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A THEORETICAL STUDY OF THE MECHANISM
FOR THE HAEFFNER EFFECT

BY

DAVID CHARLES JACOBS



A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of
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ABSTRACT

In 1953, E. Haeffner reported ⁽¹⁾ that when he had passed a direct electric current through a length of capillary filled with liquid mercury, the lighter mercury isotopes were enriched at the positive terminal and the heavier mercury isotopes were enriched at the negative terminal. This phenomenon is referred to as the Haeffner Effect. Since Haeffner's original experiment, other investigators have obtained similar results in other liquid metal systems.

When a direct electric current passes through a metallic conductor a free energy gradient is established. The direction of the negative free energy gradient is in the direction of the positive terminal. In accordance with basic diffusion theory the metallic atoms will, therefore, migrate toward the positive terminal.

The diffusion rate of a specific isotopic species is proportional to the mean vibrational frequency of the atoms of that species. Since the mean vibrational frequency is inversely proportional to the square root of the mass of the oscillator, the rate of diffusion toward the positive terminal will be greater, the less the isotopic mass. As a result, there will be an enrichment of the light isotopes at the positive terminal and a corresponding enrichment of the heavy isotopes at the negative terminal.

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I INTRODUCTION

Most of the naturally occurring elements consist of a mixture of two or more isotopes. All the isotopes of a given element have the same number of protons and differ from one another in their number of neutrons.

The fundamental chemical behavior of an atom is determined by the number of electrons bound to that atom. Since the number of electrons bound to an atom is determined by the number of protons contained within that atom's nucleus, it is obvious that all isotopes of a given element will have essentially the same chemical behavior. Because of the similarity in the chemical behavior of the isotopes of a given element, any method of separating isotopes of the same element from one another must involve a reaction or process the mechanism of which is mass dependent.

With the advent of the utilization of nuclear energy it has become increasingly necessary to increase the abundance (percentage) of a given isotopic species within certain elements above that of their natural abundance. One familiar case is that of the enrichment of Uranium with respect to the fissionable U^{235} .

To date there are three fundamental methods for isotopic enrichment in common use. The first of these fundamental methods involves processes in which atoms, ions or molecules migrate in a definite direction. In these processes the rate of migration is mass dependent. When a mixture of isotopes of an element are subjected to any of these migration processes, an isotopic enrichment in the direction of migration occurs. The migration processes presently in common use include gaseous diffusion, thermal diffusion, electrolytic processes

and the centrifuge process.

The second type of fundamental method for isotopic enrichment is the method of chemical exchange. The chemical exchange processes make use of the fact that the kinetics of certain chemical reactions are sufficiently mass dependent so that these reactions may be used as a means of isotopic enrichment.

The third fundamental method used to obtain an isotopic enrichment is the electromagnetic method. The principal upon which the electromagnetic method is based is the fact that the radius of an ion's circular path in a magnetic field is mass dependent. In the electromagnetic processes charged plates are placed at various predetermined positions so that they may intercept the circular paths of specific isotopes, thereby collecting those isotopes. This method is used principally as a means of performing isotopic analyses in the form of the familiar mass spectrometer.

In order for a given isotopic enrichment process to be economically feasible, the enrichment must be accomplished in a cascade type, multi-stage system. By their very nature the migration type processes lend themselves well to cascade type, multi-stage systems.

In most cases, isotopic enrichment by any of the aforementioned migration type processes necessitates that the substance used in the system be a gas except, of course, in the case of the electrolytic processes in which the substance is an electrolyte. The use of a gas in the process is highly inconvenient if the element for which the isotopic enrichment is desired happens to be a metal. In such cases a gaseous compound of the metal must first be formed. The other element in the compound must consist of only one isotope. After the desired enrichment is obtained, the pure metal must be reclaimed from its

gaseous compound.

In light of the obvious objections to the use of migration type processes necessitating the use of a gas, an aqueous solution or a molten mixture of salts, it is obvious that a migration type process involving the pure metal in its solid or liquid form would be highly desirable. Such a process involving metals in the liquid state may be possible by utilizing the Haeffner Effect.

In 1953, E. Haeffner reported ⁽¹⁾ that when he had passed a direct electric current through a length of capillary filled with liquid mercury held at constant temperature, the lighter mercury isotopes were enriched at the positive terminal and the heavier mercury isotopes were enriched at the negative terminal. This phenomenon has been referred to as the Haeffner Effect. Since Haeffner's original experiment, similar results have been obtained using liquid lithium ⁽²⁾, gallium ⁽³⁾, rubidium ⁽⁴⁾, potassium ⁽⁵⁾ and solid uranium ⁽⁶⁾.

By its very nature the Haeffner Effect seems well suited for the isotopic enrichment of liquid metals. Since liquid metals potentially have a highly important role to play in the nuclear energy field, a fundamental understanding of the Haeffner Effect is needed so that its potential utilization as a means of isotopic enrichment for liquid metals may be scrutinized.

It is the purpose of this paper to propose a mechanism for the Haeffner Effect and to analyze this mechanism in light of experimental data obtained from the literature.

II THEORY PROPOSING A MECHANISM FOR THE HAEFFNER EFFECT

A. DEVELOPMENT OF THE DIFFUSION EQUATION

Consider a system consisting of a homogeneous mixture of isotopes of a given metallic element. Each isotopic species will have a chemical potential (g), defined as the free energy per atom of the isotopic species in question. The system will be in thermodynamic equilibrium only if the chemical potential of each isotopic species is the same at every point in the system. If the chemical potential of a given species is greater at one point in the system than at another, the atoms of that species will tend to migrate from the point of high free energy to the point of low free energy. This migration is commonly referred to as diffusion.

Assume that the chemical potential of the i th isotopic species (g_i) varies in a single, given direction through the system and let this direction be referred to as the x direction. Hence a chemical potential gradient (dg_i/dx) is established.

According to diffusion theory the atoms of the i th isotopic species will migrate in the direction of the negative chemical potential gradient. The diffusing force (f_i) acting on each atom of the i th isotopic species will be

$$f_i = -dg_i/dx. \tag{1}$$

The minus sign in equation 1 implies that the diffusing force is acting in the direction of the negative chemical potential gradient.

