = \frac{G_1}{m(1 - m)^2}$$

(10)

where

$$G_1 = -\frac{N_o(m_o)}{AU}$$

and

$$t_1 = G_1 \left[ \ln \frac{(1 - m_o)m}{m_o(1 - m)} + \frac{m - m_o}{(1 - m_o)(1 - m)} \right]$$

(11)

When $m \sim m_o$, the second term in the bracket is nearly 0. The evaporation time for this first case, $t_1$, is then a logarithmic function of $m$, as has been experimentally observed (see e.g., Ref. 3).

Also, when $m \sim m_o \sim 0$,

$$t_1 \sim \frac{N_o}{AU} \ln \frac{m_o}{m}$$

(12)
Case II: The solvent is much more evaporative than the solute, i.e., $V \gg U$; or $\alpha = -2$ and $\beta = -1$. In this case

$$dt_2 = \frac{G_2 \, dm}{(1 - m)^2 m}$$  \hspace{1cm} (13)

where

$$G_2 = \frac{m \, N}{AV}$$

and

$$t_2 = G_2 \left[ \ln \frac{(1 - m) m}{m_0 (1 - m)} + \frac{m - m_0}{m_0 m} \right]$$  \hspace{1cm} (14)

For dilute solutions (i.e., $m \approx m_0 \approx 0$), $t_2$ also becomes a logarithmic function of $m$, as has been observed.

Case III: $\alpha = (2V - U)/(U - V) = 0$, i.e., $U = 2V$ and $\beta = -3$

$$t_3 = G_3 \left[ (1 - m)^{-2} - (1 - m_0)^{-2} \right]$$  \hspace{1cm} (15)

where

$$G_3 = -\frac{N_0 (1 - m_0)^2}{2AVm_0}$$

Case IV: $\beta = (V - 2U)/(U - V) = 0$, i.e., $V = 2U$ and $\alpha = -3$. In this case

$$t_4 = G_4 \left( m^{-2} - m_0^{-2} \right)$$  \hspace{1cm} (16)
where

\[ G_4 = - \frac{N_m^2}{2A\mu(1 - m_o)} \]

Equations (15) and (16) show that under some conditions, the evaporating time, \( t \), is more adequately represented by linear functions of \( (1 - m)^{-2} \) or \( m^{-2} \), rather than by logarithmic functions of \( m \).

Case V: For relatively dilute alloys, i.e., \( m \) and \( \beta m \ll 1 \), the following solution by series expansion can be obtained from Eq. (6):

\[
dt_5 = Gm \alpha \left[ 1 - \beta m + \frac{(\beta m)^2}{2!} + \cdots + (-1)^i \frac{(\beta m)^i}{i!} + \cdots \right] \tag{17}
\]

and

\[
t_5 = G \left[ \frac{m^{\alpha+1} - m_o^{\alpha+1}}{\alpha + 1} - \frac{m^{\alpha+2} - m_o^{\alpha+2}}{\alpha + 2} + \cdots + (-1)^i \frac{m^{\alpha+i+1} - m_o^{\alpha+i+1}}{(\alpha + i + 1)i!} \beta^i \right] \tag{18}
\]

For computer calculations, it is desirable to know the ratio of the \( i \)th term to the \( (i - 1) \)th term, thus

\[
- \frac{T_i}{T_{i-1}} = \frac{\beta(\alpha + 1)(m^{\alpha+i+1} - m_o^{\alpha+i+1})}{i(\alpha + i + 1)(m^{\alpha+i} - m_o^{\alpha+i})} \tag{19}
\]

which is generally less than \( \beta m/i \) or \( \beta m_o/i \).
Because $\beta m \ll 1$ and $i$ constantly increases with each additional term, this series converges rapidly unless $\beta$ is very large, i.e., unless $U = V$, which leads to the following interesting case:

Case VI: The solute and solvent are evaporating at equal rates, i.e., $U = V$. In this case, we would expect

$$m = m_0 \quad \text{for all} \quad t.$$  \hspace{1cm} (20)

There is, then, no evaporative segregation, that is, there is neither solute enrichment nor depletion in the evaporating source.

