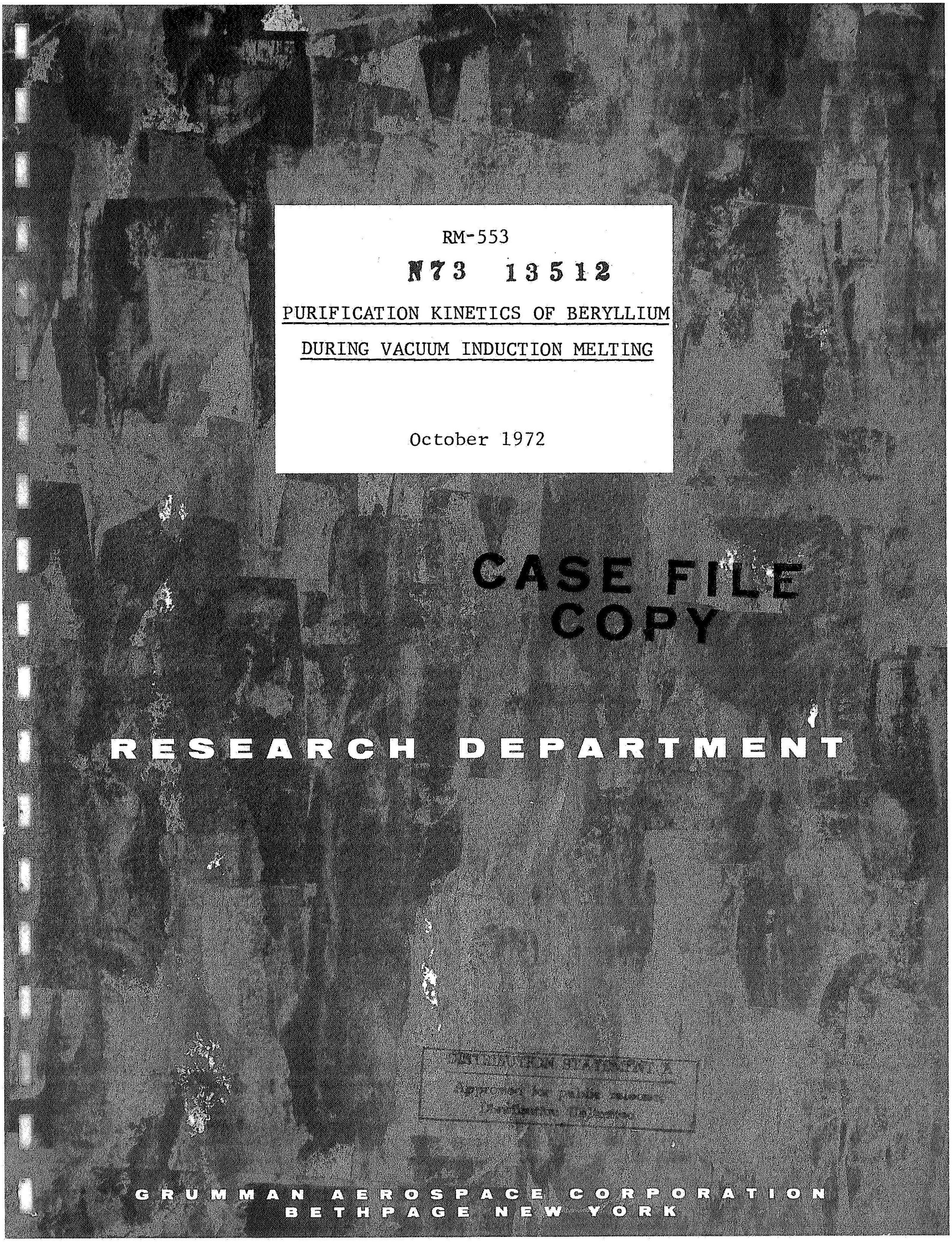

RM-553

N73 13512

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October 1972

RESEARCH DEPARTMENT

GRUMMAN AEROSPACE CORPORATION
BETHPAGE NEW YORK

Grumman Research Department Memorandum RM-553

PURIFICATION KINETICS OF BERYLLIUM DURING VACUUM INDUCTION MELTING

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October 1972

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ACKNOWLEDGMENT

This work was done under NASA Contract No. NAS 8-27891.

