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Study of the temperature dependence of the Haeffner effect in mercury

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STUDY OF THE TEMPERATURE DEPENDENCE

OF THE HAEFFNER EFFECT IN MERCURY

BY

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_____ (advisor)   _____

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ABSTRACT

In 1953, E. Haeffner (1) reported that after he had passed a direct electric current through a capillary tube filled with mercury, he obtained a separation of the isotopes of mercury. It was found that the heavier isotopes were enriched at the negative terminal and the lighter isotopes at the positive terminal. This effect has since been referred to as the Haeffner Effect. Since this original experiment, other investigators have observed this effect in many other liquid and some solid metal systems.

The work of J. N. Baysden (2) showed that the separation of the isotopes in mercury could be followed by the use of mercury (203) as a radioactive tracer.

In this investigation of the Haeffner Effect in mercury a radioactive tracer, mercury (203), was used to follow the separation of the isotopes in a capillary system that did not contain an attached reservoir. The separation was followed near the cathode and near the anode by determining the change in counting rate. The change in counting ratio with time and the time necessary to reach equilibrium conditions were determined at several temperatures to determine whether these factors were temperature dependent.

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I. INTRODUCTION

In 1953 Haeffner (1) successfully demonstrated that the separation of isotopes, in a liquid metal, could be obtained by the passage of direct current through a capillary tube containing the liquid metal. Since that time, this phenomenon has been observed in many liquid metals and some solid metals. In all cases it was demonstrated that the heavier isotopes were concentrated in the direction of current flow, while the lighter isotopes were concentrated in the direction of electron flow. With very few exceptions these investigations were conducted in such a manner that it was not possible to follow the instantaneous separation of the isotopes. Since the separation could not be followed it was impossible to determine, with any degree of accuracy, when an equilibrium condition had been attained. In most cases the investigations were conducted in a system in which a reservoir was attached to the capillary tube at either the middle or at one or both ends.

In 1963 Baysden (2) successfully followed the separation of the isotopes in a capillary system without attached reservoirs. His results showed that, with this type of system, an equilibrium condition could be attained in a time much shorter than the 50 to 120 days used in previous investigations.

It is the purpose of this investigation to:

(1) Determine if the time necessary to reach equilibrium is dependent on the temperature of the system.

(2) Determine if the amount of separation attained, at equilibrium, is dependent on the temperature of the system.

(3)   Follow the separation of the isotopes, as it was progressing, and, if possible, find a relationship between time, separation, and temperature.

II. REVIEW OF LITERATURE

The previous work in the field of the Haeffner Effect will herein be examined by looking at the experimental techniques, the results and the proposed mechanisms of earlier investigators. It is felt that by doing this a clearer insight into the phenomenon may be gained.

Mass transport, induced by the passage of an electric current, as well as isotope separation, by the same method, in both the liquid and the solid state will be considered as the result of the Haeffner Effect.

A. Experimental Techniques and Results

In the first successful experiment, preformed on mercury, by Haeffner (1) a vertical diaphragm tube, 140 mm in length and 2 mm inside diameter, was fitted with tungsten electrodes and used as a separation cell (Figure 1). The tube was filled with glass beads (0.09-0.15 mm diameter) between two sintered glass plates, forming the top and the bottom of the diaphragm. A quantity of mercury (1.430 grams) above the top diaphragm was used to connect the diaphragm area to the top electrode. This mercury was analysed by a mass spectrometer after a current of 22.6 amperes had been passed through the separation cell for about 2000 hours. During the experiment the cell was held at $15^{\circ}C$ in a constant temperature bath. The experiment was then repeated with the direction of current flow reversed. When the top electrode was positive the ratio of Hg^{198}/Hg^{204} was found to be 10.35/6.44, and when the top electrode was negative the ratio was found to be 9.68/6.94.

In 1956 Haeffner, Sjoborg and Lindhe (3) reported the re-

Figure 1. Separation Cell used in Haeffners' original experiment.

Figure 2. Separation Cell used in the experiment by Haeffner, Sjoborg and Lindhe on mercury.

sults of another investigation on mercury, at a higher temperature (47.0±0.5°C), and of one on uranium wire. In the investigation on mercury they used a vertical diaphragm tube, 170 mm in length and 1 mm inside diameter, filled with glass spheres. In this investigation, reservoirs were used at both the cathode and the anode (Figure 2). A current of 4.3 amperes was passed through the separation cell for 42 days. The tube was broken into sections with a length of about 10 mm. The ratio Hg^{198}/Hg^{204} of the mercury contained in the anode and cathode volumes and six of the tube samples was determined with a mass spectrometer. The ratio Hg^{198}/Hg^{204} of the anode volume was 1.548, it then went up to 1.603 at a distance of 5 mm from the anode, followed by 1.608 at 15 mm from the anode, then decreased lineally to 1.526 at 119 mm from the anode and then to a minimum of 1.472 in the cathode volume (170 mm from the anode).

