A continuous method for determination of the evaporation rate of zinc

Paul Alan O'Neill

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A CONTINUOUS METHOD FOR DETERMINATION
OF THE EVAPORATION RATE OF ZINC

BY

PAUL ALAN O'NEILL, 1943-

A

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ABSTRACT

A method for determination of the evaporation rate of zinc using a continuous recording balance has been devised. Tests were carried out under an inert gas over the range $600^\circ C$ to $750^\circ C$ with a total pressure of 1 atmosphere. It was found that the rate of evaporation doubled with an increase of $50^\circ C$ in this range.

Scanning electron microscope photographs show the crystalline nature of the condensate and the presence of a thin oxide layer on some solidified test samples. This oxide layer reduced the rate of evaporation by retarding the zinc vapor escape from the evaporating surface.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. REVIEW OF THE LITERATURE</td>
<td>2</td>
</tr>
<tr>
<td>III. EXPERIMENTAL</td>
<td>21</td>
</tr>
<tr>
<td>A. Apparatus</td>
<td>21</td>
</tr>
<tr>
<td>B. Procedure</td>
<td>29</td>
</tr>
<tr>
<td>IV. RESULTS</td>
<td>36</td>
</tr>
<tr>
<td>V. DISCUSSION</td>
<td>47</td>
</tr>
<tr>
<td>VI. CONCLUSIONS</td>
<td>65</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>66</td>
</tr>
<tr>
<td>Appendix 1. Summary of Data Used in Calculation of Results</td>
<td>68</td>
</tr>
<tr>
<td>Appendix 2. List of Symbols</td>
<td>69</td>
</tr>
<tr>
<td>VITA</td>
<td>71</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figures</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cahn Model RH Automatic Recording Electrobalance</td>
<td>22</td>
</tr>
<tr>
<td>2. Furnace, Hangdown Tubes, Condenser and Outside Thermocouple</td>
<td>24</td>
</tr>
<tr>
<td>3. Boiler, Deflector Plate and Nichrome Wire</td>
<td>25</td>
</tr>
<tr>
<td>4. Experimental Apparatus</td>
<td>30</td>
</tr>
<tr>
<td>5. Schematic of the Experimental Apparatus</td>
<td>31</td>
</tr>
<tr>
<td>6. Chart Trace of Weight Loss</td>
<td>37</td>
</tr>
<tr>
<td>7. Comparison of Some Observed Rates of Evaporation by Solidified Surface Color</td>
<td>46</td>
</tr>
<tr>
<td>8. ((\log W_{Zn} + 1.78 \log T)) in Argon and Vacuum vs (1/T)</td>
<td>50</td>
</tr>
<tr>
<td>9. Comparison of the Observed Rate of Evaporation of Zinc in Argon with the Maximum Rate of Zinc</td>
<td>52</td>
</tr>
<tr>
<td>10. Crack in Oxide Layer 1000X</td>
<td>54</td>
</tr>
<tr>
<td>11. Zinc Condensate Crystals 3000X</td>
<td>56</td>
</tr>
<tr>
<td>12. Zinc Condensate Crystals 3000X</td>
<td>57</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Tables</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Boiler Temperature Calibration</td>
<td>27</td>
</tr>
<tr>
<td>II. Evaporation of Zinc in Argon Atmosphere</td>
<td>40</td>
</tr>
<tr>
<td>III. Evaporation of Zinc in Argon Atmosphere</td>
<td>41</td>
</tr>
<tr>
<td>IV. Evaporation of Zinc in Argon Atmosphere</td>
<td>42</td>
</tr>
<tr>
<td>V. Evaporation of Zinc in Argon Atmosphere</td>
<td>43</td>
</tr>
<tr>
<td>VI. Evaporation of Zinc-Alloy in Argon Atmosphere</td>
<td>44</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

Evaporation of one molten metal from a mixture of metals has long been used as a refining technique. Although zinc can be refined electrolytically its low boiling point makes it very suitable for separation from other metals by evaporation. Previously, most studies of evaporation phenomena have concentrated on vacuum techniques which were found to give results closer to the theoretical values than those studies in the presence of an atmosphere. Previous work by Su\(^{(7)}\) and Wu\(^{(9)}\) indicated that the rate of evaporation of zinc at one atmosphere was dependent on the type of atmosphere used.

The object of this experiment was to develop an apparatus and technique to measure the evaporation rate of molten zinc, and some alloys, using an instrument that would continuously record the weight loss. It is felt that with some knowledge of the mechanism of evaporation and the factors involved, it might be possible to carry out more selective refining of certain metal combinations by varying residual atmospheres and pressure.
II. REVIEW OF THE LITERATURE

Evaporation may be defined as the process of conversion of a liquid into a vapor, without necessarily reaching the boiling point.

Purification of a metal by evaporation is one of the major methods of purifying many non-ferrous metals (cadmium from zinc; zinc from lead; bismuth or antimony from tin). This process is only feasible when there is a significant difference between the vapor pressure of the impurity or impurities A and the base metal B. If the impurities possess the higher vapor pressure, the gas phase will contain a greater A to B ratio than the liquid phase. In other words, the liquid metal B is refined by decreasing the amount of A impurity. Such is the case in eliminating cadmium from zinc. Conversely, if the impurity A is not volatile, the base metal B can be purified by vaporizing it while the impurity A is left behind, as is done in refining lead from zinc.

In approaching the theory of evaporation, one can examine Raoult's Law, a generalization, which states that:-

The equilibrium vapor pressure that is exerted by a component in a solution is proportional to the mole fraction of that component.

\[ P_A = X_A \cdot P_A^0 \]

where

- \( P_A \) is the vapor pressure of component A in a solution.
- \( X_A \) is the mole fraction of A in the solution.
- \( P_A^0 \) is the vapor pressure of A in the pure state.

From the kinetic theory of equilibrium vapor pressure, it would be expected that this generalization would be correct when
the following conditions exist:

1. No chemical combination or molecular association between unlike molecules takes place in the formation of the solution.

2. The sizes of the component molecules are approximately equal.

3. The attractive forces between like and unlike molecules are approximately equal.

4. The component molecules are non polar, and no component is concentrated at the surface of the solution.

When a liquid is evaporating into the atmosphere above its surface, there is a net transfer of the substance from the liquid to the gaseous state. The presence of a residual gas and the partial pressure of the evaporating species, if not removed, has a retarding effect upon the process of evaporation.

As the vapor phase accumulates, the two states, liquid and vapor, may coexist in equilibrium such that, under definite conditions of pressure and temperature, the rate of evaporation exactly equals the rate of condensation back upon the surface of the liquid. When two phases are confined in a container, the vapor phase exerts a very definite pressure within the enclosure. The pressure of a vapor in equilibrium with a liquid (about to condense) is commonly called the "saturation vapor pressure" (1).

Evaporation phenomena for a liquid metal at atmospheric pressure involves the same mechanism as that for any other liquid, except for the effect of the greater density of metals. Evaporation of a metal is largely a surface phenomena, because the hydrostatic
pressure, even at exceedingly shallow depths, is greater than the saturated vapor pressure of most metal vapors, thus preventing the formation of vapor bubbles below the surface.

The evaporation process can be described as one in which molecules diffuse \(^{(1)}\) through the liquid at various velocities, depending on the surface temperature. If the velocity of the molecule is great enough and in the direction of the surface, it will leave the body of liquid and travel into the space above. Gases above the surface form a barrier into which some of the evaporating molecules collide, causing many of them to rebound to the evaporating surface.

Evaporation of a liquid metal at reduced pressure is quite different in many respects from the process described above. Reducing the system pressure removes the residual gas molecules, and the atmosphere is then composed primarily of the metal vapor.

The theory of the rate of evaporation may best be explained by considering a volume of gas \(V\) cubic centimeters containing \(N_t\) molecules.

Probability theory \(^{(2)}\) indicates that the chance \(P_s\) of a particular molecule striking the walls of the container in a time interval of one second when the area of the walls is \(S\) square centimeters is:

\[
P_s = \frac{SC}{4V}
\]

where

- \(P_s\) is the probability
- \(S\) is the area of walls, square centimeters
- \(C\) is the average velocity of particles, centimeters per
second

V is the volume of container, cubic centimeters

With $N_t$ molecules enclosed in $V$ cubic centimeters the number of molecules striking the walls per second ($N_s$) is given by

$$N_s = P_s N_t$$  \hspace{1cm} (2)

Introducing equation (1) into (2)

$$N_s = N_t \left( \frac{SC}{4V} \right)$$

Calling $N_t/V$, the number of molecules per cubic centimeter, $N$, then

$$N_s = N \left( \frac{SC}{4} \right)$$

If $N_s/S$, the number of molecules striking a square centimeter per second is represented by $n$ then

$$n = NC/4$$  \hspace{1cm} (3)

where

- $n$ is the number of molecules striking one square centimeter per second
- $N$ is the number of molecules per cubic centimeter
- $C$ is the average velocity of molecules, centimeter per second

Now for a gas composed of molecules with mass $m$ and an average velocity $C$ the number of molecules passing through a cross section of 1 square centimeter per second is given by equation (3).