ABSTRACT

The kinetics of evaporation in binary alloys have been quantitatively treated. The formalism so developed works surprisingly well for several systems so far studied, notwithstanding the several major assumptions involved. In this memorandum, we have studied the kinetics of purification of beryllium through evaporation data actually acquired during vacuum induction melting. This study shows that normal evaporation equations are generally valid and useful for understanding the kinetics of beryllium purification. The normal evaporation analysis has been extended to cover cases of limited liquid diffusion. It has been shown that under steady-state evaporation, the solute concentration near the surface may be up to six orders of magnitude different from the bulk concentration. Corrections for limited liquid diffusion are definitely needed for the highly evaporative solute elements, such as Zn, Mg, and Na, for which the computed evaporation times are improved by five orders of magnitude. The commonly observed logarithmic relation between evaporation time and final concentration further supports the validity of our normal evaporation equations.

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INTRODUCTION

The kinetics of evaporation in binary alloys have been quantitatively treated by C. H. Li (Refs. 1,2). The formalism so developed works surprisingly well for the several systems so far studied, notwithstanding the several major assumptions involved. Specifically, in this normal evaporation approach, it is assumed that a) the evaporating alloy is always homogeneous in composition, b) the alloy follows Raoult's law, and c) the vapor is instantly removed. In this work, we have studied the kinetics of purification of beryllium through evaporation data actually acquired during vacuum induction melting by R. F. Bunshah and R. S. Juntz (Ref. 3).

EXPERIMENTAL DATA

The details of the vacuum induction melting procedure are as follows. Beryllium (SR grade flakes) in the form of a cylindrical compact was crucible-free induction melted under an ambient pressure of 10^{-6} torr. The cylindrical compact was 1-3/4 inches in diameter and 4 inches high, and weighed about 100-130 g. Since the actual temperature of the melt was not known, for the purpose of our computations, the temperature was assumed, for the sake of comparison, to be 1500°C, a temperature commonly used in Be melting (Ref. 3).

EQUATION OF NORMAL EVAPORATION

The solutions of the kinetic equations for two important cases are given in papers by Li and Mukherjee et al. (Refs. 2,4). In Case I, the solute evaporating rate, U, is much greater than the solvent evaporating rate, V, i.e., $U \gg V$. The equation relating the evaporating time t_1 to final concentration, m, is, for this case,

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

and in Case II when $U \ll V$, the evaporation time is given as follows:

$$t_2 = G_2\left[\ln \frac{(1 - m_o)m}{m_o(1 - m)} + \frac{m - m_o}{mm_o}\right] , \tag{2}$$

where

$G_1 = - N_o(1 - m_o)/AU$

$G_2 = + N_o m_o/AV$, and

m, m_o = mole fractions of solute at $t = t$ and $t = 0$, respectively.

G's are the time constants of evaporation. For Case I when $U \gg V$, solute depletion takes place (or $m < m_o$) and, therefore, the logarithmic term in the parentheses is negative (the second term in the parentheses is, for small values of m and m_o, negligible by comparison with the logarithmic term). Since the evaporating time t_1 must be positive, G_1 must be negative. G_2, on the other hand, is always positive.

In Table 1 the times t_i, to reach the final concentrations m from initial concentration m_o (through evaporation from area A and with an initial total of N_o moles of both solute and solvent) for each element in the melt have been compiled using Eqs. (1) and (2) above. In the table, the ideal evaporation rates at temperature T°K of each element have been computed using the formula given in Ref. 5, viz.,

for the solute:

$$U = K\ 10^{A_u - B_u/T} \Big/ \sqrt{M_u T}$$

and (3)

for the solvent:

$$V = K\ 10^{A_v - B_v/T} \Big/ \sqrt{M_v T}\ ,$$

where $K = 5.833 \times 10^{-5}$ for metals; A_u, B_u, A_v, and B_v are elemental evaporation constants given in Ref. 5; and the M's are molecular weights.

Table 1

PURIFICATION KINETICS OF BERYLLIUM DURING CRUCIBLE-FREE VACUUM INDUCTION MELTING

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

*for $U \gg V$

**for $U \ll V$

$V_i(\text{Be}) = 2.4287 \times 10^{-4}$ moles/cm^2/sec

$T = 1500°C$

Ambient Pressure = 10^{-6} torr

TYPES OF IMPURITIES

Three types of impurities can be distinguished:

Type I. - The impurities that have much higher evaporating rates U than the solvent Be. For these impurities, such as Zn, Na, and Mg, evaporation Eq. (1) should be used.