In the work of Lundén, Reuterswärd, and Lodding (4) on molten potassium, a folded vertical tube (Figure 3) with a central reservoir was used. The separation cell was filled by placing the molten metal in the upper chamber, evacuating the cell and then slowly allowing the pressure to return to one atmosphere under an inert gas. In this way the liquid metal was forced into both ends of the cell. A direct electric current with a density of 2900 A/cm^2 was passed through the cell for 14.8 days. Each end of the cell was broken into five equal sections and the contents of these were analysed by a mass spectrometer. It was found that the cathode section contained 7.025% K^{41} and the anode section contained 6.30% K^{41}.

In the investigations of the Haeffner Effect on indium (5),

Figure 3.   Separation Cell used in the experiment by Lundén, Reuterswärd, and Lodding on molten potassium. Sections 1 to 10 were analysed by mass spectrometer.

lithium (6), rubidium (7), tin, cadmium, and zinc (8), all in the liquid state, a horizontal capillary system with a central reservoir was used. Figure 4 is an example of this type of separation cell, the central reservoir was varied slightly by different investigators but was essentially the same as that shown. The separation cell was filled in the same manner as the folded vertical tube which was mentioned earlier. Current was passed through the cells for a predetermined length of time. The separation cells were then broken into sections and their contents were analysed by a mass spectrometer to determine the amount of separation.

In the investigation of Bogoiavlenskii, Grigor'ev, Rudenko, and Dolgopolov (9), on mercury, a folded vertical tube with a reservoir at the positive terminal was used (Figure 5). The experimental procedure and the method of analysis was similar to the methods used by the investigators mentioned earlier.

When compared with the remainder of the separation cell, the volume of metal which is contained in the reservoirs is quite large. This large volume, relative to that of the rest of the separation cell, will introduce a large amount of dilution and will thus increase the time necessary for the separation to reach equilbrium. The results of the experiment by Haeffner, Sjoborg and Lindhe (3), on mercury, clearly show the dilution which is introduced by reservoirs. In 1963 Baysden (2) showed, in a system which did not contain reservoirs, that it was possible to reach an equilibrium condition in a time which was much shorter than previously expected.

It has been found by Lodding (10) that temperature

Figure 4. Separation Cell used in the investigations of the Haeffner Effect in indium, lithium, rubidium, tin, cadmium, and zinc.

Seal

Tungsten
Electrodes

Figure 5. Separation Cell used in the investigation of the
Haeffner Effect on mercury by Bogoiavlenskii, Grigor'ev,
Rudenko and Dolgopolov.

can vary up to 20°C over the length of a vertical separation cell. He also found that with a horizontal separation cell the variation in temperature will be only from 1°C to 6°C. In gallium (11) the separation factor increases from 0.049 at 325°K to 0.077 at 560°K. In indium (5) the ratio In^{115}/In^{113} in the cathode volume was found to increase from 22.5 at 210°C to 23.9 at 530°C. In rubidium (7) the separation of the isotopes increases with increasing temperature to about 142°C, increasing the temperature above 142°C will cause the separation to decrease. In tin (8) the ratio Sn^{125}/Sn^{112} of the cathode volume increases from 5.43 at 285°C to 6.05 at 590°C. In cadmium (8) the ratio Cd^{116}/Cd^{106} increases from 5.32 at 370°C to 5.43 at 590°C. The above data shows that the Haeffner Effect is temperature dependent for some metals. Since the effect is temperature dependent the use of vertical separation cells with their large temperature variations is not good practice.

The use of glass spheres inside a capillary tube will cause the effective cross sectional area of the tube to be continually changing over its length. Because the effective cross sectional area changes, the current density will also change from one location to another within the tube. The results of localized changes in current density will be localized changes in temperature and also in the electrical force which causes separation. Localized temperature changes can easily set up convection currents and thus mixing which will increase the time necessary to reach equilibrium.