The weight $W$ of a substance striking one square centimeter per second is given by

$$W = mn = NmC/4$$  \hspace{1cm} (4)

Since $Nm$ equals the density of the gas then using the
ideal gas law

\[ P = Nm = \frac{M}{V} = \frac{pM}{RT} \]  

(5)

where

- \( p \) is the pressure of the gas dynes per square centimeter
- \( V \) is the volume in cubic centimeters
- \( M \) is the molecular weight, grams
- \( R \) is the gas constant, ergs per mole. degree
- \( T \) is the absolute temperature, °K.

The kinetic theory shows that the root mean square velocity \( u \) in centimeters per second is

\[ u = \left( \frac{3p}{\rho} \right)^{\frac{1}{2}} \]  

(6)

The average velocity according to the Maxwell distribution law is equal to \( C \) centimeters per second where

\[ C = u \left( \frac{8}{3} \pi \right)^{\frac{1}{2}} \]  

(7)

Combining (5) and (6) with (7) gives

\[ C = \left( \frac{8RT}{\pi M} \right)^{\frac{1}{2}} \]  

(8)

Substituting equations (5) and (8) into (4) gives the following expression known as the effusion formula \(^3\)

\[ W_0 = p \left( \frac{M}{2\pi RT} \right)^{\frac{1}{2}} \]  

(9)

where

- \( W_0 \) is the weight of gas striking one square centimeter of surface per second
- \( p \) is the partial pressure of gas
- \( T \) is the temperature

Hence, if the vapor pressure of a liquid at any given temperature is known, it may be substituted for \( p \) in equation (9) to calculate the rate of evaporation into a vacuum. Under
these conditions, molecules evaporating from the surface do not collide with other molecules and return to the liquid phase since there are no residual gas molecules present. This rate of evaporation will be the theoretical maximum rate.

The equation (9) for the maximum rate of evaporation can be simplified by inserting the values of the constants to obtain

\[ W = p \left( \frac{M}{2RT} \right)^{\frac{1}{2}} = p \left( \frac{M}{2} \right)^{\frac{1}{2}} (3.14) (8.314) (10^7) (T)^{\frac{1}{2}} \]

\[ W = (43.74 \times 10^{-6}) (p) \left( \frac{M}{T} \right)^{\frac{1}{2}} \]

where

- \( W \) is the maximum rate of evaporation, grams per square centimeter per second
- \( p \) is the vapor pressure of the evaporating liquid at temperature \( T \) in dynes per square centimeter.
- \( M \) is the molecular weight of the liquid, grams.

This shows that the maximum rate of evaporation of a particular liquid is determined by the vapor pressure of the evaporating liquid and the temperature.

Evaporation of liquid metal may be pictured as a two-step process. In the first step, atoms of metal escape from the liquid phase into the space above the liquid surface. The second step involves diffusion of the metal vapor away from the liquid surface into infinite space or to a condensing surface.

If liquid metal evaporates into a vacuum, the rate is a maximum because every atom that crosses the liquid - vacuum interface escapes from the liquid phase. However, when a gas phase is present over the liquid surface every metal atom that crosses the liquid - gas interface does not escape from the
liquid phase in the sense that it moves out into infinite space or is captured by a condensing surface. Some of the atoms that leave the liquid phase collide with gaseous atoms or molecules and as a consequence are knocked back into the liquid phase. Furthermore, the atoms or molecules in the gas phase interfere with the movement of the metal atoms away from the liquid, that is, they reduce the rate of diffusion of the metal. Thus, the presence of a residual gas should slow down both steps in the evaporation process.

The kinetic theory of gases\(^2\) has been used to make certain calculations which indicate how the two steps in the evaporation process are affected by residual gases.

It is assumed that the effect of the residual gas on the net rate of escape of metal atoms from the liquid is proportional to a force exerted by atoms or molecules in the gas phase on the metal atoms immediately above the liquid metal surface. The force under consideration is responsible for returning some of the metal atoms to the liquid phase. This force is the result of the collision between the metal atoms and molecules of residual gas. The kinetic theory of gases permits calculation of the ratio of the forces exerted by the different residual gases on the metal atoms.

The forces exerted on the metal atoms will be proportional to the rate of change of momentum of the metal atom as a consequence of collisions with the residual gas. A number that should be approximately proportional to the force is obtained by calculating the change of momentum in a particular kind of
collision and multiplying this by the total number of collisions between metal atoms and residual gas atoms or molecules that occur in a unit of volume per second. Both quantities of this product are calculated rather easily.

The collision for which the change of momentum of the metal atoms is most easily calculated is one in which the metal atoms and residual gas atoms collide head-on and each has its root mean square velocity \( u \) which is given by

\[
 u = (3 \, RT/M)^{1/2} \tag{10}
\]

where

- \( u \) is the root mean square velocity in centimeters per second
- \( R \) is the gas constant in ergs per gram mole, degrees Kelvin
- \( T \) is the absolute Kelvin temperature,
- \( M \) is the molecular weight in grams.

The velocities of the metal atom and the residual gas atom or molecule after the collision can be calculated by solving the two simultaneous equations for the conservation of energy and of momentum. Thus,

\[
\frac{1}{2} M \, u^2 + \frac{1}{2} M_G \, u_G^2 = \frac{1}{2} M \, u'{}^2 + \frac{1}{2} M_G \, u_G'{}^2 \tag{11}
\]

and

\[
M \, u + M_G \, u_G = M \, u' + M_G \, u_G' \tag{12}
\]

where

- \( M \) and \( M_G \) are the molecular weights of the metal and residual gas respectively, in grams
- \( u \) and \( u' \) are velocities of the metal before and after the collision, respectively, in centimeters per second.
The change in momentum of the metal atom in this collision will be

\[ M u' - M u \]  \hspace{1cm} (13)

The total number of collisions in one second between all the atoms of metal and all the atoms or molecules of residual gas in one cubic centimeter, \( Z_{M,G} \) as given by Su(4) is

\[
Z_{M,G} = \frac{1}{4} n_M n_G (d + d_G)^2 \left( \frac{8 \pi R T (M_M + M_G)}{M_{M_G}} \right)^{\frac{3}{2}} \]  \hspace{1cm} (14)

where

- \( n \) is the number of metal atoms per cubic centimeter,
- \( n_G \) is the number of atoms or molecules of residual gas per cubic centimeter,
- \( d \) is the diameter of a metal atom in centimeters
- \( d_G \) is the diameter of the atom or molecule of residual gas, and the other symbols are as defined above.

It is assumed that the force exerted by the residual gas on the metal atoms is at least approximately proportional to the product, \( F_{M,G} \), of the change in momentum in the one kind collision and the total number of collisions

\[ F_{M,G} = Z_{M,G} (M u' - M u) \]  \hspace{1cm} (15)

The force factor, \( F_{M,G} \) can be calculated for various residual gases and comparison of force factors will give the relative force exerted by any residual gas on a particular metal.

The effect of the residual gas atmosphere on the rate of evaporation of liquid metals has been demonstrated in several instances. Turkdogan, Grieveson and Darken (5) showed that the rates of vaporization of metals under isothermal conditions were
increased by several orders of magnitude by introducing some reacting gas into the inert atmosphere surrounding the metal. They suggested that this enhanced vaporization is basically a vaporization - oxidation process involving the counter diffusion, for example, of oxygen and metal vapor within the gaseous boundary layer. As a result of the reaction forming a metal oxide mist which acts as a sink for the metal vapor in the gas close to the metal-gas interface, the partial pressure of oxygen influences the rate of vaporization of the metal. As the partial pressure of oxygen increases, the thickness of the boundary diffusion layer for metal vapor decreases, resulting in an increased rate of vaporization. At a critical pressure of oxygen, the vaporization of the metal is close to the maximum rate obtainable in vacuum. When the oxygen pressure exceeds this critical value (60 mm Hg for Fe), the flux of oxygen towards the surface is greater than the counter flux of the metal vapor, and, consequently, a liquid or a solid layer forms on the metal surface and vaporization practically ceases. The validity of this concept was verified by measuring the rates of vaporization of several metals (Cu, Co, Mn, Ni, Fe, Cr) in a stream of argon plus oxygen under isothermal conditions. Turkdogen(6)(7) in two later papers noted that the extent to which a given oxygen partial pressure can affect the vaporization in a given system depends on the degree of forced convection. He used equations derived by Ranz and Marshall(8) for the forced convection around a single sphere and calculated the value of the average film mass-transfer coefficient for oxygen transfer through the
boundary layer for isothermal conditions of the vaporization of an iron sphere in an oxygen enriched helium atmosphere and showed by his results that at an oxygen pressure of less than 0.1 atmosphere, the flux of oxygen towards the metal surface is retarded by a thermal-diffusion effect brought about by the temperature gradient from metal surface to gas interface.