The mobility of an i th type atom (M_i) is by definition that atom's

mean velocity (\bar{v}_i) per unit force, i.e., $M_i = \bar{v}_i/f_i$. Using the expression for f_i given by equation 1, it is readily seen that

$$\bar{v}_i = -M_i(dg_i/dx). \quad (2)$$

Let n_i be the number of atoms of the *i*th isotopic species per unit volume and let J_i be the flux of the *i*th type atoms, i.e., the number of atoms of the *i*th isotopic species crossing a unit area in a unit of time in the direction of the negative chemical potential gradient. Then by definition,

$$J_i = n_i \bar{v}_i = -n_i M_i (dg_i/dx). \quad (3)$$

Equation 3 should be familiar to all who have studied diffusion theory as the general expression of the basic diffusion equation.

B. THE MASS DEPENDENCE OF THE DIFFUSION EQUATION

In order for equation 3 to be useful in describing an isotopic enrichment process it must, of course, be mass dependent. The only possible mass dependent members of equation 3 are M_i , the mobility, and g_i , the chemical potential. Prior to determining the manner in which the mobility is mass dependent, the basic diffusion process in solids and in liquids held near their melting points must be understood.

The accepted models of both the solid and liquid states assume that at any given instant most of the atoms in the solid or liquid system occupy equilibrium positions. These equilibrium positions

represent positions of minimum potential energy for the atoms. It is generally assumed that midway between each equilibrium position the potential energy is a maximum so that each equilibrium position is separated from the next by a potential energy barrier.

The solid or liquid system is believed to be permeated with holes or vacancies into which the atoms may move. In order for an atom to move from one equilibrium position to the next, it must, at that instant, have sufficient energy to overcome the potential energy barrier between equilibrium positions. The height of the potential energy barrier is referred to as the activation energy (Q). Therefore, no atom can move from one equilibrium position to the next unless its energy is equal to or greater than the activation energy.

LeClaire ⁽⁷⁾ has shown that the mobility of an atom is proportional to

$$(1/KT)(1/6) \nu_i (n_v/n) \exp(-Q_i/KT), \quad (4)$$

where ν_i is the mean vibrational frequency of an atom of the i th kind, n_v is the number of vacancies or holes per unit volume, n is the number of atoms of all species per unit volume and Q_i is the activation energy required of the i th type atom.

In equation 4 the term $(1/6) \nu_i \exp(-Q_i/KT)$ is the probability per unit time that an i th type atom has an energy equal to, or greater than, the required activation energy. The ratio (n_v/n) is related to the probability that a new equilibrium position is available to the migrating atom.

The activation energy in a diffusion process is essentially that energy required by an atom to rupture the chemical bonds holding it

in its equilibrium position. The magnitude of the activation energy is, therefore, more than likely dependent only upon the chemical nature of the atom and not upon its mass. The ratio of vacancies to atoms is dependent only upon the temperature and pressure of the system and is also mass independent.

The frequency of a harmonic oscillator is inversely proportional to the square root of the mass m_i of the vibrating body according to the relationship

$$B/m_i = 4\pi^2\nu_i^2, \quad (5)$$

where B is the force constant, which in the case of a vibrating atom, is dependent upon the chemical nature of the atom, and upon the temperature of the system.

In light of the foregoing, the mobility of the i th isotopic species may be written as

$$M_i = Z/m_i^{\frac{1}{2}}, \quad (6)$$

where Z is a proportionality constant incorporating all the mass independent terms of equation 4, and is dependent only on the nature of the elemental species in question and upon the temperature and pressure of the system.

The insertion of equation 6 into equation 3 yields the following mass dependent expression for the flux of the i th isotopic species

$$J_i = -n_i Z/m_i^{\frac{1}{2}}(dg_i/dx). \quad (7)$$

C. THE CHEMICAL POTENTIAL GRADIENT FOR THE HAEFFNER EFFECT

The physical significance of equation 7 is extremely important and, therefore, equation 7 warrants some degree of analysis. Equation 7 states that the flux of a given isotopic species in the direction of a negative chemical potential gradient is inversely proportional to the square root of the isotopic mass of that species. A chemical potential gradient can be provided by placing one or more constraints upon the system in such a way that the constraints vary in a given direction throughout the system. These varying constraints may be a temperature gradient, a centripetal force, a pressure gradient, an applied electric field, etc. It should be obvious that with suitable adjustment of the chemical potential term, equation 7 can be made to be applicable to all the migration type isotopic enrichment processes discussed in the introduction.

In the specific case of the Haeffner Effect the general expression for the chemical potential of the ith isotopic species is

$$\xi_i = g(T) + g(V) + g(p) + KT \ln(n_i/n), \quad (8)$$

where $g(T)$ is some temperature dependent function, $g(V)$ is a function dependent upon the electrical potential applied to the system, $g(p)$ is a pressure dependent function, K is Boltzmann's constant, n_i is the number of i type atoms per unit volume and n is the number of atoms of all species per unit volume. It follows from equation 8 that the general expression for the chemical potential gradient of the ith species is

$$dg_i/dx = dg(T)/dx + dg(V)/dx + dg(P)/dx + K \ln(n_i/n) (\delta T / \delta x) + (KT/n_i) (\delta n_i / \delta x). \quad (9)$$

In the case of the Haeffner Effect, the temperature and pressure remain constant throughout the length of the system. Therefore, equation 9 reduces to

$$dg_i/dx = dg(V)/dx + (KT/n_i) (\delta n_i / \delta x). \quad (10)$$

Prior to determining the exact form of the function $g(V)$ a system of conventions concerning the applied electricity must be adapted. The conventions to be adapted are based on the following definitions:

- (1) The direction of the electric field (F) at a point in the system is the direction of the force on a positively charged body placed at that point.
- (2) Point B is said to be at a higher potential than point A if the potential energy of a positively charged body is greater at B than at A.
- (3) The terminal with the higher potential is referred to as the positive terminal and the terminal with the lower potential is referred to as the negative terminal.
- (4) The direction of the current in a conductor is that direction which would be taken if all the current carrying, moving charges were positive.