For any pair of solvent and solute, there is a unique temperature, $T_s$, at which $U = V$ and, hence, the alloy concentration remains stable or constant. Equations (2) and (3) give:

$$T_s = \frac{B_u - B_v}{A_u - A_v - 0.5 \log(M_u/M_v)}$$  \hspace{1cm} (21)

Case VII: With extremely dilute alloys, i.e., $m \ll m_0 \ll 0$, we have (Ref. 2)

$$F = N/N_0 = (m/m_0)^{\alpha+1}$$  \hspace{1cm} (22)

Hence,

$$t_7 = \frac{N}{AV} \left[ 1 - (m/m_0)^{\alpha+1} \right]$$  \hspace{1cm} (23)
EXAMPLES OF COMPUTATION

- The Ni-Al System:

As an example of the use of the various derived equations, the evaporation behavior of an alloy containing 8 percent by weight of Al in Ni at the melting point of pure Ni (i.e., 1453°C) is computed. Here, the solute element (Al) is comparatively highly evaporative relative to the solvent (Ni). Equation (11), therefore, applies, and the time, $t_1$, to reach a final solute concentration $m$ from a specified initial concentration, $m_0$, is directly proportional to $N_0A/U$ (in the $G_1$ constant). Table 1 gives the times to reach various final Al concentrations for one mole (53.66g) of the 8 percent Al in Ni alloy ($m_0 = 0.159$) evaporating at 1453°C from its (supposedly constant) 10 cm$^2$ surface.

Table 1

NORMAL EVAPORATION OF 8% BY WEIGHT ALUMINUM IN NICKEL AT 1453°C

<table>
<thead>
<tr>
<th>Final Solute Concentration</th>
<th>Alloy Remaining</th>
<th>Evaporation Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Fraction</td>
<td>Mole Fraction</td>
<td>Weight (g)</td>
</tr>
<tr>
<td>0.080</td>
<td>0.1590</td>
<td>53.66</td>
</tr>
<tr>
<td>0.079</td>
<td>0.1573</td>
<td>53.60</td>
</tr>
<tr>
<td>0.078</td>
<td>0.1555</td>
<td>53.53</td>
</tr>
<tr>
<td>0.077</td>
<td>0.1536</td>
<td>53.47</td>
</tr>
<tr>
<td>0.076</td>
<td>0.1518</td>
<td>53.41</td>
</tr>
<tr>
<td>0.075</td>
<td>0.1500</td>
<td>53.34</td>
</tr>
<tr>
<td>0.074</td>
<td>0.1481</td>
<td>53.28</td>
</tr>
<tr>
<td>0.073</td>
<td>0.1463</td>
<td>53.22</td>
</tr>
<tr>
<td>0.072</td>
<td>0.1444</td>
<td>53.15</td>
</tr>
<tr>
<td>0.071</td>
<td>0.1426</td>
<td>53.09</td>
</tr>
<tr>
<td>0.070</td>
<td>0.1407</td>
<td>53.03</td>
</tr>
</tbody>
</table>
Iron Alloys:

The evaporation behavior of binary iron alloys containing 20 different solute elements has also been studied. Table 2, listing

Table 2

EQUI-EVAPORATIVE TEMPERATURES FOR TWENTY BINARY IRON ALLOYS

<table>
<thead>
<tr>
<th>Solute</th>
<th>U/V at 1600°C</th>
<th>T_s, °C</th>
<th>Solute</th>
<th>U/V at 1600°C</th>
<th>T_s, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>3.765 x 10^6</td>
<td>13,540</td>
<td>W</td>
<td>4.412 x 10^{-12}</td>
<td>-69,590</td>
</tr>
<tr>
<td>Zn</td>
<td>2.065 x 10^6</td>
<td>15,610</td>
<td>C</td>
<td>8.210 x 10^{-8}</td>
<td>5,263</td>
</tr>
<tr>
<td>Mg</td>
<td>9.074 x 10^5</td>
<td>19,610</td>
<td>Mo</td>
<td>1.879 x 10^{-7}</td>
<td>-12,130</td>
</tr>
<tr>
<td>Ca</td>
<td>5.503 x 10^4</td>
<td>9,335</td>
<td>Zr</td>
<td>1.950 x 10^{-6}</td>
<td>-47,790</td>
</tr>
<tr>
<td>Pb</td>
<td>3.333 x 10^3</td>
<td>4,976</td>
<td>B</td>
<td>6.832 x 10^{-5}</td>
<td>9,510</td>
</tr>
<tr>
<td>Mn</td>
<td>1.070 x 10^3</td>
<td>20,740</td>
<td>V</td>
<td>3.804 x 10^{-3}</td>
<td>8,574</td>
</tr>
<tr>
<td>Al</td>
<td>45.65</td>
<td>7,918</td>
<td>Ti</td>
<td>2.254 x 10^{-2}</td>
<td>34,650</td>
</tr>
<tr>
<td>Cu</td>
<td>12.25</td>
<td>5,613</td>
<td>Co</td>
<td>4.362 x 10^{-1}</td>
<td>4,318</td>
</tr>
<tr>
<td>Sn</td>
<td>9.978</td>
<td>2,686</td>
<td>Si</td>
<td>5.238 x 10^{-1}</td>
<td>2,825</td>
</tr>
<tr>
<td>Cr</td>
<td>3.158</td>
<td>-215</td>
<td>Ni</td>
<td>5.897 x 10^{-1}</td>
<td>3,036</td>
</tr>
</tbody>
</table>