The results of Su\(^{(4)}\) show that the rate of evaporation of zinc was markedly decreased in atmospheres of an oxidizing residual gas, which would exceed the critical value set by Turkdogan, Grieveson and Darken\(^{(5)}\). Su and also Wu\(^{(9)}\) showed that the rate of evaporation is dependent upon the physical nature of the non oxidizing residual gas, in particular, the size and mass of its atoms or molecules. Further, Wu\(^{(9)}\) found that there was a difference in the rate of evaporation with the heat conductivity and the accommodation coefficient of the inert gas, while Wada \(^{(10)}\) in evaporating a series of metals in helium and argon found that the evaporated particles grow larger in argon than in helium provided that the gas pressures are the same.

There have been several derivations of practical equations for rate of evaporation. Firstly, for pure metals, St. Clair and Spendlove\(^{(3)}\) showed by experiment, that for a fixed power input the rate of evaporation, at reduced pressures ranging from 0.5 to 5.0 millimeters Hg, decreased as pressure increased. They also recognized that the effusion formula could be used to calculate the rate of condensation of zinc \(W_C\) if \(p\) was replaced by the partial pressure of the actual zinc vapor \(p_C\). Thus, the
net rate of evaporation of zinc $W_n$ is the difference between the maximum rate of evaporation $W$ and the rate of condensation $W_c$:

$$W_n = (p - p_c) (M/2\pi RT)^{1/2}$$  \hspace{1cm} (16)

This equation is only applicable when the gas phase is pure zinc. Epstein(11) derived an equation giving the rate of evaporation of a metal from a liquid bath when a residual gas is present:

$$\frac{W_E}{W} = (2.736 T/ p) (1/b)^{2/3} (1 + M_A/M_B)^{1/2} \times$$

$$\left(1 + (\rho_B/\rho_A)^{1/3}\right)^2$$  \hspace{1cm} (17)

where

$W_E$ is Epstein rate of evaporation of the metal A into a gaseous atmosphere containing the metal A, and a residual gas B in grams per square centimeter per minute

$W$ is the rate of evaporation of a metal A into a perfect vacuum (i.e. maximum) in grams per square centimeter per minute

$T$ is absolute temperature degrees Kelvin

$P$ is total pressure, dynes per square centimeter

$\lambda$ is the distance between the evaporating and condensing surface, centimeters

$M_A$ molecular weight of metal A, in grams

$M_B$ is the molecular weight of residual gas B, in grams

$\rho_A$ is the density of metal A, grams per cubic centimeter, at the boiling point

$\rho_B$ is the density of the residual gas B, grams per cubic centimeter.

$b$ is Van der Waals constant for the gas.
Unfortunately, the derivation of this equation is reported as a private communication and its derivation is not really known. The correctness of this equation is doubtful, but it does make allowance for the forces exerted by the residual gas.

Luchak and Langstroth\(^{(12)}\) have derived an equation giving the rate of evaporation of a substance from a liquid surface when air is present (assuming no oxidation on the liquid surface)

\[ W_L = (9.60) \times (10^{-6}) \times (p) \times (M_A D / T \lambda) \]  \hspace{1cm} (18)

where

- \( W_L \) is the Luchak rate of evaporation of the metal A, in grams per square centimeter per minute.
- \( P \) is the vapor pressure of liquid at temperature \( T \) in millimeters Hg.
- \( T \) is the temperature degrees Kelvin.
- \( M_A \) is the molecular weight of metal A in grams.
- \( \lambda \) = Distance between the evaporating and condensing surfaces in centimeters.
- \( D \) is the diffusivity in the gas, square centimeters per second.

Diffusivity, \( D \), may be calculated from the following equation which has been derived from the kinetic theory of gases by Maxwell\(^{(13)}\) and modified by Sutherland\(^{(14)}\) to allow for the effect of inter-molecular forces in increasing the resistance to diffusion

\[ D = B(T)^{5/2} \times (1/M_A + 1/M_B)^{1/2} \times \frac{p}{(V_A^{1/3} + V_B^{1/3}) (T + C)} \]  \hspace{1cm} (19)

where
D is the diffusivity in the gas, square centimeters per second.

$M_A$ is the molecular weight of metal A in grams.

$M_B$ is the molecular weight of residual gas B in grams.

$P$ is the total pressure atmospheres.

$T$ is the absolute temperature in degrees Kelvin.

$V_A$ and $V_B$ are molal volumes of A and B in the liquid state at their boiling points in cubic centimeters per gram mole.

The term $C$ is from the Sutherland constant\(^{14}\) and is obtained from an expression in terms of the corresponding constants for viscosity of the individual components of the system. The term $B$ is most often given the value 0.00837 after Jean's experimental determination,\(^{15}\) but an often used equation for diffusivity by Gilliland\(^{16}\) omits the Sutherland constant and uses 0.0043 for $B$. It is thought this latter value was deliberately chosen to give somewhat low values of $D$, thus compensating for the probability that some experimental values are too large because of the difficulty in eliminating convection in gas diffusivity experiments.

The necessity of the Sutherland constant in equation (19) to take into account the effect of inter-molecular forces can be seen by considering the relative forces exerted by residual gases. Su\(^{(4)}\) calculated that the force exerted on evaporating zinc atoms by argon is 2.1 times higher than the force exerted by helium.
Another equation for calculating the rate of evaporation has been derived by Maxwell and Stefan\(^{(17)}\).

\[
W_M = 60 P M_A D_G (P_{A_1} - P_{A_2}) / T_{A_1} R \lambda (P_{BM}) \tag{20}
\]

where

- \(W\) is the Maxwell rate of evaporation of metal \(A\) in a stagnant gas in grams per square centimeter per minute.
- \(P\) is the total pressure, in atmospheres.
- \(D_G\) is the diffusivity of metal \(A\) in residual gas \(B\), square centimeters per second.
- \(P_{A_1}\) is the partial pressure of the metal \(A\) at the evaporating surface for a given temperature \(T_{A_1}\), in atmospheres.
- \(P_{A_2}\) is the partial pressure of metal \(A\) at the condensing surface for a given temperature \(T_{A_2}\), in atmospheres.
- \(M_A\) is the molecular weight of metal \(A\) in grams.
- \(\lambda\) = Distance between evaporating and condensing surfaces, in centimeters.
- \(R\) is the gas constant.
- \(T_{A_1}\) is the absolute temperature of metal \(A\) at the evaporating surface degrees Kelvin.
- \(P_{BM}\) is the log mean partial pressure of residual gas \(B\).

It is felt that since the Maxwell-Stefan equation makes allowance for the fact that the vapor pressure of the metal above the condenser is lower than that directly above the evaporating metal, this equation is better than the Luchak and Langstroth\(^{(12)}\) equation.

Evaporation from a mixture of two molten metals was
considered by Spendlove (1). When two molten metals are mixed, the respective vapor pressures are diminished in proportion to the degree of molal concentration if they behave as perfect liquids. In other words, the vapor pressures are proportioned to the respective molal fractions, and the partial pressures follow Raoult's Law for molten metal solutions. It is not possible therefore, to predict the partial pressures for a binary system without first knowing the respective activities or fugacities for the range of compositions to be considered.

The maximum rate of evaporation of a single metal is given in Equation (9) which, if expressed in terms of mass, will be proportional to \( p(M)^{1/2} \). It is evident, therefore, that the composition of the vapor will vary depending on whether the vapor is in equilibrium or being completely removed as fast as it evaporates. If the equilibrium partial pressures of two metals are \( P_A \) and \( P_B \), the ratio of the two components A and B in the vapor at equilibrium will be \( \frac{P_A M_A}{P_B M_B} \).

The ratio of their rates of evaporation from the surface is then given by

\[
\frac{P_A}{P_B} \frac{M_A}{M_B}^{1/2}
\]

Therefore, if the subscript e denotes equilibrium conditions and m indicates maximum evaporation, then

\[
\frac{A_e}{B_e} \frac{M_A}{M_B} = \frac{A_m}{B_m} M_A M_B^{1/2} \quad (21)
\]

Thus, some variation of vapor composition will occur in a system of two metals having slightly different molecular weights such as aluminum and zinc.

Any deviation between an observed evaporation rate and that
calculated from the kinetic theory is described by an accommodation coefficient (18).