The Haeffner Effect deals specifically with metallic conductors in which the moving, current carrying charges are electrons. In metallic conductors the electrons move in a direction opposite to that of the conventional current as defined in 4, i.e., the direction of the

electronic motion is from the negative terminal to the positive terminal.

As defined in 1 the electric field is directed toward the negative terminal. Hence in a metallic conductor the electrons move in a direction opposite to that of the conventional electric field.

If V_+ is the potential at the positive terminal and V_- is that at the negative terminal then the potential difference (V) between the two terminals will be $V = V_+ - V_-$. If $(-e)$ is the electronic charge, the decrease in an electron's potential energy (W) in moving against the electric field from the negative to the positive terminal is $W = (-e)(V_- - V_+) = eV$. In other words, because the electron bears a negative charge, it will lose potential energy in moving in a direction opposite to that of the conventional electric field. Obviously, therefore, in a metallic conductor, if one assumes the origin of the system to be the negative terminal and that x increases in the direction of the positive terminal, $dV = Fdx$, i.e., the electron gains potential energy when moving in the direction of the conventional electric field.

If n_{eff} is the effective number of conduction electrons per atom for the element in question, then the function $g(V)$ appearing in the preceding equation is $g(V) = \phi n_{\text{eff}} eV$, where ϕ is a mass independent constant related to the degree of interaction between the electrons and the atoms of the metal. Since, for a metallic conductor, $dV/dx = F$, it is readily seen from equation 10 that the chemical potential gradient of the i th isotopic species is

$$dg_i/dx = \phi n_{\text{eff}} eF + (KT/n_i)(\delta n_i/\delta x). \quad (11)$$

In a metallic conductor $I = -F/r$, where I is the current density and r is the resistivity of the metallic element in question. By

substituting the preceding relationship into equation 11, the following expression for the chemical potential gradient of the ith isotopic species is obtained.

$$dg_i/dx = -\phi n_{\text{eff}} e r I + (KT/n_i)(\delta n_i/\delta x). \quad (12)$$

D. THE DIFFUSION EQUATION FOR THE HAEFFNER EFFECT

From equations 7 and 12 it is readily seen that the flux of the ith isotopic species is

$$J_i = n_i Z/m_i^{\frac{1}{2}} \left[\phi n_{\text{eff}} e r I - (KT/n_i)(\delta n_i/\delta x) \right]. \quad (13)$$

The holes or vacancies which permeate the solid or liquid system are capable of motion. Their motion is accomplished by the migration of neighboring atoms into the vacancy. Obviously, therefore, at any instant a vacancy's direction of migration will be opposite to the direction of the atom moving into the vacancy.

When a chemical potential gradient is applied to the system, the net flux of the migrating vacancies will be directed toward the positive chemical potential gradient. If the diffusion process is allowed to continue for a sufficiently long period of time and if the system is closed, the vacancies will be disproportionately distributed throughout the system, the vacancy population increasing in the direction of the positive chemical potential gradient.

Similarly, in the closed system, there will be a disproportionate distribution of the atomic population, the atomic population increasing

in the direction of the negative chemical potential gradient. This disproportionate distribution of the atomic population is due to the fact that the atoms, migrating toward the negative chemical potential gradient, will at any instant, occupy positions formerly occupied by the vacancies or portions thereof.

In light of these phenomena, the physical significance of equation 13 can be obtained. The first term in equation 13 describes a migration process in the direction of the electric current in a metallic conductor, i.e., toward the positive terminal. The second term in equation 13 describes a self-diffusion process in the direction of a negative concentration gradient.

Since, initially, the system consists of a homogeneous isotopic mixture there is at the time the current is applied, no concentration gradient and, therefore, the second term in equation 13 will be zero. Thus, the flux of the diffusing material will be directed toward the positive terminal. As the diffusion in the direction of the positive terminal continues there will be a continual increase in the atomic population in the direction of the positive terminal. Hence a concentration gradient will appear and will continually increase.

The direction of the negative concentration gradient will be opposite to that taken by the diffusing material. As a result the net flux of material in the direction of the positive terminal will fall off continually as the time after the application of the electric current increases.

Since the magnitude of the second term in equation 13 is dependent upon the first in the manner described above, it should be obvious that the second term in equation 13 will never exceed the first, but will only tend to approach it after a sufficiently long

period of time has elapsed. In most cases the magnitude of the second term will not approach that of the first since the diffusion in a closed system will be limited by the incompressibility of the material in question, i.e., the flux will drop to zero when the maximum number of allowable vacancies are filled. At any rate, it should be obvious that the net flux of diffusing material will always be directed toward the positive terminal.

Since the net flux of a given isotopic species in the direction of the positive terminal is inversely related to the square root of the isotopic mass of that species, it is logical to assume that, at any instant, the abundance of a given isotopic species at the positive terminal will increase, the less the isotopic mass of that species. Therefore, an enrichment of the lighter isotopes at the positive terminal and thus an enrichment of the heavier isotopes at the negative terminal should be expected.

E. SOLUTION OF THE DIFFUSION EQUATION

Consider an element of volume in the system. Since the system is closed and there are no reservoirs of material at either the positive or negative terminals, then in accordance with equation 13 it is seen that the rate of change of the concentration of the ith isotopic species in the element of volume is

$$\delta n_i / \delta t = \delta J_i / \delta x. \quad (14)$$

For simplification, the obvious effect the number of vacancies per unit volume at any x and t , $n_v(x,t)$, will have upon $n_i(x,t)$ will be ignored. Therefore, the constant Z in equation 13, which contains

the ratio (n_v/n) will be treated as a constant independent of time and position. Any expression for $n_i(x,t)$ obtained under these conditions will be approximately valid at all values of x and for values of $t < t'$, where t' is the time at which all permissible vacancies are filled and an equilibrium condition is established.