In his investigation of the Haeffner Effect in mercury Baysden (2) used a thin wall glass capillary tube, without

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In his investigation of the Haeffner Effect in mercury Baysden (2) used a thin wall glass capillary tube, without

attached reservoirs, for the separation cell. A radioactive tracer, mercury (203), was used to follow the separation. The separation was followed by determining the change in radiation level with time at 20 positions along the length of the separation cell while passing a current with a current density of 509.3 A/cm^2. These positions were 1 cm apart over the entire length of the separation cell. Due to the distance between the separation cell and the detector and also to the collimation of the radiation from the radioactive mercury, at each position a 2 cm length of the separation cell was counted. It is felt, by this author, that the length of separation cell that was counted at each position was excessive as it would be more desirable to have this length approach a point source.

The work of Baysden was the first successful attempt to actually follow the separation as it occured and as such was a significant breakthrough in research technique in this field.

In 1956 the first successful investigation of the Haeffner Effect in the solid state was reported by Haeffner, Sgoborg, and Lindhe (3). This investigation was performed on a uranium wire which was 347 mm in length and 1 mm $\pm$ 0.1 mm in diameter. The wire was inserted in a "Pyrex" glass tube which was then filled with argon. The argon was purified by circulation through heated uranium turnings. A current of 16.8 amperes was passed through the wire for 171 days. The temperature of the wire, as determined with an optical pyrometer, varied between 750°C and 870°C due to the varying diameter.

After the current had been shut off the wire was removed and divided into 35 pieces. Thirteen of these samples were

dissolved in nitric acid and treated chemically to obtain samples of known weight of uranium oxide. The specific α-activity, in counts/mg-min., of the uranium was then determined by an α-scintillation counter. The original specific α-activity of the samples was not determined and thus it is not possible to calculate the amount of separation that occured, but when plotting the specific α-activity versus the distance from the positive electrode it was found that the specific α-activity reached a maximum at a distance 10 mm from the positive electrode. the maximum in the specific α-activity is a very good indication that more U^{234} and U^{235} are present here than in the rest of the wire.

Huntington and Grone (12) studied mass transport in a gold wire by following the movement of light transverse scratches, which were used as markers. The experiments were performed inside a brass box under an argon atmosphere, at a positive pressure. A 3 inch diameter window in the lid of the box allowed continuous measurements to be made of the marker motion during the course of a run. Measurements of marker motion were made with a Hilger linear comparator microscope with a 1 μ lease count. The wire was supported, inside the brass box, in a horizontal plane and both ends were held in cooled clamps. A current with a density of 10^4 A/cm^2 was passed through the wire and gave low temperatures at the cooled ends with a symmetric maximum of 860°C at the center. Temperature was measured by an optical pyrometer and remained within 15 $^{\circ}$C limits. It was found that the velocity of the markers increased with an increase in temperature and was proportional to current

density, at least in the range of their experiment. The marker
motion varied from 1μ per day at about $860^{\circ}C$ to 8μ per day
at about $970^{\circ}C$. The experiment was repeated and the current
density was doubled. For each scratch, in both experiments,
the ratio of the velocity to current density was logarithmi-
cally plotted against the reciprocal of the absolute tempera-
ture. The agreement between the results of the first and second
experiments was sufficiently good to warrant the conclusion
that the marker velocity is proportional to current density.

Similar investigations were performed using copper (13)
and platinum (14) wires. These investigations were carried
out using either the same equipment or slightly modified equip-
ment. In copper the marker velocity increased with increasing
temperature to a maximum of 2μ per day at about $900^{\circ}C$ and then
decreased with additional increases in temperature until $1000^{\circ}C$
where the marker velocity became zero. Above $1000^{\circ}C$ the marker
velocity, in copper, was in the reverse direction. In platinum
it was found that marker velocity increased with increasing
temperature in the range from about $1480^{\circ}C$ to $1670^{\circ}C$.

In the investigations on solid wires the movement of the
markers toward the negative electrode has been explained by
Huntington et al (12) to be due to the vacancies created in
the lattice as mass is transported toward the positive elec-
trode. As mass is transported toward the positive electrode
the vacancies are in turn transported toward the negative elec-
trode. As the vacancies join together, the pressure created
by them is relieved by the markers and the markers are thus
transported toward the negative electrode.

B. Mechanisms

There have been many mechanisms proposed, since the original experiment, to explain the isotopic concentration by a direct current. None of the proposed theories have gained unanimous support but experimental findings give more weight to some theories than to others. In the following the prominent theories will be discussed and, when available, the experimental results will be noted.