It has been shown on the basis of the kinetic theory that, when a uniform gas with no mass motion is bounded by a fixed surface, the mass of molecules that strike unit area of the surface in unit time is given by

\[ W = p \left( \frac{M}{2\pi RT} \right)^{\frac{1}{2}} \]  

(9)

If the bounding surface consists of a liquid (or solid) condensate that is in equilibrium with its saturated vapor, and if the pressure of the saturated vapor is denoted by \( p_v \) then the rate at which the vapor molecules strike the surface is found to be given by the above equation with \( p = p_v \). If a fraction \( \alpha \) of the molecules condense on the surface (and the fraction \( 1-\alpha \) is reflected) it is necessary, in order to maintain a stationary condition, to have \( W \) molecules evaporate from unit surface in unit time where

\[ W_{\text{Exp}} = \alpha p_v \left( \frac{M}{2\pi RT} \right)^{\frac{1}{2}} = \alpha W \]  

(22)

The above equation gives the unilateral rate of evaporation from a surface in contact with its saturated vapor when both surface and vapor are at temperature \( T \). The coefficient \( \alpha \) is referred to as the accommodation coefficient and since it has been defined as a fractional value, it follows that \( W \) is maximum when \( \alpha = 1 \), in which case it will be designated by \( W \) and referred to as the "theoretically maximum" rate of evaporation. In practice, the apparent rate of evaporation \( W_{\text{Exp}} \) may be measured and \( W \) calculated as in equation (9) from a knowledge of vapor pressure and temperature. The evaporation coefficient may then be
calculated from the relationship
\[ \alpha = \frac{W_{\text{EXP}}}{W} \]  
(23)

The fact that experimentally observed values of \( \alpha \) practically never exceed unity lends some support to the interpretation of \( \alpha \) as the fraction of the impinging molecules which condense in the equilibrium condition.

If some of the molecules that come off the condensate are not immediately removed so that a vapor cloud develops above the condensate surface, the net rate of evaporation will be given by
\[ W_n = \alpha (p_v - p_a) \left( \frac{M}{2\pi RT} \right)^{\frac{1}{2}} \]  
(24)
where \( p_a \) is the pressure of the vapor cloud. When a foreign gas is present above the condensate surface this effect may be compensated for by interpreting \( p_a \) as the partial pressure of the evaporated vapor.

The effect of what we have now called the accommodation coefficient was first noticed by Smoluchowski\(^{(9)}\) who found that in some gases, particularly hydrogen and helium, the amount of heat given up to the gas by the solid was only a fraction of that which should be delivered if each molecule striking the surface reached thermal equilibrium with it before leaving.

Knudsen\(^{(19)}\) considering that when a molecular stream at temperature \( T_i \) strikes a surface at temperature \( T_w \), the molecules may, on the average, make a great many collisions within the fissures and asperities on the surface and thereby come into thermal equilibrium with the surface, or they may make relatively few collisions before leaving the surface. In the former case, the molecules will leave the surface with temperature \( T_w \); in the latter case, they will recede from the surface with a
temperature $T_r$ that would be expected to be intermediate between $T_i$ and $T_w$. The ratio

$$A_T = \frac{(T_r-T_i)}{(T_w-T_i)}$$

(25)

was introduced by Knudsen (19) as a measure of the energy exchange between the incident stream and the surface and was called the accommodation coefficient.
III. EXPERIMENTAL

A. Apparatus

The apparatus used in this investigation consisted of four major components: (1) automatic recording Electrobalance, (2) resistance furnace and temperature controller, (3) evaporation unit - boiler and condenser, (4) gas purification system.

The Electrobalance

The Cahn Model RH Automatic Recording Electrobalance is shown in Figure 1. The capacity of this unit when set in the HI position was a maximum load on the sample suspension of 100 grams with 20 grams maximum weight change measurable and a sensitivity of $10^{-5}$ grams equal to a weight change of 0.5% on a 1 MV recorder.

The Electrobalance is based on the null-balance principle. When the sample weight changes, the beam tends to deflect momentarily. The flag moves with it, changing the light to the phototube and the phototube current. This is amplified in a 2-stage servo amplifier and the amplified current is applied to a coil attached to the beam, which is in a magnetic field. The current in the coil acts like a d.c. motor, exerting a force on the beam to restore it to the original balance position. Thus, the change in electromagnetic force is equal to the change in sample weight. The beam is always in dynamic equilibrium, with the sum of the moments on it equal to zero. By Amphere's law, the electromagnetic restoring force is exactly proportional to the current which caused it. The voltage that this current develops across the coil is measured. After subtracting and measuring a part of the weight voltage with circuits inside the
Figure 1: Cahn Model RH Automatic Recording Electrobalance
balance, the excess is applied to the recorder.

**Furnace Construction**

The electrically heated Hevi-Duty hinged tube furnace is shown as F in Figure 2. The 18 inch long shell was mounted vertically on a steel frame to be in a position to close around the Vycor hangdown tube from the Electrobalance. Two semi-circular heating units, 690 watts capacity and 8 inches in length, formed of chrome-aluminum-iron alloy embedded in high thermal conductivity cement were placed in position 2.5 inches from the top of the shell and the remaining 10 inches of length was filled in with blank units.

The temperature of the furnace was controlled by a Bristol Controller using a chromel-alumel thermocouple. This controller held the boiler at the desired temperature ± 2° C as indicated by another chromel-alumel thermocouple whose hot junction was between the outer wall of the Vycor hangdown tube and the heating unit.

**The Boiler**

The boiler, A in Figure 3, was a recrystallized alumina crucible, Coors CN5. One crucible was used for 3 runs then discarded. The dimensions of an average crucible were 14.5 millimeters inside diameter and 25.0 millimeters deep. This gave an average liquid bath with 1.65 square centimeters surface area. Recrystallized alumina was chosen as the crucible material only after several runs using a graphite crucible failed because of a heavily oxidized metal surface. It was shown that the graphite introduced adsorbed oxygen into the system and released it at higher temperatures.
F. Furnace  
C. Condensor  
H. Aluminum Cap  
B. Vycor Hangdown Tube  
O. Outer Thermocouple  
T. Inner Vycor Tube

Figure 2: Furnace, Hangdown Tubes, Condenser, and Outside Thermocouple
A. Boiler  
D. Deflector Plate  
E. Nichrome Wire

Figure 3: Boiler, Deflector Plate and Nichrome Wire.
The Vycor hangdown tube, B in Figure 2, was designed with top joint TS 75/50 to fit the vacuum bottle of the Electrobalance. The total length of the tube was 930 millimeters and the inside diameter was 51 millimeters. The bottom 100 millimeters of the tube were tapered slightly to a TS 50/50 joint. The inner Vycor tube, T in Figure 2, was held in place by the aluminum cap, H in Figure 2, and served to prevent condensate accumulation on the hangdown wire.

The temperature of the molten bath was indicated by the chromel-alumel thermocouple (0) between the outer wall of the Vycor hangdown tube and the heating unit. To indicate the adjustment needed to record the true temperature of the bath, a temperature calibration was conducted from $400^\circ C$ to $800^\circ C$ with a separate chromel-alumel thermocouple (I) in place of the crucible and a potentiometer in a position to read alternately from thermocouple (0) and (I). The results of this calibration which were calculated under test conditions are given in Table 1. This procedure showed that the boiler temperature differed from the temperature indicated by the outside thermocouple (0) by a constant value of $-70^\circ C$. The potentiometer was left in the circuit to use as an accurate check on the controller.

The boiler was suspended from the hangdown wire by a holder made from 19 gauge nichrome wire as shown, E in Figure 3. A tantalum deflector plate, D in Figure 3, was used to prevent evaporated zinc particles from being swept up the inner Vycor tube into the balance mechanism.
### Table I: Boiler Temperature Calibration

<table>
<thead>
<tr>
<th>Controller Set Point °C</th>
<th>Time Controlling At Set Point Minutes</th>
<th>Thermocouple I °C</th>
<th>Thermocouple O °C</th>
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</tr>
<tr>
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<td>4</td>
<td>500</td>
<td>428</td>
</tr>
<tr>
<td></td>
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<td>500</td>
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</tr>
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<td></td>
<td>6</td>
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</tr>
<tr>
<td></td>
<td>6</td>
<td>800</td>
<td>730</td>
</tr>
</tbody>
</table>
The Condenser System

The water cooled condenser, C, is shown in Figure 2. It consisted of 0.25 inch inside diameter copper tubing spiral wound to fit snugly against the outside of the Vycor hangdown tube. Rubber tubing was used for connection to the cooling water supply and to the drain.

The Gas Atmosphere System

Argon was used as the residual gas. The gas flow rate was adjusted by a needle valve on the gas cylinder to give 1 centimeter per second flow as indicated on a flow meter after the outlet gas bubbler. Leaving the cylinder, the gas passed through 0.25 inch inside diameter rubber pressure tubing into a Vycor tube one inch in outside diameter and 42 inches long. The Vycor tube was filled with an alloy 87.5 atomic percent zirconium and 12.5 atomic percent titanium, and heated to 700° C.