From equations 13 and 14 it is seen that

$$\delta n_i / \delta t = a(\delta n_i / \delta x) - b(\delta^2 n_i / \delta x^2) \quad (15)$$

where

$$a = Z' n_{\text{eff}} \text{erf} I / m_i^{\frac{1}{2}},$$

and

$$b = ZKT / m_i^{\frac{1}{2}}.$$

Assume that equation 15 yields a product solution, that is

$$n_i(x,t) = X(x) \cdot T(t), \quad (16)$$

where $X(x)$ is a function of x alone and $T(t)$ is a function of t alone. Then equation 15 will take the form

$$\frac{1}{T} T' = \frac{a}{X} X' - \frac{b}{X} X'' = k, \quad (17)$$

where k is a constant independent of position and time.

From equation 17 it is seen that

$$T(t) = C_1 e^{kt} \quad (18)$$

and that

$$X(x) = C_2 e^{\frac{x}{2}\left(\frac{a}{b} + y\right)} + C_3 e^{\frac{x}{2}\left(\frac{a}{b} - y\right)}, \quad (19)$$

where C_1 , C_2 and C_3 are arbitrary constants and where

$$y = \left[\left(\frac{a}{b}\right)^2 - \frac{4k}{b} \right]^{\frac{1}{2}} \quad (20)$$

Therefore, in accordance with equation 16,

$$n_i(x,t) = \left[C_4 e^{\frac{x}{2}\left(\frac{a}{b} + y\right)} + C_5 e^{\frac{x}{2}\left(\frac{a}{b} - y\right)} \right] e^{kt}. \quad (21)$$

When $t = 0$, $I = 0$ and, therefore, $a = 0$. Also, $n_i(x,0) = n_{i0}$, where n_{i0} is the natural concentration of the i type atoms. If $n_i(x,0)$ is to be equal to n_{i0} then y must be zero and, therefore,

$$k = a^2/4b. \quad (22)$$

Also

$$n_i(x,0) = n_{i0} = C_4 + C_5. \quad (23)$$

Therefore,

$$n_i(x,t) = n_{i0} e^{\frac{a}{2b}(x + \frac{at}{2})}. \quad (24)$$

Obviously, equation 24 is not a complete solution of the diffusion equation. A more complete solution is given by

$$n_i(x,t) = n_{i0} \left[1 + \frac{a}{b}(C_6 + x) e^{\frac{a}{2b}(x + \frac{at}{2})} \right]. \quad (25)$$

Let L = length of the system in the direction of migration. If the system is closed and if there is no reservoir of material at the positive or negative terminals, then, by symmetry considerations, the flux of the i th species at $x = L/2$ will equal that fraction of the vacancy flux caused by the migration of the i type atoms. Therefore, the concentration of the i type atoms at $x = L/2$ will remain unchanged for all values of t . In other words,

$$n_i(L/2,t) = n_{i0}. \quad (26)$$

Obviously, therefore, $C_6 = -L/2$ and hence,

$$n_i(x,t) = n_{i0} \left[1 + \frac{a}{b}(x - \frac{L}{2}) e^{\frac{a}{2b}(x + \frac{at}{2})} \right]. \quad (27)$$

Recalling that $a = Z'n_{\text{eff}}erI/m_i^{\frac{1}{2}}$ and that $b = ZKT/m_i^{\frac{1}{2}}$, it is seen that the only mass dependent term in equation 27 is the exponent $at/2$ which is inversely proportional to $m_i^{\frac{1}{2}}$. Therefore, the exponent $at/2$ decreases with increasing isotopic mass. Hence, increasing isotopic mass results in a decrease in the absolute value of the second term in equation 27.

For values of x less than $L/2$ the second term in equation 27 is negative. Therefore, in that half of the system toward the negative terminal, the concentration of a given isotopic species is larger, the larger the isotopic mass for all values of $0 < t < t'$.

For values of x greater than $L/2$ the second term in equation 27 is positive. Hence, in that half of the system toward the positive terminal, the concentration of a given isotopic species is larger, the less the isotopic mass for all values of $0 < t < t'$.

For $x = L/2$ the concentration of a given isotopic species remains unchanged and equal to the natural concentration (n_{i0}) for all values of $0 \leq t \leq t'$.

F. CHANGE IN THE ISOTOPIC ABUNDANCES DUE TO THE HAEFFNER EFFECT

From equations 4, 5 and 13, it is seen that

$$J_i \propto \frac{m_i^{-\frac{1}{2}}}{KT} \cdot B(T)^{\frac{1}{2}} \cdot \frac{n_v(T)}{n} \cdot e^{-\frac{Q}{KT}} \left[n_i n_{\text{eff}} e^{rI} - KT \left(\frac{\delta n_i}{\delta x} \right) \right], \quad (28)$$

where T is temperature and B(T) is the force constant of the harmonic oscillator.

For most metals, the resistivity (r), can, to a good approximation, be assumed to be directly proportional to temperature. Therefore, the constants a and b, previously defined, are both functions of mass and temperature so that

$$a_i(m, T) = \frac{a'}{m_i^{\frac{1}{2}}} \cdot B(T)^{\frac{1}{2}} \cdot \frac{n_v(T)}{n} \cdot e^{-Q_i/KT},$$

and

$$b_i(m, T) = \frac{b'}{m_i^{\frac{1}{2}}} \cdot B(T)^{\frac{1}{2}} \cdot \frac{n_v(T)}{n} \cdot e^{-Q_i/KT}.$$

The terms a' and b' are constants independent of mass and the temperature. In light of the preceding two equations, it is obvious that all terms in equation 27 containing the ratio a/b are independent of mass and temperature.