Klemm (15) was the first to propose a theory of the Haeffner Effect. Assuming that a metal consists of a mixture of mobile and immobile ions and electrons, he proposed that, since they are a part of an orderly lattice arrangement, the immobile ions were less likely to suffer as many interactions with the conduction electrons as were the mobile ions which are in disorderly arrangement. The mobile ions were thus concentrated toward the anode as a result of numerous interactions with electrons. Both the light and heavy isotopes are among these mobile ions, but since the lighter ions have a greater degree of ionization they interacted more strongly with the electrons and were thus concentrated in the direction of electron flow.

Klemm mentions the fact that in tungsten (16) transport occurs toward the cathode while Cu-Al (17) shows transport toward the anode in the   phase and toward the cathode in the phase but his mechanism fails to explain this. His mechanism also fails to take the temperature of the system into account.

Bresley and Pikus (18) proposed that the heavy isotopes would be concentrated toward the negative electrode. The basis

of their mechanism was that, since the vibrational frequency
of a light isotope of a given element is greater than that of
a heavy isotope, effective radius or wave function of the lighter
isotope is larger than that of a heavier isotope and thus the
lighter isotope will interact to a greater degree with its
neighbors than the heavier isotope. From this they assumed
that the net flux of material is towards the cathode or in the
direction of the electric field. The heavier isotope would
thus be concentrated in the direction of the electric field
because of greater mobility due to its smaller degree of inter-
action.

The mechanism proposed by de Gennes (19) considered the
relationship between the coefficient of diffusion and viscosity,
together with the mean frequency of oscillation of an ion and the
energy transitions of free electrons whereby they impart en-
ergy to the ions of the liquid metal. This mechanism predicts
that the lighter isotopes have a greater cross sectional area
and will be carried along in the direction of electron flow.
Calculations based on his proposals give results that are a
factor of two lower than the experimentally determined separa-
tion in gallium.

Huntington (12) based his mechanism on the interactions
between the charge carriers and the moving atoms as a means of
influencing the direction of jumping via momentum transferred
to the atoms at the saddle point. This mechanism takes temp-
erature into account and can be used to explain the results of
the investigation of the Al-Cu system (17) in which mass trans-
port of both constituents took place toward the anode in the

β-phase (which is an electron conductor) but the direction of transport was reversed in the γ-phase where the current carriers are holes.

Jacobs (20) proposed a negative free energy gradient and that the diffusion rate was proportional to the vibrational frequency of the ions. Jacobs proposed that the negative free energy gradient was in the direction of the positive terminal. Since the vibrational frequency was inversely proportional to the mass of the oscillator, the rate of diffusion toward the positive terminal would be greater for a light isotope than for a heavier isotope thus there would be an enrichment of the light isotopes near the positive electrode and a corresponding enrichment of the heavier isotopes near the negative electrode. This mechanism takes into account the effects of temperature on separation.

III. EXPERIMENTAL PROCEDURE

Mercury was used in this investigation of the Haeffner Effect for the following reasons: (1) a radioisotope, mercury (203), emits β-radiation which is readily detectable, is readily available, has a sufficiently long half-life and a mass that is sufficiently different from that of the average atomic mass of stable mercury and can thus be used as a tracer to detect and follow the separation of the isotopes; (2) mercury is in the liquid state between -38.36°C and 357°C, giving a fairly wide range of temperatures which could be investigated without the necessity of extensive equipment as a heat source; (3) a comparison can be made with the work of Baysden (2) and others.

The radioisotope was purchased from the Isotopes Division, Oak Ridge National Laboratory. The isotope was received in the form of mercuric nitrate in a nitric acid solution with a normality of 2.95 and a volume of 14.6 milliliters. The radioactive properties of the isotope are listed in Table 1.

A. Preparation of the Tagged Mercury

In order for the radioactive mercury isotope to be used as a tracer in this investigation, it was necessary to reduce it to its elemental form from the acid solution. The recovery was accomplished by electrolysis (Figure 6) in the following manner: A small amount of stable triple distilled mercury was placed in the bottom of a 250 ml, wide-mouth, separatory funnel and used as the cathode of the electrolysis cell. Electrical connection was made by placing a platinum wire inside a glass tube and inserting one end of the tube below the surface

TABLE 1

The Radioactive Properties of Mercury-203

Half-life	Energies of Radiations (in Mev)	
47.2 ± 0.7 days	β^-	0.208
	γ	0.286
	e^-	0.20, 0.27

Glass
Tube

Platinum
Electrode

Platinum
Electrode

Mercurous
Nitrate in
Nitric Acid

Stable
Mercury

Figure 6. Electrolytic Cell

of the mercury. This insulated the wire from the solution above the surface of the mercury. A small piece of platinum screen served as the anode of the electrolysis cell. The radioactive solution was mixed with 100 milliliters of 2 normal nitric acid and placed in the separatory funnel. A current of 0.2 ampere was passed through the solution for 72 hours in an effort to recover as much of the radioactive isotope as practical. The tagged mercury was withdrawn from the funnel by opening the stopcock. It was then cleansed by successive washing and decanting in distilled water.