To eliminate the remaining oxygen and moisture a special copper base getter R-3-II from B.A.S.F. Chemical Company was placed in series with the previous getter and heated to 200° C. After passing over this second getter the gas entered the sample hangdown tube via another length of pressure tubing and the top part of the Cahn Electrobalance bottle.

The gas outlet from the bottom of the hangdown tube was through a Pyrex cap necked to fit a further section of 0.25 inch diameter pressure tube which connected to a bubbler filled with Dibutyl Phthalate and then a Matheson 600 flowmeter tube which exhausted to the air.

It should be noted that both sets of getters were kept at
the appropriate temperature between each run and a slow stream of gas kept moving through the tubes to prevent the possibility of any condensation of water vapor within the system or back diffusion of oxygen. This combination of two separate getters was chosen to provide the best elimination of oxygen. The special copper base getter which operates at low temperature was added at a later stage of the experiments because it could be placed quite close to the balance mechanism without any fear of heat damage. The advantage of both getters over the commonly used copper chips was their longer working life. The copper base getter was re-generated periodically with carbon monoxide gas by attaching a cylinder of this gas in place of argon gas and passing it over both the getters then out of the system. The excess carbon monoxide was burnt on exit.

B. Procedure

The complete experimental apparatus is shown in Figure 4 and a schematic diagram of the apparatus is shown in Figure 5. The following procedure was used to determine the rate of evaporation of zinc and zinc alloys at various temperatures below their boiling points.

The starting samples weighed between 6 and 7 grams, and filled the boiler to a depth of approximately 6 millimeters, giving an average exposed liquid evaporation surface of 1.65 square centimeters. The analysis of the zinc used was:-

zinc 99.99, iron 0.0002, lead 0.0019, cadmium 0.0017.

Preparation of samples of pure zinc involved heating about 50 grams of the zinc in an open ceramic crucible and drawing it up under vacuum through a 1 centimeter diameter Vycor tube
Figure 4: Experimental Apparatus
Figure 5: Schematic of the Experimental Apparatus
inserted in the bottom of the crucible. The zinc was drawn up to a height of about 60 centimeters then allowed to solidify in the tube. At this point, the Vycor was smashed, the rod of zinc removed and cut up into approximately 8 gram pieces. Each piece was filed on all surfaces then heated to 450°C in a recrystallized alumina crucible enclosed in the Vycor hangdown tube attached to the balance. This procedure gave a button of pure zinc of the desired weight and shape to use in a run.

The first aluminum alloy was made by weighing out 99 grams of the previously prepared zinc and 1 gram of aluminum and encapsulating this material under vacuum in a Vycor tube which was then heated to at least 700°C and left at this temperature for 30 minutes, during which time the Vycor tube was turned and shaken within the furnace to produce a uniform alloy. The alloy was quenched in water while still encapsulated then broken out of the Vycor and cut up into the required weight for samples. Lower percentage aluminum alloys were made by repeating the procedure and diluting the 1 percent alloy.

Examination of a 1 percent alloy under the microscope at 100 X magnification showed a uniform grain size of about half the size of the pure zinc samples. Before finally placing the samples in the boiler they were again filed on all surfaces to remove any impurities or oxide layer. The boilers were all previously outgassed by heating to 500°C in argon.

The length of the hangdown wire set the position of the boiler in the furnace. Since the same hangdown wire was used throughout, this position was always the same. Care was taken
to keep the axis of the boiler vertical because if the boiler was tilted, the evaporation surface would not be perpendicular to the axis of the boiler and the exposed surface area would be increased. The internal diameter of each recrystallized alumina boiler was measured before each run with a pair of Vernier calipers.

Loading of the sample and positioning the boiler in the hangdown tube was carried out with the hangdown tube detached from the balance and furnace. The first step in loading was to insert one end of the hangdown wire through the 0.125 inch diameter hole in the aluminum cap, which was stuck with epoxy resin onto the top end of the inner Vycor tube, then the tantalum deflector plate and boiler were attached. This entire assembly was then lowered carefully into the Vycor hangdown tube and supported in position by three alligator clips attached to the top cap. The top end of the hangdown wire was prevented from falling through the hole in the aluminum cap by a length of wire used as a cross piece over the top of the cap.

The loaded hangdown tube was then placed in the furnace and held below the balance while the hangdown wire was attached to the balance hook and the aluminum cap screwed into position onto a metal brace from the base of the balance. With the boiler secured in position in the above manner, the Vycor hangdown tube was clamped in position onto the balance vacuum bottle and the bottom Pyrex cap pushed onto the bottom joint to complete the system.

In order to obtain the best oxygen and moisture free inert
gas atmosphere it was found necessary to first close off the hang-
down tube and balance assembly and evacuate by a vacuum pump.
The purified inert gas was then passed slowly into the system and
after reaching one atmosphere pressure, the system was allowed
to purge for at least 2 hours.

The Cahn Electrobalance and the recorder were switched on
at least two hours before the start of a run to give the electrical
components time to stabilize. The procedure for heating the
boiler to the correct temperature was to first move the controller
set point to $380^\circ$ C. and once the temperature was raised to this
point the controller was allowed to control for 10 minutes. The
purpose of this was to allow for some temperature lag inside the
system and to decrease some of this lag at a temperature below
the melting point of the sample, thus decreasing the dead time at
higher temperatures where the sample would be losing weight at a
much faster rate. After 10 minutes at $380^\circ$ C., the set point was
moved to $50^\circ$ C. above the highest required temperature for the
run and the temperature was allowed to reach this point. Then
the set point was turned down to control at the desired temperatures.
At this time the trace of weight loss versus time was followed
closely and data was not collected from the trace until the
controller had been controlling for five minutes at the required
temperature, which was monitored by the potentiometer set in the
controller thermocouple circuit. For readings at lower temperatures
in the same run, this five minute period was observed at each
temperature.

The 1 millivolt recorder chart was checked every few
minutes during a run to examine the trace of weight loss versus time. The chart speed was set at 1 inch per hour during the initial heating up period then set at 1 inch per minute or 2 inches per minute depending on the slope of the trace and a recorder range of 100 milligrams full scale was used throughout. Temperature readings as indicated by the circuit potentiometer were taken every few minutes and marked on the chart.

On completion of a run, the furnace was turned off and the sample allowed to cool to room temperature in the purified inert atmosphere before it was removed.

During an average run, there was from 0.3 to 0.5 grams of metal evaporated. In cases where the amount of metal evaporated was less than 0.1 gram due to interruption of the run, the sample was cleaned and reused. The difference in weight of sample in the crucible caused by taking out and cleaning was less than 2 millimeters.
IV. RESULTS

A series of evaporation experiments was made to determine the rate of evaporation of zinc in an argon atmosphere at temperatures ranging from 600° C. to 750° C. The effect of various oxide layers on the rate of evaporation was also determined over this temperature range.

Calculation of the rate of evaporation of the sample at each temperature was done by taking the slope of the chart trace at each temperature and dividing by the surface area of the sample. Figure 6 shows a sample of the trace as recorded during a run. It can be seen that with a recorder chart speed of one inch per minute the mean of the trace was a straight line. The fluctuations on the chart are due to convection currents within the hangdown tube causing the sample to move slightly. The sensitivity of the instrument made it necessary to change the recorder scale about every five minutes at 750° C. and every ten minutes at 700° C. For data at 750° C. and 700° C. the average of two 5 minute traces was taken, and an average of three 8 minute traces at 650° C. and 600° C. At higher temperatures of 750° C. and 700° C. the times for evaporation were kept to one 10 minute period while a 650° C. a 24 minute period of evaporation was used. The shorter period at higher temperatures was to minimize the possibility of zinc powder collecting in the balance mechanism.

At any set temperature the established rate of evaporation of a zinc sample with a clean surface did not vary with time. All the rates quoted were measured first at the highest temperature
Figure 6: Chart Trace of Weight Loss
then moving down the temperature range for any one run. Some initial tests showed that there was no variation when rates were measured at temperatures moving up the temperature range.

A sample which by visual observation was heavily oxidized did require a higher temperature before an appreciable rate was established. This is attributed to the fact that an oxide layer on the surface of the molten metal had to be broken to allow the exposure of a clean surface from which the metal would evaporate. The cracking of the oxide layer is borne out by Figure 9 and discussion in the next section of this thesis.

The results given are not meant to be absolute rates of evaporation of zinc in argon at one atmosphere pressure because the rates are dependent on such characteristics of the apparatus as convection within the hangdown tube and the retarding effects of the hot deflector plate above the sample, but these characteristics were constant from run to run and the results reported are truly relative to the chosen base of the bright clean surface obtained and reported as tests 10 and 23.