Consider any two isotopic species, 1 and 2, in the system and let $m_1 < m_2$. Define $R(x, t)$ as the ratio of the concentration of the

lighter species at any point in the system to the concentration of the heavier isotope at the same point for all values of $0 < t < t'$. Then by definition

$$R(x, t) = n_1(x, t)/n_2(x, t). \quad (29)$$

From equations 27 and 29 it is seen that

$$R(x, t) = R_0 \frac{1 + (x - \frac{L}{2})D(x) \left[\exp \left\{ \Theta(T) \cdot t/m_1^{\frac{1}{2}} \right\} \right]^Y}{1 + (x - \frac{L}{2})D(x) \left[\exp \left\{ \Theta(T) \cdot t/m_2^{\frac{1}{2}} \right\} \right]^Y}, \quad (30)$$

where

$$R_0 = n_{10}/n_{20}, \text{ i.e., the natural ratio,}$$

$$\Theta(T) = B(T)^{\frac{1}{2}} \cdot \frac{n_v(T)}{n} \cdot \exp(-Q/KT)$$

and

$$D(x) \left[\exp \left\{ \Theta(T) \cdot t/m^{\frac{1}{2}} \right\} \right]^Y = (a/b) e^{\frac{a}{2b}(x + \frac{at}{2})}.$$

Since by definition, $m_1 < m_2$, the absolute value of the second term in the numerator of equation 30 is greater than the second term in the denominator at any given temperature. Therefore;

- (1) when $x < L/2$, $R(x < L/2, t)/R_0 < 1$
- (2) when $x > L/2$, $R(x > L/2, t)/R_0 > 1$
- (3) when $x = L/2$, $R(L/2, t)/R_0 = 1$.

III DISCUSSION

A. COMPARISON WITH EXPERIMENT

According to equation 13, when a direct electric current passes through a metallic conductor there will be an atomic migration (diffusion) toward the positive terminal. This prediction is in complete agreement with the experimental findings of Huntington and Grone (8,9). By observing marker motion in gold and copper wires, Huntington and Grone found that there was atomic migration toward the positive terminal when an electric current was made to pass through the wires. Huntington and Grone's results showed that the velocity of migration was proportional to the current density. This phenomenon is in agreement with equation 13 if one considers the concentration gradient to be negligible.

In light of equation 30, it is seen that the ratio of the concentration of the lighter isotope to that of the heavier isotope is:

- (1) less than the natural ratio in that half of the system toward the negative terminal, i.e., $x < L/2$,
- (2) greater than the natural ratio in that half of the system toward the positive terminal, i.e., $x > L/2$,
- (3) equal to the natural ratio midway between the negative and positive terminals, i.e., $x = L/2$.

The experimental results obtained by Nief and Roth (3), in their study of the Haeffner Effect in liquid gallium are shown in figure 1. In their experiment, Nief and Roth used no reservoir of material at either the positive or negative terminals and, therefore, the conditions of their experiment conform to the conditions imposed upon the deriva-

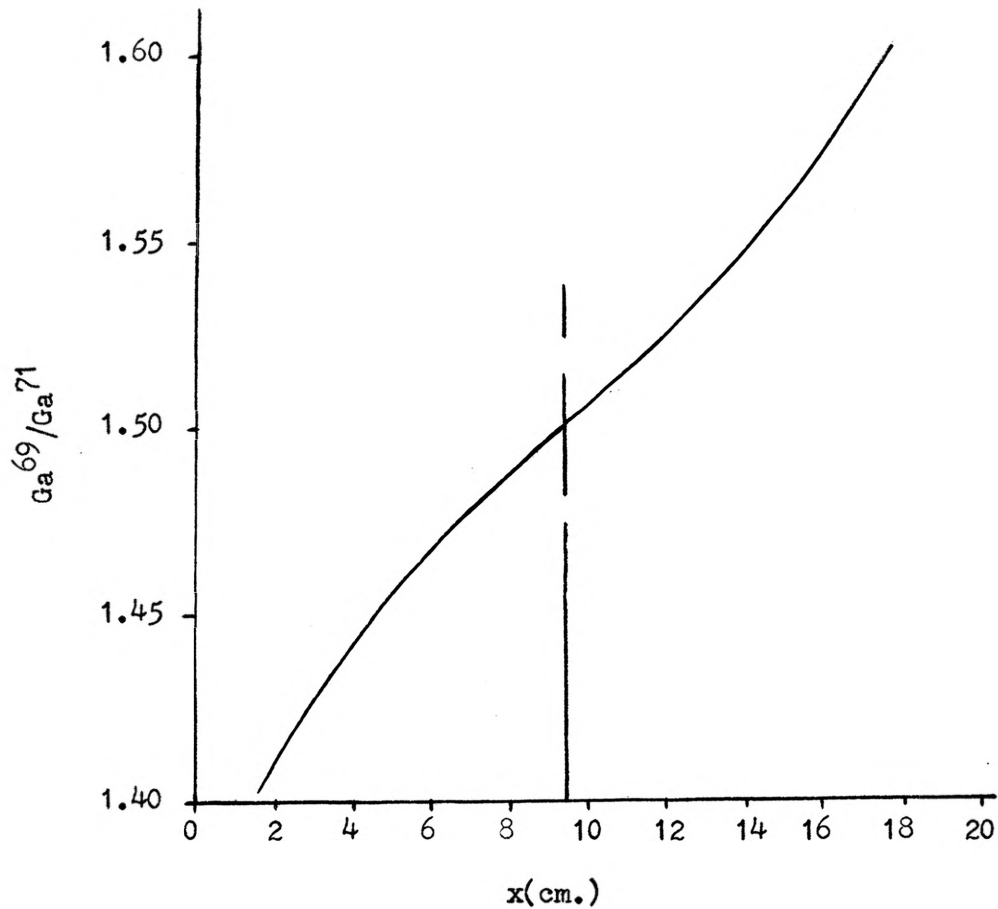


Figure 1 - The Haeffner Effect in liquid gallium. Data from Nief and Roth⁽³⁾.

Inside diameter of capillary: 0.2 mm

Length of capillary: 188 mm

Current: 2.52 amp.

Time: 248 hrs.

Temperature: 48°C

$\text{Ga}^{69}/\text{Ga}^{71}$ (initial): 1.510

tion of equation 30. It is encouraging to note that equation 30 successfully predicts, in a general fashion, the results obtained by Nief and Roth.

B. THE HAEFFNER EFFECT IN SOLID METALLIC CONDUCTORS

In the derivation of equation 13 the assumption was made that the metallic element in the system was either in the solid or liquid state. Hence, equations 27 and 29 are equally valid for solid or molten metallic conductors and, therefore, one should expect to observe the Haeffner Effect in solid metals under suitable conditions.