B. Purification of the Tagged Mercury

The tagged mercury was purified by triple distillation, under vacuum, in a pyrex distillation tube. The condensate was collected in a water cooled trap and thoroughly mixed before use in this study.

C. Description of Separation Cell

The separation cell for studying the Haeffner Effect was made from a capillary tube 1 mm inside diameter, 1.65 mm outside diameter and 25 cm in length. The diameters are the average values obtained by microscopic measurement using a filar eyepiece. Three centimeters of each end were bent at an angle of 45° giving the separation cell a straight portion with a length of 20 cm. Two centimeters at each end of the tube were then bent back 45° so they were parallel with the straight portion of the tube (Figure 7). This was done so the separation cell could be placed in a rack prepared for it and this placement repeated in further experiments.

A capillary tube was used in this investigation for two

Figure 7. Separation Cell

Figure 8. Lead Shield

A. Side view, cut away
B. Top view

reasons: (1) current density is expressed in units of amperes per square centimeter, thus with a given current, the current density increases as the cross sectional area of the conductor decreases making it possible to have a high current density without excessive power consumption; (2) to avoid as much as possible any convection due to thermal gradients within the cell. Thin walls were needed in the capillary tube to rapidly dissipate any heat that resulted from the current passing through the mercury.

D. Filling of the Separation Cell

Before filling the capillary tube it was heated to drive out any possible moisture. After it had cooled, a short plastic tube with an attached syringe was placed over one end of the capillary tube.

A quantity of tagged mercury, 0.157 milliliters or 2.127 grams, sufficient to fill the straight portion of the capillary tube was withdrawn, with the syringe, from the prepared mixture of stable and radioactive mercury. Tungsten electrodes were then inserted at each end of the separation cell and pushed inward until they made contact with the mercury in the straight portion of the tube.

E. Counting

An Ekco Electronics Limited automatic decade scaler, type N530F, was used for all counting performed during this investigation. A NaI (Tl) crystal scintillation counter, which was β-sensitive, was used to detect the activity of the radioisotope.

The length of the straight portion of the separation cell

and thus the distance between its anode and cathode was 20 centimeters. The counting was performed at two locations over this length, at the first and the nineteenth centimeters. By using these locations both the maximum increase and the maximum decrease in radiation level could be observed and followed as separation proceeded. The counting was performed by taking 50 readings of the number of seconds per one thousand counts at both locations. These values were then averaged and converted to a counting rate of counts per one hundred seconds. The time between counts at all temperatures is shown in Table 2.

F.   Mounting of the Scintillation Counter

The scintillation counter was placed in an upright position over the separation cell by putting it in a lead shield (Figure 8) mounted above the capillary tube. While constructing the equipment for this investigation it was found that a lead shield, with the wall thicknesses shown in Figure 8, was necessary to keep the background count low enough to be able to successfully follow the separation. As can be seen in Figure 8 the lead shield had a 1 mm diameter hole drilled in the center of its' bottom making it possible to count a 1 mm length of the separation cell at each position.

An assembly (Figure 9) consisting of a piece of ply-wood placed in a metal holder was used to mount the lead shield in a vertical position over the separation cell. The shield was mounted through a hole cut in the ply-wood by means of three bolts placed through holes in the ply-wood and into nuts which were mounted on the side of the shield. Figure 9-A shows the entire assembly with the shield supported by the nuts. In

TABLE 2

Time between readings of radiation level at experimental temperatures.

Temperature °C	Time between readings in hours
30	2
40	4
50	4
60	3
65	2

A.

B.

Figure 9.   Metal Holder Assembly

A.   Side View
B.   Top View

Figure 9-B the shield and nuts have been removed for clarity but their mounting holes are shown. It can easily be seen that by turning the bolts the shield could be raised or lowered without its removal.