The classification of the amount of oxide on the surface was done by observing the diffraction color on the solidified surface and the presence of any visible skin on the solidified surface. The results are grouped accordingly.

Two tests were made with 1% aluminum-zinc alloy and another with 1% tin-zinc alloy as a further comparison of rates of evaporation. The major portion of this thesis was spent on the design and calibration of an apparatus and the establishment of a procedure to measure these rates.
The average results of each run are set out in Tables II to VI according to temperature of evaporation and condition of sample surface. Complete results are tabulated in Appendix 1.

It can be seen from Table II that at 750°C, the highest temperature tested, the rate decreased as the surface of the sample became more oxidized. At lower temperatures this was also the general rule, but there was some slight variation in rates which did not conform exactly to the variation in surface oxide.
<table>
<thead>
<tr>
<th>TEST NO.</th>
<th>SURFACE COLOR</th>
<th>BOILER TEMP. °C</th>
<th>EVAPORATION RATE GM/CM² - MIN.</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>Bright Clean</td>
<td>750</td>
<td>0.01090</td>
</tr>
<tr>
<td>10</td>
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<td>Gold</td>
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</tr>
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<td>0.00773</td>
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<tr>
<td>29</td>
<td>Dull Wrinkled Skin</td>
<td>750</td>
<td>0.00530</td>
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### TABLE III: EVAPORATION OF ZINC IN ARGON ATMOSPHERE

<table>
<thead>
<tr>
<th>TEST NO.</th>
<th>SURFACE COLOR</th>
<th>BOILER TEMP. °C</th>
<th>EVAPORATION RATE GM/CM² - MIN.</th>
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<tbody>
<tr>
<td>23</td>
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### TABLE IV: EVAPORATION OF ZINC IN ARGON ATMOSPHERE

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<th>BOILER TEMP. °C</th>
<th>EVAPORATION RATE GM/CM² - MIN.</th>
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<td>-----------------</td>
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<tr>
<td>10</td>
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</tr>
<tr>
<td>9</td>
<td>Blue</td>
<td>600</td>
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</table>
TABLE VI: EVAPORATION OF ZINC-ALLOY IN ARGON ATMOSPHERE

<table>
<thead>
<tr>
<th>TEST NO.</th>
<th>ZINC ALLOY</th>
<th>SURFACE COLOR</th>
<th>BOILER TEMP. °C</th>
<th>EVAPORATION RATE GM/CM² - MIN.</th>
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<tbody>
<tr>
<td>27</td>
<td>1% Aluminum</td>
<td>Bright</td>
<td>750</td>
<td>0.0101</td>
</tr>
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<td>0.01040</td>
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<td>Bright</td>
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<td>Bright</td>
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<td>0.00274</td>
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<td>Bright</td>
<td>650</td>
<td>0.00257</td>
</tr>
<tr>
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<td>1% Aluminum</td>
<td>Dull Blue</td>
<td>650</td>
<td>0.00156</td>
</tr>
<tr>
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<td>0.00920</td>
</tr>
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</tr>
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<td>1% Tin</td>
<td>Blue-Black</td>
<td>650</td>
<td>0.00164</td>
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</table>
As a general rule, an increase in temperature of 50°C increased the rate of evaporation by a factor of about 2 which followed closely the factor for variation of vapor pressure over the same temperature range. Figure 7 shows a plot of rate of evaporation versus temperature with results grouped according to color of solidified surface. Test 29 was the obvious exception to this general rule, with a factor of about 4 for every 50°C increase but it was noted that this particular sample was the most heavily oxidized of all the tests and a leak in the apparatus was suspected. The results of Test 29 are not included in Figure 7.

The difficulty of obtaining a clean bright surface for every test was thought to be due to the presence of adsorbed oxygen on the inside of the hangdown tube. This oxygen was not removed by the vacuum obtained but was released during a run at the higher temperatures.
Figure 7: Comparison of Some Observed Rates of Evaporation by Solidified Surface Color
V. DISCUSSION

Thermodynamic considerations can give a relationship between the rate of evaporation and temperature. The Clausius-Clapeyron equation is

$$\Delta H = T \frac{dP_o}{dT} (V_G - V_L)$$  \hspace{0.5cm} (26)

where

- $\Delta H$ is the latent heat of evaporation per mole of zinc,
- $V_G$ is the volume of zinc vapor, and
- $V_L$ is the volume of liquid zinc.

Since $V_L$ is negligibly small compared to $V_G$ and if the gas phase is assumed to be ideal $V_L = 0$ and $PV = RT$. The Clausius-Clapeyron equation becomes

$$\frac{d \ln P_o}{dT} = \frac{\Delta H}{RT^2}$$  \hspace{0.5cm} (27)

In general, $\Delta H$ is a function of temperature such that

$$\frac{d(\Delta H)}{dT} = C_P(V) - C_P(L)$$  \hspace{0.5cm} (28)

where $C_P(V)$ and $C_P(L)$ are the heat capacities of zinc vapor and liquid zinc respectively. Since zinc evaporates as monatomic vapor its heat capacity at constant pressure is

$$C_P(V) = 2.98 + R = 4.98 \text{ cal/gm-atom}$$

The heat capacity of liquid zinc $C_P(L)$ is 7.5 cal/gm-atom according to Kelley (20). Substituting $C_P(L)$ in equation (28) and integrating we obtain

$$\Delta H = \Delta H_0 - 2.52T$$  \hspace{0.5cm} (29)

where $\Delta H_0$ is an integration constant.

Substituting (29) in (27) and integrating again, we obtain

$$\log P_o = A - \frac{0.218}{T} \Delta H_0 - 1.28 \log T$$  \hspace{0.5cm} (30)
where \( A \) is a constant of integration.

Taking the logarithm of equation (9) for zinc gives

\[
\log W_{Zn} = \log P_0 + \frac{1}{2}(\log \frac{M_{Zn}}{2\pi R}) - \frac{1}{2} \log T
\]

(31)

Combining this with (30),

\[
\log W_{Zn} = A' - \frac{0.218 \Delta H_0}{T} - 1.78 \log T
\]

(32)

where

\[ A' = A + \frac{1}{2} \log \frac{M_{Zn}}{2\pi R} \]

(33)

Equation (32) gives the rate of evaporation of zinc as a function of the temperature. There are two empirical constants \( A' \) and \( \Delta H_0 \) to be determined from the experiments. Equation (32) shows that for zinc \( \log W_{Zn} + 1.78 \log T \) is a linear function of \( 1/T \). In Figure (8) the quantity \( \log W_{Zn} + 1.78 \log T \) for the evaporation of zinc in argon according to Wu(9) and this experiment and evaporation in perfect vacuum are plotted against \( 1/T \). The lines of best fit were calculated by the least squares method. The slopes of these lines are equal to the quantity \( 0.218 \Delta H_0 \). The equation of the line for the evaporation of zinc in argon was found from the experimental data, to be

\[
\log W_{Zn}(Ar) = \frac{-6558.0}{T} - 1.78 \log T + 9.790
\]

(34)

since \( 0.218(\Delta H_0)_{Ar} = 6558.0 \)

then \( (\Delta H_0)_{Ar} = 30.08 \) Kcal/mole

In a perfect vacuum the equation for the rate of evaporation of zinc was found to be
\log W_{Zn} = - \frac{6709}{T} - 1.78 \log T + 8.95 \quad (35)

since \(0.218(\Delta H_0)_{\text{vac}} = 6709\)

then \((\Delta H_0)_{\text{vac}} = 30.7 \text{ Kcal/mole}\)

At the boiling point of zinc, 907° C, \(\Delta H\) is the heat of vaporization \(\Delta H_v\). From Equation (29) we have

\[\Delta H_v = \Delta H_0 - 2.54 \times 1180\]

In argon \((\Delta H_v)_{\text{Ar}} = 30.09 \times 10^3 - 2.54 \times 1180\)

\[= 27.08 \text{ Kcal/mole}\]

In a perfect vacuum \((\Delta H_v)_{\text{vac}} = 30.7 - 2.54 \times 1180\)

\[= 27.7 \text{ Kcal/mole}\]

The heat of evaporation of zinc obtained from the data from the argon runs is closer to the theoretical value (vacuum value) than is the value of 29.4 Kcal/mole as found by Wu\(^9\).

Figure 9 shows a plot of rate of evaporation of zinc in argon according to Wu\(^9\) and the results of this experiment. A plot of rate of evaporation under vacuum is also added for comparison. All values are plotted, versus the reciprocal temperature. The fact that all three graphs have approximately the same slope is an indication that there is no change in the mechanism of evaporation from perfect vacuum to one atmosphere pressure of inert gas.