Type II. - The impurities that have much lower evaporating rates U than the solvent Be. For these impurities, such as Fe, Cr, Ni, Cu, Ti, and Si, Eq. (2) should be used.

Type III. - The impurity that evaporates at about the same rate as the solvent Be, i.e., $U \simeq V$. Only a single element, Al, is in this group. For this impurity, a different evaporation equation in infinite series form should be used (Ref. 2).

PRELIMINARY DATA ANALYSIS

Since the exact temperature of the melt was not known, the exact evaporation rates could not be computed. However, since all the solute and solvent elements were evaporating from the same liquid-gas interface of a fixed area A for the same length of time, we can compute, from the measured m_o's and m's, the values of P, which is the product of the evaporating time and evaporation rate for a given solute with the help of Eqs. (1) and (2). The value of P should be constant for all the solutes.

$$t_1^i = t_1^{ideal} = \frac{-N_o(1 - m_o)}{AU_i}\left[\ln \frac{(1 - m_o)m}{m_o(1 - m)} + \frac{m - m_o}{(1 - m)(1 - m_o)}\right] , \qquad (4a)$$

or

$$t_1^i U_i = t_1^{ideal} U_i = \frac{-N_o(1 - m_o)}{A}\left[\ln \frac{(1 - m_o)}{m_o(1 - m)} + \frac{m - m_o}{(1 - m)(1 - m_o)}\right] = P , \qquad (4)$$

where t_i is the estimated evaporation time computed separately for each element at the assumed temperature of 1500°C. Similarly, from Eq. (2) and the ideal evaporation rate of the solvent V_i at the same temperature, we have:

$$t_2^{ideal} V_{ideal} = P .$$

In Table 1 are listed the value of P's for each element. P is defined, as shown, such that

$$P = t_i \times U_i \quad \text{when} \quad V_i < U_i$$

$$P = t_i \times V_i \quad \text{when} \quad V_i > U_i .$$

It can be seen from Table 1 that P is almost constant for the low vapor pressure (Type II) impurities except for copper.

Because of our three assumptions of normal evaporation, and because of the assumed evaporating temperature of 1500°C, the computed values of t_i vary from element to element, even though they should be identically the same. The variations in t_i, however, are not very large so that the equations presented here are still useful.

The high vapor pressure (Type I) impurities (Mg, Na, Zn) also have uniform P values, which are roughly one order of magnitude higher than those for the low vapor pressure (Type II) elements. The negative value of P for aluminum shows that aluminum cannot be treated by Eqs. (1) and (2) because for this element $U \simeq V$ and a different evaporation equation in infinite series form should be used.

STEADY-STATE EVAPORATION

To explain the large variation in P values among different types of impurity elements, one should consider limited liquid diffusion. The concept of effective evaporation rates, U_e and V_e upon reaching a steady-state condition is now introduced.

$$P = t_e V_e = \text{constant} \tag{1a}$$

or

$$t_i V_i = P = \text{constant} \cong t_e V_e \ , \tag{2a}$$

where the subscripts i refer to ideal or normal evaporation values, while the subscripts e refer to effective or nonnormal values.

In the following paragraphs, the concept of U_e will be developed.

In normal evaporation, we assume that the evaporating alloy is always homogeneous, i.e., the liquid diffusion constant $D_\ell = \infty$. But because of the large (orders of magnitude) differences in evaporation rates of elements, the surface concentration of the solute m_s in the melt is not the same as the bulk concentration m_o due to the limited liquid diffusion. Figure 1 depicts the situation (at $t = 0$) (i.e., initial), and after reaching steady states, for the case $U \gg V$.