The metal holder, in which the ply-wood was placed, had a vee-grove on one side, a flat surface on the other side and two nuts welded to the bottom as shown in Figure 9. This assembly was placed on a large metal rack with a vee-grove and a flat surface corresponding to those of the holder (Figure 10). A long threaded rod was placed through the nuts on the bottom of the holder and connected to the rack as shown in Figure 10 so that turning the rod would move the holder assembly and thus the scintillation counter continuously over the length of the separation cell.

G. Temperature Control

In order to keep the temperature of the separation cell within $\pm 0.1^{\circ}C$, at all of the temperatures, an oil filled plexiglass tank was used as a temperature control bath. A 750 watt flexible immersion heater was controlled with a mercury thermoregulator and a relay was used to supply the current to the heater to maintain the bath temperature. The flexible heater was coiled below the separation cell so that heating would be as uniform as possible. The oil was stirred to keep the temperature constant throughout the entire bath.

H. Separation

The filled separation cell was placed on racks in the plexi-glass tank and a direct electric current of 4.3 ampere, obtained from 6 volt storage batteries, was passed through the

Thermoregulator
Stirrer
Lead Shield in metal holder
Threaded Rod
Oversize nut welded to rack
Washer
Nuts welded to the threaded rod

Separation Cell
Flexible Heater
Plexi-glass Tank

A.

Lead Shield

Metal Holder Assembly

Metal Rack

B.

Figure 10.   Assembled Apparatus

A.   Side View, cut away
B.   Front View, bottom cut away

separation cell. The above mentioned current will give a calculated current density of 547.8 A/cm^2.

IV.   EXPERIMENTAL RESULTS

The data presented was obtained as follows: The number of seconds to record 1000 counts on the scaler was obtained 50 times for each reading. The results were averaged and converted to the number of seconds per 100 counts. The counting rate at time x was corrected for radioactive decay to give C_x. The original count at time zero, C_o, was subtracted from C_x and this quantity was divided by C_o to give a dimensionless ratio which will be called the counting ratio. The values of the counting rates, both uncorrected and corrected for half-life, and counting ratios may be found in Appendix I.

The radioactive isotope, Hg 203, used as a tracer in this investigation, is the second heaviest isotope of mercury and thus an increase in counting ratio will show an increase or enrichment of the heavier isotopes. In like manner a decrease in counting rate will show an enrichment of the lighter isotopes. The separation of isotopes by the Haeffner Effect is retarded by self diffusion and thus it may be said that the measured separation is the net separation and is equal to the total separation minus the opposing effect of self diffusion. If the counting ratio is plotted versus time the net separation of the isotopes may easily be followed.

When the counting ratio is plotted versus time (Figures 11 to 15) the result is a sloping line during the period in which separation is occurring, from time zero to the equilibrium time. When the equilibrium time has been exceeded, and separation is no longer occurring, the plot of counting ratio versus time results in a horizontal straight line.

At $30^\circ C$ and $50^\circ C$ the sloped portion of the plot of counting ratio versus time gradually merges with the horizontal portion as shown in Figures 11 and 13. At $40^\circ C$, $60^\circ C$ and $65^\circ C$ the plot of counting ratio versus time results in a pronounced knee between the sloped and the horizontal portions of the curves.

Figure 11. Counting Ratio Versus Time, 30°C.

⊙— Near negative electrode
⬓— Near positive electrode

Figure 12. Counting Ratio Versus Time, 40°C.