Some variation in the absolute values can be explained by considering that Wu used a value of 0.0043 for \(B\) to calculate the diffusivity of zinc in argon. After calculating the theoretical rate of evaporation using equation (20) he found his experimental results to be approximately 2.1 times higher than the theoretical rate.
\[ \log W_{obs} = -\frac{6558.0}{T} - 1.78 \log T + 9.79 \]

\[ \log W_{Wu} = -\frac{7070.6}{T} - 1.78 \log T + 9.575 \]

\[ \log W_{vac} = -6709 \times \frac{10^{-5}}{T} - 1.78 \log T + 8.95 \]

**Figure 8:** (log $W_{Zn}$ + 1.78 log $T$) in Argon and Vacuum vs $1/T$
The theoretical rate could be manipulated to coincide very closely with \( W_{\text{Exp}} \) rate by simply choosing a higher value of the empirical constant \( B \) to use in the theoretical equation. Applying Sutherland's constant to the theoretical equation increases the value of \( B \) to 0.0057 a factor of 1.32 which may be directly applied to increase the theoretical rate.

The factor of 5 by which the results of this experiment differ from those of Wu can be explained by considering the enhancing effect of convection currents in removing vapor away from the liquid vapor interface as discussed by Turkdogan\(^{(6)}\) above. This effect can be easily understood by considering equation (24)

\[
W_n = \alpha (p_v - p_a) (\frac{M}{2\pi RT})^{\frac{1}{2}}
\]

(24)

This equation which applies to the evaporation of liquid metal at a liquid-gas interface shows that the rate of evaporation is directly dependent on the value of the vapor pressure, \( p_a \) of the vapor cloud directly above the liquid surface. If the value \( p_a \) is decreased, because of the removal of zinc molecules by convection, there will be a corresponding increase in the rate of evaporation \( W_n \).

The presence of oxygen in the system resulted in the formation of zinc oxide and a decrease in rate of evaporation. The fact that an oxidized surface of zinc gave a constant rate of evaporation at a set temperature even in the presence of more oxygen indicates that after an initial film of oxide formed on the surface and cracked to allow some clean surfaces for evaporation, the evaporating zinc acted as a getter above the
Figure 9: Comparison of the Observed Rate of Evaporation of Zinc in Argon with the Maximum Rate of Zinc
clean surfaces and any further build up of oxide was on top of that oxide remaining. As the temperature of the melt was decreased, the getter effect of the evaporating zinc became less, allowing a narrowing of the clean cracks.

Figure 10 shows a section of the surface of Test 23 pure zinc sample, at magnification 1000X, after the sample had solidified. This photograph is representative of the entire surface as observed under the Scanning Electron Microscope. The darker areas are clean zinc, and the lighter areas are the zinc oxide layer. Other test samples examined showed surfaces ranging from ten percent oxide covering to a continuous unbroken oxide layer. The oxide content as seen under the microscope was indicative of the color observed.

The addition of one percent aluminum to zinc did not have any noticeable effect on the rate of evaporation. The findings of Wada and Sasagawa(9) that the observed temperature at which evaporation began would be decreased by addition of aluminum was not found to be true for this experiment. Two attempts to run a 0.1 percent aluminum alloy failed because of what appeared to be separation of the aluminum to the top of the sample where it formed a skin like unbroken cover over the surface. This separation was not explained by phase diagram considerations, but the sudden decrease in rate of evaporation in these cases suggest a leak in the apparatus. Also, a one percent tin alloy sample did not produce markedly different results compared with pure zinc of an equivalent surface coloration, but in this case there was only one sample run and its surface was heavily
Figure 10: Crack In Oxide Layer 1000X
The transfer of vapor from the surface of the bath to the condenser results from a pressure difference \(^{(21)}\). This pressure difference is brought about by a reduction in the vapor pressure of the evaporated metal surrounding the cooler condenser.

In this experiment the zinc condensate was in the form of loosely compacted crystals as shown in Figure 11. From the general appearance of the crystals it would seem they had condensed from the gaseous state directly to the solid state. A dull appearance of the crystals may result from some surface oxidation. The hexagonal shape of the crystals magnified in photographs taken on a Scanning Electron Microscope, Figure 12, appeared to be the predominant feature even in the formation of what, at lower magnification, appeared to be round particles. The condenser in these experiments was really the inside of the Vycor hangdown tube extending from only a few inches above the crucible over a length of approximately 1 foot. The copper coil around the outside of the hangdown tube served mainly to cool the tube in the immediate vicinity of the furnace top. The remainder of the tube was cooled above and below the furnace by two small fans which kept these parts of the tube at room temperature. The convection currents within the tube swept some of the condensate up into the balance mechanism even through a 1/8 inch diameter hole in the aluminum cap, H in Figure 2, and a great deal of trouble was experienced with this condensate until the inner Vycor tube, T in Figure 2, was devised, and successfully kept the condensate from being swept into the
Figure 11: Zinc Condensate Crystals 3000X
Figure 12: Zinc Condensate Crystals 3000X
mechanism or clinging to the hangdown wire. The tantalum deflector plate, D in Figure 3, was used to prevent the condensate from escaping up the inner Vycor tube and also to prevent condensate carried by convection currents from falling back into the molten bath. This deflector plate was kept well within the hot zone of the furnace to prevent any chance of condensation on its surface. It is not surprising that with the convection currents and a deflector plate above the molten bath there was a considerable amount of condensate on the bottom cap. This condensate was much finer than that on the upper parts of the tube, but on examination it was found to be composed of the same hexagonal shaped crystals.

Previous attempts to collect all the evaporated zinc powder in some loosely packed glass wool held above the sample in a colder zone failed because the glass wool became heavily coated and the smaller pieces fell to the bottom of the tube or fell into the sample.

The path of travel of a molecule as it leaves the surface of molten metal is governed by the cosine law of molecular flow which may be stated thus: The number $N$ of molecules which cross an incremental plane surface $S$ per second and flow into an incremental solid angle $W$ which lies at the angle $A$ from the normal to the surface is given by

$$N = \dot{6}V_s \cos \Theta \cdot W. \quad (36)$$

in which $V$ is the number of molecules which impinge each second on a unit surface in the gas and $\dot{6}$ is a proportionality constant. This law has been verified by Mayer in probing the gas flow field in front of an effusion orifice and could be considered
to hold for the initial direction of molecules in this experiment. The cosine law becomes important if one tries to calculate the rate of evaporation by measuring the weight of condensate produced. The procedure of this experiment did not involve or warrant any calculation of the cosine law.

The level of molten metal within the boiler must be kept constant because at any fixed level there is a certain probability that atoms will rebound from the wall above the liquid back into the melt; this probability will increase with the height of the wall above the liquid level and is theoretically derived from the Clausius factor \( l \) which indicates the probability of passage of a gas stream through a tube of diameter \( d \) and height \( h \). Also, any meniscus formed by the molten metal against the wall of the boiler will cause an increase in surface area. The concave meniscus formed by zinc in this experiment was not taken into account. It is calculated the increase in area would be less than 2.5 percent.

The role of diffusion through a stationary layer, called the Langmuir layer \( ^{22} \), above a molten bath during evaporation is not well known.

Elenbaas \( ^{22} \) found that both the heat transfer and the speed of evaporation of a heated tungsten filament as a function of gas pressure could be calculated to agree with experimental results by considering the tungsten transport as a concentration diffusion of the tungsten atoms, whereby the vapor pressure at the wire is equal to the saturation vapor pressure of tungsten at the temperature of the wire and the tungsten concentration at the border of the Langmuir layer is taken to be zero. With
a filament of 2.4 millimeters diameter and a calculated Langmuir diameter of 5.4 millimeters a further calculation showed that a contribution of 18 percent thermal diffusion with respect to the concentration diffusion should also be considered and added to obtain a total tungsten transport.

In the case of evaporation from the surface of a molten metal bath, the usual observation of vapor within the tube above the bath indicates that the concentration gradient would be much less and thus the effect of concentration diffusion would be decreased and thermal diffusion increased.

The enhancement of vaporization of a molten metal by a small partial pressure of oxygen present in the residual inert gas as found by Turkdogan, Grieveson and Darken was not found to hold for the vaporization of zinc at the temperatures considered. Molten zinc has a high affinity for oxygen and by a consideration of the standard free energy of formation of the oxide as given by Richardson and Jeffes (23) the partial pressure of oxygen required to form zinc oxide at 700°C is of the order of 10^{-28} atmospheres as compared with the partial pressure of oxygen required to form iron oxide (FeO) at the considered temperature of 2000°C of 10^{-6} atmospheres.

The critical value at which oxygen enhancement ceased and the surface of molten iron became oxidized was of the order of 10^{-1} atmospheres and without any consideration of the kinetics involved it could be assumed that the critical value for oxidation of the zinc surface occurs within a range of partial pressure of oxygen that was always present in this experiment, and for practical purposes a partial pressure of oxygen below this
critical value is not attainable.