The "hole" theory of the liquid state predicts that the ratio of the number of vacancies (holes) to the number of atoms in a liquid metal, held near its melting point, is in the order of 10^{-1} . Corresponding theories of the solid state predict that the vacancy to atom ratio in metallic solids is in the order of $10^{-3} - 10^{-5}$.

Since the constant Z appearing in equation 13 is directly proportional to the ratio n_v/n , it should be obvious that J_i , the flux of a given isotopic species in the direction of the positive terminal, will be $10^2 - 10^4$ times greater for a given liquid metal than for its corresponding solid. Obviously, therefore, if any detectable variations in isotopic concentrations are to be achieved across the length of a solid metallic conductor at reasonable current densities, the process must be allowed to continue for extremely long periods of time.

It is interesting to note that the Haeffner Effect has indeed been observed in solid metals. Haeffner, Sjöborg and Lindhe have reported ⁽⁶⁾ that they were able to detect a variation in the concentrations of U^{234} and U^{238} along the length of a fine wire of pure

natural uranium after passing an electric current through the wire for 171 days (4.1×10^3 hrs.) at temperatures between 750°C and 870°C . The experimental results showed that there was an increase in the abundance of U^{234} at the positive terminal and an increase in the abundance of U^{238} at the negative terminal.

C. THE TEMPERATURE DEPENDENCE OF THE HAEFFNER EFFECT

When the temperature derivative of equation 30 is set to zero, i.e., $dR/dT = 0$, a finite solution is obtained. This, of course, indicates that there is an optimum temperature (T') at which the quantity $R(x,t)$ will be a maximum at a given position in the system for given values of time, current density, etc. In other words, at temperatures less than or greater than T' , $R(x,t)$ will be less than $R(x,t)_{\max}$ at a given position in the system, at a given time and under a given set of conditions.

It can be shown that $T = T'$ when

$$\begin{aligned} & 1/m_1^{\frac{1}{2}} \left[(x - \frac{L}{2})D(x) + \exp\{-\Theta(T') \cdot ty/m_2^{\frac{1}{2}}\} \right] \\ & = 1/m_2^{\frac{1}{2}} \left[(x - \frac{L}{2})D(x) + \exp\{-\Theta(T') \cdot ty/m_1^{\frac{1}{2}}\} \right] . \end{aligned}$$

The preceding equation shows that, under a given set of conditions, T' is dependent upon position, time and upon the function $\Theta(T)$ which is solely dependent upon the properties of the metallic element in question. As should be expected, the preceding equation becomes ambiguous at $x = L/2$ indicating that no temperature dependent

maximum exists for $R(L/2, t)$.

Such optimum temperatures, as described above, have in fact, been found by Lodding in his studies of the Haeffner Effect in liquid rubidium ⁽⁴⁾, potassium ⁽¹⁰⁾ and indium ⁽¹¹⁾. The results obtained by Lodding in his indium studies are shown in figure 2.

Goldman, Nief and Roth claim ⁽¹²⁾ that no optimum temperature exists for gallium within the temperature range $325^{\circ}\text{K} - 560^{\circ}\text{K}$. This, of course, is not to say that no such optimum temperature for gallium exists above 560°K . Mention should be made of the fact that gallium is unusual in that its resistivity decreases upon melting. If this latter phenomenon has any effect upon the optimum temperature, similar effects should be observed with antimony and bismuth since the resistivities of both these metals also decrease upon melting.

D. THE STATE OF EQUILIBRIUM IN THE HAEFFNER EFFECT

Previous mention has been made of the fact that the migration of atoms toward the positive terminal is a process in which the atoms "jump" from an equilibrium position to a neighboring vacant equilibrium position and that the vacancies migrate toward the negative terminal. Since the metallic element in question will have a definite limit to its compressibility, it should be obvious that, in a closed system with no infinite reservoir of material available, an equilibrium condition will eventually be obtained. This equilibrium condition corresponds to a situation in which all permissible vacancies at the positive terminal are filled.

The quantity t' was defined as the time at which the equilibrium condition is obtained. Obviously, at values of $t \geq t'$ migration in the