⊙ — Near negative electrode
▫ — Near positive electrode
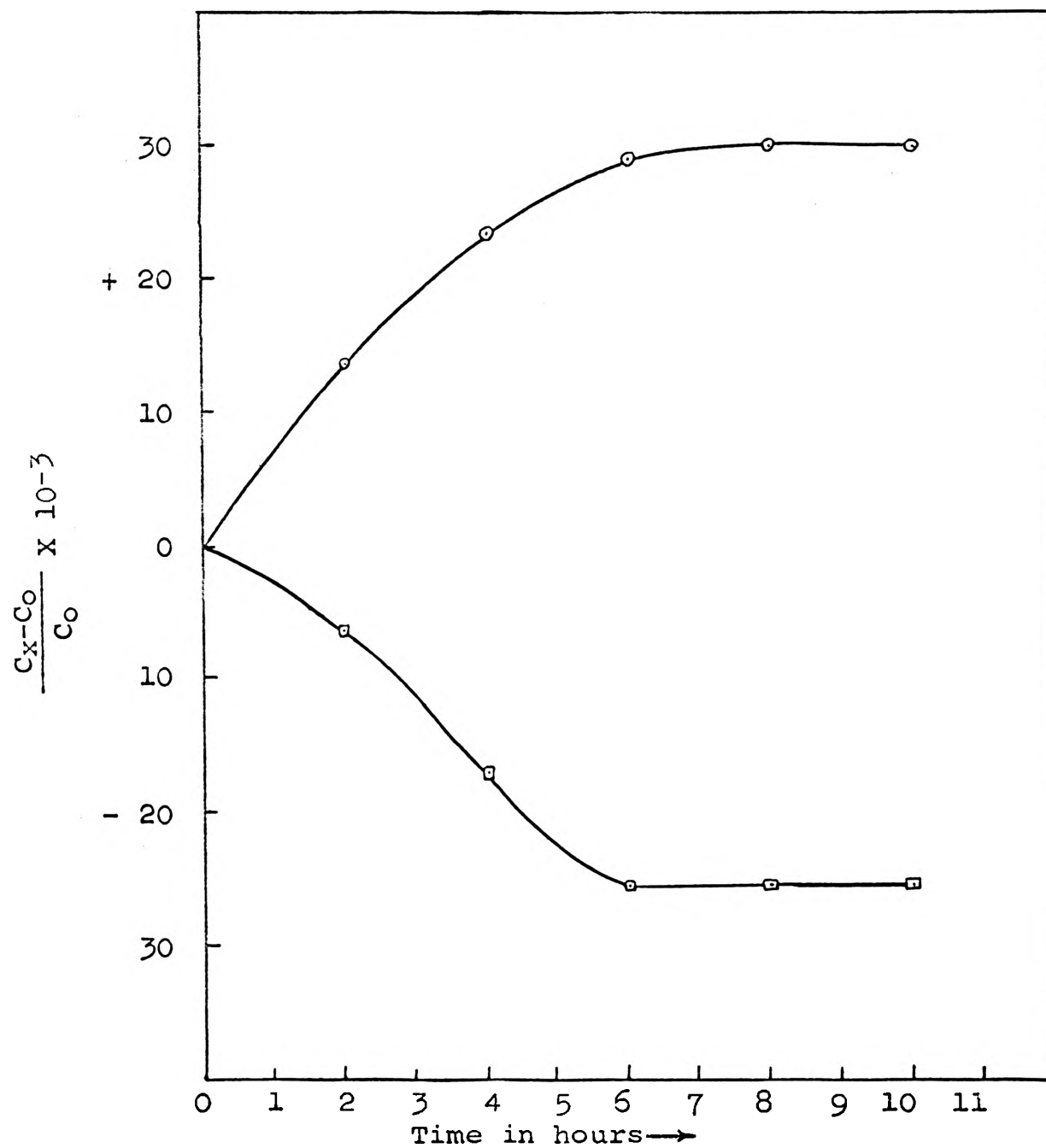
Figure 13. Counting Ratio Versus Time, 50°C.

⊙— Near negative electrode
⊡— Near positive electrode

Figure 14.   Counting Ratio Versus Time, 60°C.

⊙— Near negative electrode
⊡— Near positive electrode

Figure 15. Counting Ratio Versus Time, 65°C.

⊙— Near negative electrode
▣— Near positive electrode

V. DISCUSSION OF RESULTS

In this investigation of the Haeffner Effect the light isotopes were enriched at the positive electrode. In mercury the charge carriers are electrons and thus the light isotopes were enriched in the direction in which the charge carriers flowed. This work is the same as that of all other investigators in so far as the direction of separation is concerned.

In all respects other than the direction of separation this investigation is quite different from all others. Baysden (2) showed that a radioactive tracer could be used to follow the separation of the isotopes and in doing so opened the door to a new method of studying the Haeffner Effect. Using the radioactive tracer method it was possible to do the following things which were not possible with the research techniques that were used by the previous investigators: (1) actually follow the separation as it was occurring; (2) determine the degree of separation which had occurred at any time and at any location along the length of the separation cell.

The separation can best be explained by the so called "electron wind" effect proposed by Huntington (12) in which there is interaction between the charge carriers and the moving atoms as a means of influencing the direction of jumping via momentum transferred to the atoms at the saddle point. Bresler and Pikus (18) and de Gennes (19) state that the lighter isotopes will have a greater effective cross sectional area than the heavier isotopes. If equal numbers of heavy and light isotopes are in a given cross sectional area the lighter isotopes will occupy a larger portion of this area and thus the

charge carriers, the electrons, will encounter light isotopes more often than heavy isotopes as they move toward the positive electrode. Since momentum must be conserved, an electron will impart a higher velocity to a light isotope than to a heavy isotope. The light isotopes are thus concentrated near the positive electrode displacing the heavy isotopes and driving them toward the negative electrode.