The latent heat of evaporation of zinc at 700° C in argon from Kelley\(^{(20)}\) is 29,930 calories per mole which is 458 calories per gram. If the thermal conductivity of zinc is taken as 0.138 calories per square centimeter per second, the temperature gradient required to evaporate \(W\) grams of zinc per square centimeter per minute is given by\(^{(1)}\)

\[
\frac{dt}{dx} = \frac{458W}{60 \times 0.138} = 55.3W
\]

The experimental results for pure zinc evaporation in argon give a rate of evaporation of \(4.97 \times 10^{-3}\) grams per square centimeter per minute. Using this value in the above equation gives a temperature gradient of 0.263 degrees centigrade per centimeter which is within the values of experimental error for this experiment and may be neglected in this case, but it should be pointed out that this factor becomes a considerable source of error at temperatures approaching the boiling point of zinc where one might expect a temperature gradient of the order of 3.0 degrees centigrade per centimeter based on an extrapolation of the obtained rates of evaporation. Although the figures in this case are theoretical, Spendlove\(^{(1)}\), using an automatic instrument, was able to measure the temperature gradient in a zinc sample evaporating under vacuum and found the values to agree with the theoretical.

Another factor that can cause a considerable variation in the rate of evaporation of a molten metal is the effect of stirring the melt. St. Clair and Spendlove\(^{(3)}\) showed that the stirring of a plunger immersed just below the surface of a
molten zinc sample increased the rate of evaporation of the metal, which was under a vacuum pressure of 20 microns, by about 10 percent. The relative importance of transferring heat to the surface by agitation of the liquid as well as by thermal conduction can be shown by the following calculations. As liquid zinc has a specific heat of 0.115 calorie per gram and a density of 6.57, the heat capacity, in terms of unit volume, is $6.57 \times 0.115 = 0.755$ calorie per cubic centimeter per degree Centigrade. Therefore, the flow of 1 cubic centimeter per second across a temperature gradient of $1^\circ$ Centigrade results in a heat transfer of 0.755 calorie per second. The thermal flow of heat that would occur through the same gradient and cross section is 0.138 calorie per second (the thermal conductivity). Therefore, a flow of $0.138/0.755 = 0.183$ centimeter per second, is equivalent to the flow of heat by thermal conduction.

The vapor pressure of zinc in zinc aluminum alloys shows a positive deviation from Raoult's law; that is, the vapor pressure is greater than that calculated by multiplying the vapor pressure of pure zinc by the molal fraction of zinc in the melt. For a solution in which the concentration of aluminum is very dilute, say equal to 1 percent by weight which is an aluminum mole fraction of only 0.024, then Hultgren's(24) values indicate the activity coefficient of zinc to be very close to 1 and the activity coefficient of aluminum to be about 3.1.

To determine the fraction of aluminum evaporated with zinc from an alloy of 1 weight percent aluminum in zinc at 750$^\circ$ C, the vapor pressure data of K. K. Kelley(20) was used:--
For pure zinc
\[ \log P^0 = \frac{6754.4}{T} - 1.318 \log T - 0.06 \times 10^{-3} + 12.723 \]

and for pure aluminum
\[ \log P^0 = -\frac{14362}{T} - 1.01 \log T + 12.43 \]

where \( P^0 \) is vapor pressure of the respective pure metal expressed in millimeters of mercury and \( T \) is absolute temperature in degrees Kelvin.

Using the above equations, the vapor pressure of pure zinc at 750° C, is 122.9 millimeters of mercury and the vapor pressure of pure aluminum is \( 2.5 \times 10^{-5} \).

Using Raoult's law for an ideal solution
\[ \text{Activity} = \text{mole fraction} \]
then
\[ \frac{P_{Al}}{P_{Al}^0} = X_{Al} \quad (37) \]

where \( P_{Al} \) is vapor pressure in the solution considered

or
\[ P_{Al} = P_{Al}^0 X_{Al} \quad (38) \]

then
\[ P_{Al} = 2.5 \times 10^{-5} \times 2.4 \times 10^{-2} \]

By using the activity coefficient value for aluminum
\[ P_{Al} = 6.0 \times 10^{-7} \times 3 = 18.6 \times 10^{-7} \text{ millimeters Hg} \]

Similarly, since the solution contains 99 percent by weight zinc which is equivalent to a mole fraction of 0.975 then
\[ P_{Zn} = 122.9 \times 0.975 \]
\[ P_{Zn} = 119.8 \text{ millimeters Hg} \]

Now, considering Dalton's law, which states that the total pressure exerted by a gaseous mixture is equal to the sum of the
partial pressures, then
\[
 PT = PA + PZn
\]  (39)

The mole fraction of the aluminum component in the vapor is equal to
\[
 Y_{Al} = \frac{PA}{PT}
\]  (40)

where \( Y_{Al} \) is mole fraction of aluminum in the vapor.

Thus
\[
 Y_{Al} = \frac{(18.6 \times 10^{-7})}{(18.6 \times 10^{-7} + 119.8)}
\]
\[
 Y_{Al} = 15.5 \times 10^{-9}
\]

This mole fraction, when expressed as weight percent, becomes by approximation, \( 6.39 \times 10^{-7} \) weight percent aluminum in the vapor. From this it can be seen that the weight of aluminum in the condensate can be disregarded.
VI. CONCLUSIONS

1. The Maxwell-Stefan equation gives the closest to practical representation of the rate of evaporation of zinc in one atmosphere argon provided the empirical constant incorporated in this equation is chosen to allow for such factors as inter-molecular forces and convection currents within the apparatus.

2. An increase in temperature of 50°C increased the rate of evaporation of zinc by a factor of about 2, which followed closely the factor for variation of vapor pressure of zinc over the same temperature range.

3. A layer of oxide on the surface of the zinc decreased the rate of evaporation, at the temperatures tested, in proportion to the thickness of the oxide layer.

4. There was no enhancement of evaporation of liquid zinc by oxygen over the temperatures tested.

5. The addition of 1 percent aluminum to zinc did not have any noticeable effect on the rate of evaporation.
BIBLIOGRAPHY


21. KROLL, W. J. (1951) Vacuum No. 1, P. 166.


### APPENDIX 1

Summary of data used in calculation of results.

<table>
<thead>
<tr>
<th>TEST NO.</th>
<th>SURFACE AREA (CM²)</th>
<th>WEIGHT LOSS SLOPE (MG/MIN.)</th>
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APPENDIX 2
LIST OF SYMBOLS

English Letter Symbols

\( b \) Van der Waals constant
\( C \) average velocity
\( C_{p(L)} \) heat capacity of liquid at constant pressure
\( C_{p(v)} \) heat capacity of vapor at constant pressure
\( D \) diffusivity in gas
\( \Delta H \) heat of evaporation
\( \Delta H_0 \) integration constant
\( \Delta H_v \) heat of vaporization
\( m \) mass of molecule
\( M \) molecular weight
\( n \) number of molecules striking one square centimeter per second
\( N \) number of molecules per cubic centimeter
\( N_s \) number of molecules striking the walls per second
\( N_t \) total number of molecules in the container
\( p \) pressure of gas or vapor
\( P \) total pressure
\( P_{A} \) vapor pressure component A
\( P_{A}^0 \) vapor pressure pure A
\( P_s \) chance of a particular molecule striking the walls of the container in a time interval of one second
\( R \) gas constant
\( S \) area of walls of container
\( T \) absolute temperature
\( u \) root mean square velocity
\( V \)  total volume

\( W \)  maximum rate of evaporation

\( W_0 \)  weight of substance striking one square centimeter per second

\( W_C \)  rate of condensation

\( W_E \)  Epstein rate of evaporation

\( W_L \)  Luchak rate of evaporation

\( W_M \)  Maxwell rate of evaporation

\( W_n \)  net rate of evaporation

\( W \)  number of molecules evaporating from unit surface in unit time

\( X_A \)  mole fraction of A in solution

\( Y_A \)  mole fraction of A in vapor

**Greek Letter Symbols**

\( \alpha \)  accommodation coefficient

\( \lambda \)  distance between evaporating and condensing surfaces

\( \pi \)  3.14

\( \rho_A \)  density of the metal A

\( \rho_B \)  density of residual gas B
VITA

Paul Alan O'Neill was born in Port Pirie, South Australia, on November 10, 1943. His high school education was completed in 1960 at Rostrevor College Adelaide, South Australia. In February 1961, he was granted a Cadetship with the Broken Hill Associated Smelters, Port Pirie, which involved the part-time study towards a primary degree. After graduation in November, 1966 with a Diploma of Primary Metallurgy from the South Australian Institute of Technology, he was employed as a Technical Officer with the Broken Hill Associated Smelters for nine month.

He has been enrolled in the Graduate School of the University of Missouri - Rolla, since September, 1967.