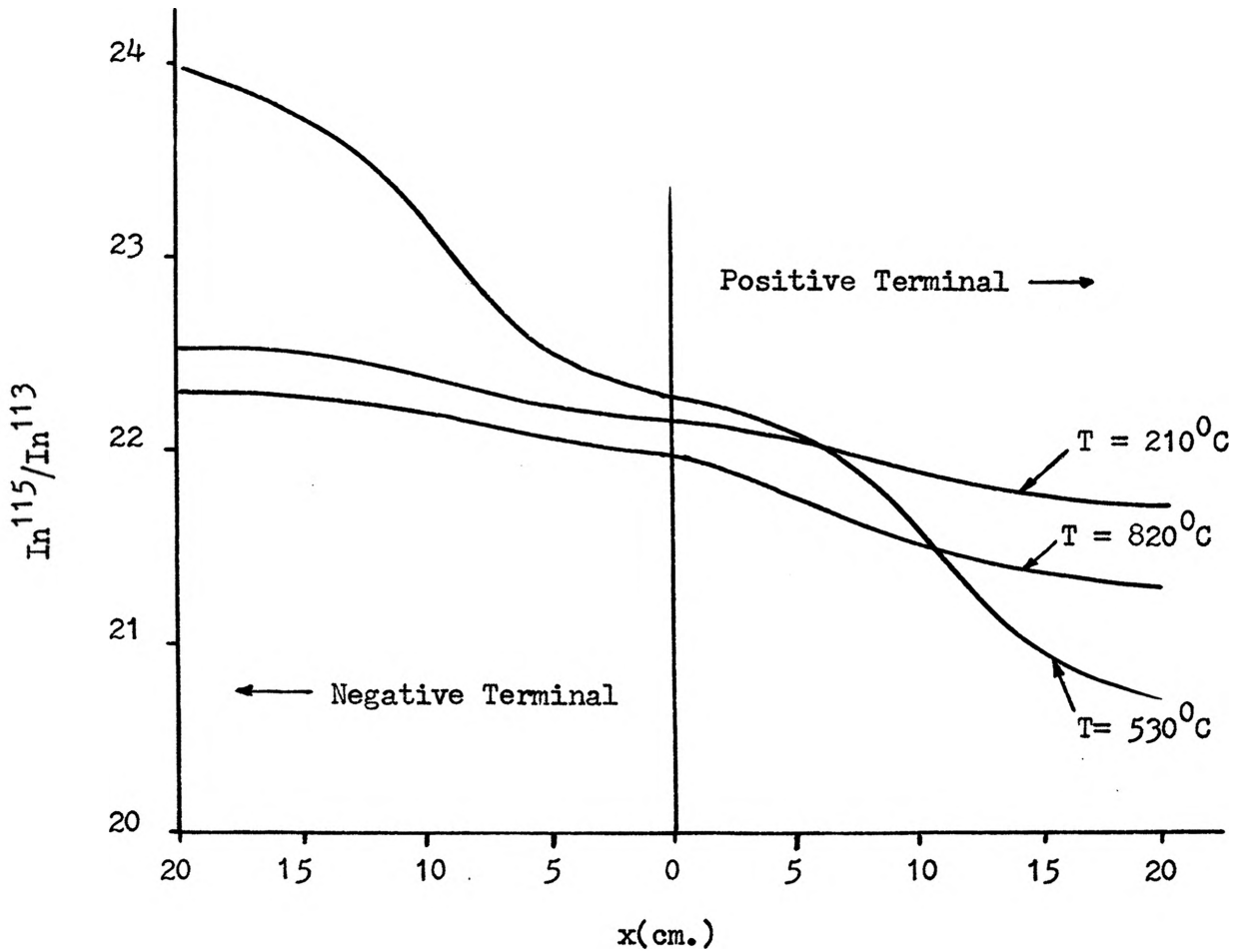


Figure 2 - The affect of temperature on the Haeffner Effect in liquid Indium. Data from A. Lodding (9). Mention should be made that $\text{In}^{115}/\text{In}^{113} = 1/R(x,t)$, where $R(x,t)$ is defined by equation 30. The curves are distorted somewhat due to Lodding's use of a reservoir midway between the negative and positive terminals.

direction of the positive terminal will cease and hence there will be no further change in $R(x,t)$.

A reservoir of material at the positive terminal will essentially act as a reservoir of vacancies. Obviously, therefore, in any such system the equilibrium condition described above will be long in coming and t' in the case of the system with the reservoir will be very much greater than the equilibrium time for the system with no such reservoir.

Bogoiavlenskii, Grigor'ev, Rudenko and Dolgoplov ⁽¹³⁾ have attempted to systematically show the affect increasing time has upon the changes in isotopic concentrations in liquid mercury. Their experimental system was such that there was a reservoir of mercury at the positive terminal. Quite naturally, therefore, Bogoiavlenskii, et al., could find no state of equilibrium. Because of their use of a reservoir of material at the positive terminal, the work of Bogoiavlenskii, et al., is valueless from the point of view of ascertaining the true conditions of equilibrium in a system with no reservoirs of material.

Unfortunately, no other investigators have yet systematically varied time in their studies of the Haeffner Effect so that the conditions for equilibrium in a closed system remains an open question.

E. THE BRESLER AND PIKUS MECHANISM FOR THE HAEFFNER EFFECT

In their mechanism for the Haeffner Effect, Bresler and Pikus propose ⁽¹⁴⁾ that, since the vibrational frequency of a light isotopic species of a given element is greater than that of a heavier species, the "radius" (wave function) of the lighter isotope is greater than

that of the heavy. Hence, according to Bresler and Pikus, the lighter isotope interacts more readily with neighboring atoms and, therefore, has a greater "friction constant" than the heavier isotope. As a result of these conclusions Bresler and Pikus assume that the mobility of the heavy isotopic species is greater than that of the light isotope.

In addition, the Bresler and Pikus mechanism assumes that the net flux of material is in the direction of the electric field, i.e., toward the negative terminal.

That the wave function of the heavier isotope is less than that of the light isotope is undoubtedly true. However, the difference in the values of the wave functions is undoubtedly negligibly small for isotopes of elements more massive than hydrogen. This is evident in the fact that the variations in the chemical reaction kinetics of isotopes of elements more massive than hydrogen are undetectable. It seems doubtful, therefore, that the differences in the wave functions of heavy and light isotopes of a given element can contribute significantly to the differences in their mobilities.

It was shown in section IIC that when an electric current passes through a metallic conductor a free energy gradient is produced in the system and that the direction of the negative free energy gradient is opposite to that of the electric field, i.e., the negative free energy gradient is directed toward the positive terminal. Obviously, therefore, migration in the direction of the negative terminal as predicted by Bresler and Pikus, is thermodynamically implausible. Furthermore, Huntington and Grone^(8,9) have shown experimentally that electric current induced atomic migration, in metallic conductors, is directed toward the positive terminal.

In light of the preceding brief discussion, the validity of the

Bresler and Pikus mechanism for the Haeffner Effect seems doubtful.

F. THE KLEMM MECHANISM FOR THE HAEFFNER EFFECT

In developing his proposed mechanism for the Haeffner Effect, Klemm assumes ⁽¹⁵⁾ that a metal consists of a mixture of "stationary" atoms arranged in a lattice and of some "mobile" atoms which are capable of motion with respect to the "stationary" lattice. According to Klemm, the "stationary" atoms, arranged in an orderly array, offer less resistance to the passage of electrons than do the disordered "free" or "mobile" atoms. Thus the "mobile" atoms suffer numerous interactions with the conduction electrons. These interactions result in a transfer of energy from the conduction electrons to the "mobile" atoms which, according to Klemm, results in a migration of the "mobile" atoms toward the positive terminal.

Klemm assumes that, in the interactions between the incident electrons and the atoms, more energy is imparted to the lighter "mobile" atoms than to the heavy and as a result, the rate of migration of the "mobile" atoms of a lighter isotopic species in the direction of the positive terminal will be greater than that of a heavier isotopic species. Therefore, Klemm concludes that there will be an increase in the abundance of the lighter isotopes at the positive terminal and an increase in the abundance of the heavier isotopes at the negative terminal.