the equi-evaporative temperatures for these 20 different alloy systems, also gives the ratios of the solute evaporating rate, U, at 1600°C, to that of the solvent iron, V. At 1600°C, 10 of these solute elements evaporate faster than the solvent (the three left columns) and 10 slower (the three right columns). Moreover, these ratios vary widely over 18 decades, from 4.41 x 10^{-12} for the slowest evaporating, W, to 3.76 x 10^6 for the fastest evaporating, Cd. Because of this wide variation in evaporating rates,
and because of the extreme sensitivities of the evaporating surface to unsuspected contaminants, predicted or experimental evaporating results cannot generally be very accurate.

The equi-evaporative temperatures in iron alloys also vary widely. Binary iron alloys containing Cr, Zr, Mo, and W have no practical equi-evaporative temperatures. One can, therefore, always expect these alloys to change compositions continuously with the evaporating time.

Table 3 shows the effect of evaporating temperature on the U/V ratios for four different solute elements Mg, Ca, Mn, and Al. In the range of 1500°C to 1900°C and beyond, increasing

<table>
<thead>
<tr>
<th>Solutes</th>
<th>Temp (°C)</th>
<th>Mg</th>
<th>Ca</th>
<th>Mn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1500</td>
<td>2132.0</td>
<td>118.2</td>
<td>1.649</td>
<td>0.06037</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>907.4</td>
<td>55.03</td>
<td>1.070</td>
<td>0.04565</td>
</tr>
<tr>
<td></td>
<td>1700</td>
<td>421.2</td>
<td>27.68</td>
<td>0.7261</td>
<td>0.03552</td>
</tr>
<tr>
<td></td>
<td>1800</td>
<td>210.5</td>
<td>14.88</td>
<td>0.5110</td>
<td>0.02831</td>
</tr>
<tr>
<td></td>
<td>1900</td>
<td>112.1</td>
<td>8.466</td>
<td>0.3719</td>
<td>0.02304</td>
</tr>
</tbody>
</table>

the evaporating temperatures always decreases the U/V ratios. This can also be seen from Table 2, as the equi-evaporative temperatures shown for these four binary iron alloys are higher than 1600°C, at which temperature the four solute elements evaporate
much faster than the solvent iron. Table 3 also shows that for the same temperature variation, the more evaporative the solute element, the more percentage variation the U/V ratio. In the case of Mg, e.g., the U/V ratio decreases by about 20 times from 1500°C to 1900°C, whereas for Al, the same ratio decreases only by less than three times over the same temperature interval.

Figure 1 shows the effect of solute elements and evaporating temperature, T, on the evaporating time, t, for a given set of initial and final solute concentrations (i.e., \( m_o = 0.01 \) and \( m = 1 \) ppm). For given \( m_o \) and \( m \), the \( \log t \) versus \( 1/T \) curves for these highly evaporative solute elements are approximately linear and have positive slopes. This can be expected from Eq. (11) since, for given \( m_o \) and \( m \), \( \log t \) is linearly related to \( B/T - 0.5 \log T \), and since \( 0.5 \log T \) is small relative to \( B/T \) within the evaporating temperature range studied. Thus, one can determine, from Fig. 1, the value of the elemental evaporating constant \( B \), or heat of evaporation \( \Delta H = 4.574B \) (Ref. 1), for the solute elements by plotting \( \log t \) versus \( 1/T \) and measuring the slope of the resultant, nearly straight lines.