For $U \gg V$, the evaporating surface region soon becomes depleted of solute, and the surface concentration of the solute, m_s, will be different from the bulk concentration, m_o, specifically, $m_s \ll m_o$. After the initial transients, a steady-state for the alloy system and evaporating conditions will be reached. The steady-

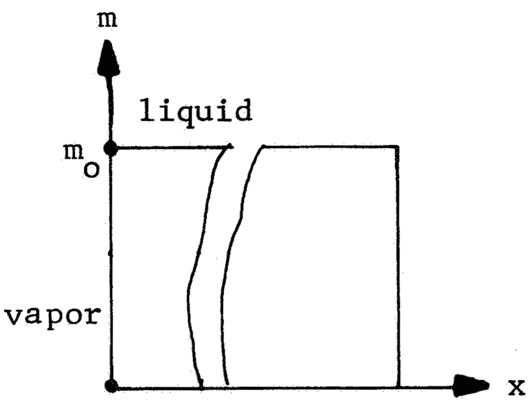

Fig. 1a Initial State, $t = 0$

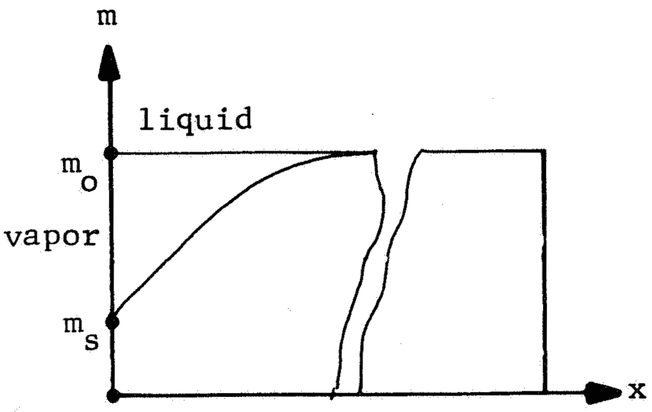

Fig. 1b Steady State, $t \geq t_s$

state concentration profile is shown in Fig. 1b. The equation of the profile, i.e., m versus x, can be derived according to a procedure used by Tiller et al. (Ref. 6) in their study of freezing with limited liquid diffusion, i.e.,

$$m = m_o \left\{ 1 + \frac{m_s - m_o}{m_o} \exp\left(\frac{-R}{D_e} x \right) \right\} , \tag{5}$$

where the receding rate R of the evaporating surface can be computed from U_i, V_i, m_s, M_u, M_v, and material densities.

In steady-state,

$$m_s U_i = m_o U_e , \tag{6a}$$

and

$$(1 - m_s) V_i = (1 - m_o) U_e , \tag{6b}$$

or

$$\frac{m_s U_i}{(1 - m_s) V_i} = \frac{m_o}{1 - m_o} . \tag{6c}$$

Solving for m_s,

$$m_s = \frac{m_o V_i}{(1 - m_o)U_i + m_o V_i} \; . \tag{7}$$

Since

$$m_s U_i = m_o U_e , \tag{8}$$

where U_e is the effective evaporation rate of the solute due to the change in surface concentration. Substituting the m_s from Eq. (7) in Eq. (8) gives

$$U_e = \frac{m_s}{m_o} U_i = \frac{U_i V_i}{(1 - m_o)U_i + m_o V_i} \; . \tag{9}$$

Similarly, for the case $V >> U$,

$$(1 - m_s)V_i = (1 - m_o)V_e \tag{10}$$

or

$$V_e = \frac{1 - m_s}{1 - m_o} V_i = \frac{V_i U_i}{(1 - m_o)U_i + m_o V_i} = U_e \; . \tag{11}$$

Thus, it can be seen mathematically that $V_e = U_e$. This means that in both cases, $U >> V$, or $V << U$, the effective value of U or V is the same. This equality means that in the steady-state, the surface concentration m_s does not change with time, as expected.

Now consider Eq. (7) in some detail. Several cases can be distinguished; these are:

I. — $U \gg V$ and $m_o \simeq m \simeq 0$

$$m_s = \frac{m_o V_i}{(1 - m_o) U_i} = \frac{m_o V_i}{U_i}$$

or (11a)

$$\frac{m_s}{m_o} = \frac{V_i}{U_i} .$$

II. — $V \gg U$

a) $$m_o V_i \gg U_i \quad \text{or} \quad \frac{U_i}{V_i} \ll m_o \qquad (11b)$$

then

$$m_s = 1 .$$

b)

$$m_o V_i \ll U_i \quad \text{or} \quad \frac{U_i}{V_i} \gg m_o \qquad (11c)$$

then

$$m_s = \frac{m_o V_i}{(1 - m_o) U_i} = \frac{m_o V_i}{U_i}$$

when

$$m_o \simeq 0 .$$

c)