In its strictest interpretation, Klemm's mechanism is inconsistent with the generally accepted theories of the solid and liquid state which do not allow for special "free" or "mobile" atoms. The theories of the solid and liquid state do, however, allow for imperfections in the atomic array, but it is doubtful that the atoms constituting

these imperfections are consistently more mobile than the atoms constituting the orderly array. In his theory Klemm also overlooks the random nature of the diffusion process as dictated by the theories of the liquid and solid state. In addition, it seems doubtful that electrons moving in an electric field of reasonable intensity can impart sufficient energy to an atom so as to dislodge that atom.

However, if one assumes that the interactions between the electrons and atoms leads to an increase in the atoms' vibrational frequency and if one liberally interprets Klemm's "mobile" atoms as being atoms which are, at any instant, undergoing diffusion, then one sees that Klemm's mechanism for the Haeffner Effect takes the appearance of the mechanism proposed by this paper.

IV SUMMARY

It was the purpose of this paper to propose a mechanism for the Haeffner Effect and to analyze the proposed mechanism in light of experimental results obtained from the literature.

It was shown in section IIC that when a direct electric current passes through a metallic conductor, a free energy gradient is established. The direction of the negative free energy gradient is the direction of the electric current in the metallic conductor, i.e., toward the positive terminal.

According to basic diffusion theory, when a free energy gradient exists in a system, an atomic migration (diffusion) will occur, the direction of which is toward the negative free energy gradient. Hence, in the case of a pure metallic conductor, through which an electric current is passing, the net diffusion will be toward the positive terminal. The fact that such current induced motion has been experimentally observed was discussed in section IIIA.

In section IIB it was shown that the rate of diffusion is directly related to the mean frequency with which the atoms vibrate in their equilibrium positions and that the vibrational frequency is inversely proportional to the square root of the mass of an atom. Obviously, therefore, the diffusion of the light isotopes in the system toward the positive terminal will be greater than that of the heavy isotopes.

In Section IIB it was pointed out that the migrating atoms move into equilibrium positions which were formerly occupied by vacancies. This results in an increase in atomic population in the direction of the positive terminal and a corresponding increase in the vacancy

population in the direction of the negative terminal.

Although the populations of all the isotopic species increase in the direction of the positive terminal, the increase in the concentration of a specific isotopic species is greater, the less the mass of that species. That this is so, was shown by equation 27 in section IIE.

In light of the preceding discussion, it should be obvious that there will be an enrichment of the lighter isotopes at the positive terminal and a corresponding enrichment of the heavier isotopes at the negative terminal.

The "diffusion" mechanism for the Haeffner Effect proposed by this paper predicts that, under suitable conditions, one should be able to observe the Haeffner Effect in solid metals. The fact that the Haeffner Effect has been observed in solid uranium was discussed in section IIIB.

It was shown in section IIIC that, for a given metal and under a given set of conditions, there is an optimum temperature at which the enrichment of a given isotopic species is a maximum at a given point in the system. At temperatures above or below this optimum temperature the obtained enrichment will be less than the maximum. The fact that such an optimum temperature does exist for liquid potassium, rubidium and indium was shown experimentally by Lodding (4,10,11).

A possible equilibrium condition for the Haeffner Effect was discussed in section IIID. It was pointed out that, in a system containing no infinite reservoirs of material, a state of equilibrium should eventually be obtained when all permissible vacancies in that half of the system toward the positive terminal are filled. Since

no systematic study of the equilibrium conditions in the Haeffner Effect has yet been made, no defense of the equilibrium hypothesis was offered.

V CONCLUSION

The "diffusion" mechanism for the Haeffner Effect proposed by this paper is merely an extension of the basic diffusion theory which is presently in general acceptance. In addition, the "diffusion" mechanism, proposed by this paper, considers no model for the liquid or solid state other than those models which are presently in general acceptance.

Since the "diffusion" mechanism for the Haeffner Effect is consistent with presently accepted theories, the fact that it predicts, in a general fashion, all the experimental results heretofore obtained is an indication of its validity.

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APPENDIX I

LIST OF SYMBOLS

- f_i = diffusion force acting on an atom of the i th species
- g_i = chemical potential of the i th species
- M_i = mobility of the i th species
- \bar{v}_i = mean migration velocity of the i th species
- n_i = concentration of the i th species (atoms/unit volume)
- J_i = flux of the i th species
- K = Boltzmann's constant
- T = temperature
- ω_i = mean vibrational frequency of the i th species
- n_v = vacancy concentration
- n = total atomic concentration
- Q = activation energy
- B = force constant
- m_i = isotopic mass of the i th species
- $Z = (1/KT)(1/12\pi)B^{\frac{1}{2}}(n_v/n)\exp(-Q/KT)$
- V = applied electric potential
- e = magnitude of the electronic charge
- F = electric field
- n_{eff} = effective number of conduction electrons per atom
- ϕ = constant related to the degree of electron-atom interaction
- I = current density
- r = resistivity
- $Z' = Z\phi$
- t = time

$$a = Z' n_{\text{eff}} e r I / m_i^{\frac{1}{2}}$$

$$b = Z' K T / m_i^{\frac{1}{2}}$$

n_{i0} = natural concentration of the ith species

L = length of the system

R = ratio of the concentration of a light species to that of a heavy species

$$\Theta(T) = B(T)^{\frac{1}{2}} \cdot (n_v/n) \cdot \exp(-Q/KT)$$

VITA

David Charles Jacobs was born on November 9, 1934 in New York City. After graduating from William Howard Taft High School in the Bronx, New York, he attended New York City Community College from where he received an Associate in Applied Sciences in Mechanical Technology in 1954. After serving in the U. S. Army from 1954 to 1956, Mr. Jacobs was employed at Bulova Watch Company as a metallurgist from August 1956 to August 1957. In September, 1957 he entered the New Mexico Institute of Mining and Technology and received a Bachelor of Science degree in Basic Sciences in 1960. In September, 1960, Mr. Jacobs entered the Missouri School of Mines and Metallurgy and was a recipient of a State Mining Experiment Station fellowship from September 1960 to February 1961.