In Fig. 2, the \( \log t \) versus \( 1/T \) relationships also appear nearly linear for all the four different initial concentrations (i.e., \( m_o = 10^{-1}, 10^{-2}, 10^{-3}, \) and \( 10^{-4} \)) of Al in Fe. This can also be seen from Eqs. (11) and (12). All these nearly straight lines have identical slopes, from which the heat of evaporation of pure Al can be evaluated.

Figures 3 and 4 display the effect on the evaporating time, \( t \), of final solute concentration, \( m_f \), and either initial concentration \( m_o \) (in Fig. 3) or solute elements (in Fig. 4).

Figure 5 indicates that Mg, Ca, and Mn in Fe alloys are so evaporative at 1600°C that practically all of these elements
Fig. 1 Evaporating Times for Different Dilute Iron Alloys to Change Concentration from $m_0 = 0.01$ to $m = 1$ ppm
Fig. 2 Evaporating Times for Dilute Iron Alloys Containing Al and Starting at Four Different Initial Concentrations, to Reach a Final Concentration of $m = 1$ ppm.
Fig. 3 Effect of Initial and Final Solute Concentrations on the Evaporating Times in Dilute Iron Alloys Containing Al at 1600°C
Fig. 4 Effect of Solute Elements and Final Concentration on the Evaporating Times in Dilute Iron Alloys at 1600°C
Fig. 5 Evaporation Loss of Dilute Iron Alloys at 1600°C As a Function of Solute Elements and Final Solute Concentrations
are removed by evaporation, without much evaporative loss of the solvent Fe atoms. On the other hand, Al is comparatively less evaporative so that much of the solvent Fe atoms are evaporated off together with Al. To achieve a purification factor of $10^7$ (i.e., to $m = 10^{-9}$) from $m_0 = 0.01$, for example, the initial evaporating alloy must lose over 30 percent of its material.
ACCURACY OF PREDICTED RESULTS

To check the validity of our derived equations for normal evaporation of binary alloys, the current literature has been searched. Several sets of alloy evaporation data have been found that are amenable to normal evaporation analysis. These sets include the following:

- The Fe-Ni and Ni-Cr Systems:

An analysis has been made of the data by Obradovic et al. (Ref. 4) for Fe-Ni and Ni-Cr alloys evaporated at 1600°C for different times under various ambient pressures. In the 80% Ni-20% Cr case, evaporation started with \( N_0 = 0.7582 \) moles of the alloy having an evaporating area \( A = 10.0 \text{ cm}^2 \). The solute and solvent evaporating rates are, respectively, \( U_{\text{Cr}} = 3.479 \times 10^{-5} \) and \( V_{\text{Ni}} = 6.386 \times 10^{-6} \text{ mol/cm}^2/\text{sec} \). This is a case where the solute, Cr, is comparatively highly evaporative relative to the solvent, Ni. Hence, the evaporating time \( t_1 \) given in Eq. (11) applies, i.e.,

\[
t_1 = G_1 \left[ \ln \frac{(1 - m_o)m}{m_0(1 - m)} + \frac{m - m_o}{(1 - m_o)(1 - m)} \right]
\]

where \( G_1 = -N_0 \frac{(1 - m_o)}{AU} \), and \( m_o \) and \( m \) are the initial and final molar solute concentrations in the alloy.

Least square fits of the Obradovic data give nearly constant values of observed \( G_1 \): \(-1.785\), \(-5.064\), and \(-5.064 \times 10^4 \text{ sec} \) for ambient pressures of 1, 100, and 500 (x \( 10^{-3} \text{ torr} \)). The calculated values of \( G_1 \), though also nearly constant, are, however, one order of magnitude smaller, indicating surface solute depletion. Similar analysis for the 60% Fe-40% Ni alloy evaporated with
and \( V_{Fe} = 1.081 \times 10^{-5} \text{ mol/cm}^2/\text{sec} \). Here, the solvent Fe is much more evaporative than the solute Ni, and Eq. (14) applies. The values of observed evaporating coefficients \( G_2 = \frac{m_o N_o}{AV} \) are 2.469, 1.369, and 8.386 \((x 10^4 \text{ sec})\), for ambient pressures of 1, 100, and 500 \((x 10^{-3} \text{ torr})\), respectively. The calculated \( G_2 \)'s are again nearly constant but also an order of magnitude smaller than the observed \( G_2 \)'s, again indicating solvent depletion (or solute enrichment) at the surface. Details of these analyses are given in Ref. 5.