$$m_o V_i \simeq U_i \quad \text{or} \quad \frac{U_i}{V_i} \simeq m_o \ .$$

then

$$m_s = \frac{1}{2 - m_o} \simeq \frac{1}{2} \tag{11d}$$

when

$$m_o \simeq 0 \ .$$

The effective evaporation rate of the solutes, U_e, can be computed by Eq. (9). The effective evaporation rates have been variably raised or lowered to equal the ideal evaporation rate of the solvent (Be). In the case of high vapor pressure impurities like Mg, Zn, Na, this means a lowering of evaporating rates by about five orders of magnitude.

The surface concentration, m_s, and the ratio of surface to bulk concentration have been computed in Table 1 by Eq. (7). These ratios must also equal V_i/U_i. Now we have

$$P = t_e U_e = t_i U_i \ .$$

The effective time t_e, to reach the final concentrations m have been computed for all the impurities in Table 1; t_e should be a constant. It can be seen that for the low vapor pressure impurities, t_e is almost constant. Again, the t_e for Cu is one order of magnitude less than others in the low vapor pressure impurity group. Among the high vapor pressure impurities, the t_e is almost constant. It can be seen that t_e for the high vapor pressure impurities is one order of magnitude larger than that of low vapor pressure impurities.

NONIDEAL SOLUTIONS

The normal evaporation equations can be further modified by introducing the concept of solvent-solute interactions. If one considers deviation from the Raoult's law, it can be shown that the evaporation rates of solvent and solute will be changed by a new factor, the activity coefficient. For very dilute solutions, which we are considering, evaporation rates for solute and solvent can be given by $U' = \gamma_u U_e$ and $V' = V_e$, respectively, where γ_u is the activity coefficient of the solute (Henry constant, in this case).

In general, such consideration should not affect the estimated time, t_e, for the type I impurities (Fe, Ni, Cr, Ti, etc.), except in the case of copper. From the available phase diagram, it is evident that Be and Cu atoms have significant interactions with each other and form many compounds (Refs. 7,8). Thus the excess free energy for the system should be negative, resulting in a lower value of γ_{Cu} compared to the ideal solution case $\left(\gamma_{Cu}^{ideal} = 1.0\right)$. In such a situation, V'_{Be} is not very much higher than U'_{Cu}, and this leads to a greater effective time, $t_{e,Cu}$ to reach the final concentration. The exact value of γ_{Cu} is difficult to evaluate because of the lack of data in this composition range.

In the cases of Zn and Mg, the solubility in beryllium is negligible (Ref. 8) and so γ_{Zn} and γ_{Mg} should be greater than one. This would lower the estimated time, t_e, meaning a better agreement with the other elements.

It is important to note that exact calculation for the deviation from the ideal solution case is difficult because of the lack of data, and such estimations are purely qualitative.

CONCLUSIONS

1. Normal evaporation Eqs. (1) and (2) are generally valid and useful for the study of beryllium purification. This agrees with a previous study on the results of Ni-Fe and Ni-Cr systems (Ref. 4).

2. The computed values of $P = t_i U_i$ or $t_i V_i$ are essentially constant for the same type of solute elements, although differing by one order of magnitude between different types of elements.

3. The normal evaporation analysis has been extended to cover cases of limited liquid diffusion. It is shown that under steady-state conditions, the solute concentration near the surface, i.e., m_s, may be up to five orders of magnitude different from the bulk concentration, m_o.

4. Corrections for limited liquid diffusion are definitely needed for the highly evaporative solute elements Mg, Zn, and Na, for which the computed evaporation times, t_e, are improved by three or four orders of magnitude.

5. After these corrections, the computed times are comparable, even between different types of solute elements.

6. The agreement among the computed times can be further improved by considering the deviation from the ideal solution condition. Because of lack of data, it is difficult to give any quantitative calculation.

7. Estimations of solute evaporation behavior are now well within one order of magnitude.

8. The commonly observed logarithmic relation between evaporation time t and final concentration m further supports the validity of our normal evaporation equations. Such relations are, however, true only for widely different solute and solvent evaporating rates and for dilute solutions, as can be seen from Eqs. (1) and (2).

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