- Beryllium Purification

The kinetics of normal evaporation for beryllium have been quantitatively checked with actual results of beryllium purification during vacuum induction melting. Details are given in Ref. 6. In these tests, beryllium was crucible-free, induction-melted under an ambient pressure of \( 10^{-6} \text{ torr} \). The actual temperature of the melt was not known, and the exact evaporating rates for the beryllium solvent and various solute elements cannot be computed. However, because all solute elements (i.e., Fe, Cr, Mn, Ni, Si, Al, Mg, Cu, Zn, and Na) and the solvent, Be, were evaporating from the same or common liquid-gas interface of a fixed area for the same length of time, we can compute the values of \( P \), defined as the product of the evaporating time, \( t \), and solvent evaporating rate, \( V \) (for \( V \gg U \)), or solute evaporating rate, \( U \) (for \( U \gg V \)); thus: \( P = tV \) or \( tU \). Table 4 gives the initial concentrations and final concentrations (in ppm) of the various solutes, together with the value of \( P \), actual surface concentrations, ratio of actual surface to bulk concentrations, and effective times to reach the final concentrations under the assumption that the evaporating temperature was 1250°C. The following conclusions can be drawn from Table 4:

\[ N_o = 0.7478 \text{ moles and } A = 10.0 \text{ cm}^2 \text{ gives } U_{Ni} = 6.386 \times 10^{-6} \text{ and } V_{Fe} = 1.081 \times 10^{-5} \text{ mol/cm}^2/\text{sec}. \]
1. The solute elements can be divided into three groups: Fe, Cr, Ni, Si, and Cu evaporate much more slowly than Be; Mg, Zn, and Na evaporate much more rapidly than Be; Al evaporates at about the same rate as Be.

2. The computed times to reach the final concentrations under normal evaporation conditions (complete liquid mixing) are fairly constant for the solute elements that evaporate much slower than Be (i.e., Fe, Cr, Ni, Si, and Cu), being about $4 \times 10^4$

3. The computed times to reach the final concentrations for the highly evaporative Mg, Zn, and Na are also fairly constant, but about four orders of magnitude smaller.

4. After correction for limited liquid mixing (Ref. 7), the effective times to reach the final concentrations are much more constant, even between the groups of solute elements. In particular, the highly evaporative elements Mg, Zn, and Na have their results improved by several orders of magnitude.

5. Limited liquid diffusion must, therefore, be considered, particularly for the highly evaporative elements.

6. The surface solute concentrations can be changed by up to six orders of magnitude, so that the effective evaporating rates can be similarly changed.
Table 4
PURIFICATION KINETICS OF BERILLIUM DURING CRUCIBLE-FREE VACUUM INDUCTION MELTING

<table>
<thead>
<tr>
<th>Solute Element</th>
<th>Initial Conc., $m_0$, ppm Atomic</th>
<th>Final Conc., $m_f$, ppm Atomic</th>
<th>Ideal Evap. Rate at 1500°C, $U_1$, moles/cm²/sec</th>
<th>Time to Reach Final Conc., $t_f$, secs</th>
<th>$P = t_f U_1$ or $= t_f V_1$ **</th>
<th>Surface Conc., $m_s$, Atomic</th>
<th>$m_s/m_0$</th>
<th>Effective Time to Reach Final Conc., $t_e$, secs</th>
<th>$t_e$, 1400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.55</td>
<td>4.5</td>
<td>$2.7885 \times 10^{-6}$</td>
<td>$2.69 \times 10^3$</td>
<td>0.655</td>
<td>$1.34 \times 10^{-4}$</td>
<td>$8.60 \times 10^1$</td>
<td>$2.69 \times 10^3$</td>
<td>3.49</td>
</tr>
<tr>
<td>Cr</td>
<td>0.65</td>
<td>2.1</td>
<td>$8.7887 \times 10^{-6}$</td>
<td>$2.84 \times 10^3$</td>
<td>0.690</td>
<td>$1.79 \times 10^{-5}$</td>
<td>$2.75 \times 10^1$</td>
<td>$2.84 \times 10^3$</td>
<td>3.48</td>
</tr>
<tr>
<td>Ni</td>
<td>4.95</td>
<td>7.5</td>
<td>$1.5353 \times 10^{-6}$</td>
<td>$1.39 \times 10^3$</td>
<td>0.340</td>
<td>$7.82 \times 10^{-4}$</td>
<td>$1.57 \times 10^2$</td>
<td>$1.40 \times 10^3$</td>
<td>3.48</td>
</tr>
<tr>
<td>Si</td>
<td>4.50</td>
<td>5.0</td>
<td>$1.3320 \times 10^{-6}$</td>
<td>$0.41 \times 10^3$</td>
<td>0.10</td>
<td>$8.19 \times 10^{-4}$</td>
<td>$1.82 \times 10^2$</td>
<td>$0.41 \times 10^3$</td>
<td>3.48</td>
</tr>
<tr>
<td>Cu</td>
<td>1.50</td>
<td>1.55</td>
<td>$4.2039 \times 10^{-5}$</td>
<td>$0.13 \times 10^3$</td>
<td>0.032</td>
<td>$8.66 \times 10^{-6}$</td>
<td>$5.77$</td>
<td>$0.13 \times 10^3$</td>
<td>3.53</td>
</tr>
<tr>
<td>Al</td>
<td>6.50</td>
<td>4.0</td>
<td>$1.6834 \times 10^{-4}$</td>
<td>$-2.57 \times 10^3$</td>
<td>-0.625</td>
<td>$9.37 \times 10^{-6}$</td>
<td>$1.44$</td>
<td>$-2.57 \times 10^3$</td>
<td>3.49</td>
</tr>
<tr>
<td>Mg</td>
<td>4.0</td>
<td>0.03</td>
<td>$5.9444$</td>
<td>$0.82$</td>
<td>4.892</td>
<td>$1.63 \times 10^{-10}$</td>
<td>$4.00 \times 10^{-5}$</td>
<td>$20.14 \times 10^3$</td>
<td>3.48</td>
</tr>
<tr>
<td>Zn</td>
<td>4.10</td>
<td>0.2</td>
<td>$14.5917$</td>
<td>$0.20$</td>
<td>3.020</td>
<td>$6.82 \times 10^{-11}$</td>
<td>$1.66 \times 10^{-5}$</td>
<td>$12.43 \times 10^3$</td>
<td>3.48</td>
</tr>
<tr>
<td>Na</td>
<td>59.0</td>
<td>8.0</td>
<td>$12.1483$</td>
<td>$0.16$</td>
<td>1.998</td>
<td>$1.17 \times 10^{-9}$</td>
<td>$1.00 \times 10^{-5}$</td>
<td>$8.22 \times 10^3$</td>
<td>3.49</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.465</td>
<td></td>
<td></td>
<td>$5.64 \times 10^3$</td>
<td>3.48</td>
</tr>
</tbody>
</table>

* for $U >> V$

** for $U << V$

$V_1(\text{Be}) = 2.4287 \times 10^{-4}$ moles/cm²/sec

$T = 1500^\circ C$

Ambient Pressure = $10^{-6}$ torr
DISCUSSION AND CONCLUSION

These and other similar analyses suggest that the normal evaporation equations presented in this Memorandum work surprisingly well for the several alloy systems studied so far. These equations generally give results accurately to within an order of magnitude of the correct values, perhaps even for highly concentrated solutions (e.g., 20% Cr in Ni or 40% Ni in Fe). Such accuracies are usually sufficient for many evaporation studies.

In other more critical studies, however, refined evaporation analyses may be needed. In particular, the effect of limited diffusion and, hence, surface depletion or enrichment of the solute, must often be accounted for. This is true especially for the highly evaporative solutes such as, e.g., Mg, Zn, and Na in the solvent Be. We already have results that confirm this conclusion. Details of these results will be published in Ref. 7 and elsewhere.
REFERENCES


Captions

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Evaporating times for different dilute iron alloys to change concentration from $m_0 = 0.01$ to $m = 1$ ppm</td>
</tr>
<tr>
<td>2</td>
<td>Evaporating times for dilute iron alloys containing Al and starting at four different initial concentrations, to reach a final concentration of $m = 1$ ppm</td>
</tr>
<tr>
<td>3</td>
<td>Effect of initial and final solute concentrations on the evaporating times in dilute iron alloys containing Al at 1600°C</td>
</tr>
<tr>
<td>4</td>
<td>Effect of solute elements and final concentration on the evaporating times in dilute iron alloys at 1600°C</td>
</tr>
<tr>
<td>5</td>
<td>Evaporation loss of dilute iron alloys at 1600°C as a function of solute elements and final solute concentrations</td>
</tr>
</tbody>
</table>