When the time necessary to reach equilibrium and the equilibrium counting ratio are plotted versus temperature as in Figures 16 and 17, it was found that the equilibrium counting ratio and time necessary to reach equilibrium both increased with increasing temperature to about 50°C and then decreased with farther rise in temperature.

Runs were made at 45°C and 55°C to see if the results would be as expected from a study of Figures 16 and 17. The results of these runs were quite close to what was expected and the data may be found in Appendix II. The equilbrium counting ratios and times of these "check" runs were plotted versus their respective temperatures in Figures 16 and 17.

An increase in separation with temperature has been reported in gallium (11), indium (5), lithium (6), mercury (9), rubidium (7), tin and cadmium (3). In potassium and rubidium (21) the separation of the isotopes was found to increase with temperature until a critical temperature was reached after which further increases in temperature will decrease the amount of separation. The temperature dependance that was obtained in this investigation was as expected from a study of previous work.

The increase in separation with temperature up to a critical temperature followed by a decrease in separation with further increases in temperature can be explained by the concept of net separation discussed earlier. As temperature is increased the effects of both the separation due to the Haeffner Effect and of self diffusion increase. Below the critical temperature the separation due to the Haeffner Effect is the predominating factor. The effect due to self diffusion increases exponentially with temperature and becomes very noticeable at the critical temperature above which it begins to become the predominant factor and causes the measured, or net separation to become less as the temperature is increased. It is expected that, at some temperature slightly above 70°C, the separation due to the Haeffner Effect and the effects of self diffusion will become equal and it will be impossible to detect separation.

A study of Figures 11 to 15 and Figure 16 clearly show that the time necessary to reach equilibrium is shorter near the positive electrode than near the negative electrode in all cases except at 30°C and 65°C. At 30°C and 65°C the times necessary to reach equilibrium are too close to each other to be able to determine which end reached equilibrium first.

The more rapid separation near the positive electrode can be best explained by Huntington's "electron wind" effect (12). The light isotopes are swept through the separation cell, by momentum transferred from the electrons, at a more rapid rate than the heavy isotopes. As the light isotopes are concentrated near the positive electrode they will displace the heavy isotopes and drive them toward the negative electrode. The

volume near the positive electrode should thus be the first to reach equilibrium and that near the negative electrode, last.

In further work on the Haeffner Effect, in mercury, the effects of current density and length of separation cell on the counting ratio should be determined. Self diffusion data should also be determined by a tracer method so a clearer insight into the Haeffner Effect may be gained.

Figure 16.   Time In Hours To Equilibrium
Versus Temperature.

⊙- Near negative electrode
△- Near positive electrode

Figure 17.   Counting Ratio At Equilibrium
             Versus Temperature.

⊙-   Near negative electrode
△-   Near positive electrode X(-1)

VI. CONCLUSION

The separation of the isotopes was found to occur in the direction previously reported by other investigators. The light isotopes are enriched in the direction of electron flow or at the positive end of the separation cell.

It was found that the separation of the isotopes is temperature dependent and that the separation increases with increasing temperature until it reaches a maximum at $50^{\circ}C$. Above $50^{\circ}C$ the separation of the isotopes was found to decrease with increasing temperature.

It was found that above $70^{\circ}C$ and below $30^{\circ}C$ it was not possible to detect separation of the isotopes when a current density of 547.8 A/cm^2 is used.

It was found that the time necessary to obtain the equilibrium separation of the isotopes is dependent on the temperature of the system. The time necessary to reach equilibrium increases with increasing temperature until $50^{\circ}C$ above which it decreases with increasing temperature.

It was found that the liquid metal near the positive electrode reached an equilibrium condition in a shorter time than the liquid metal near the negative electrode.

BIBLIOGRAPHY

1. E. Haeffner, "A Method of Changing the Isotope Concentration in Mercury", Nature, Lond., 172, 775 (1953).

2. J. N. Baysden, "A Study of the Haeffner Effect in Mercury", Master of Science Theses, Univ. of Missouri School of Mines and Metallurgy (1963).

3. E. Haeffner, Th. Sjoborg and S. Lindhe, "The Isotope Effect of a Direct Current Through Liquid and Solid Metals", Z. Naturforschung, 11a, 71 (1956).

4. A. Lunden, C. Reutersward and A. Lodding, "The Isotope Effect from Current Passage in Molten Potassium", Z. Naturforschung, 10a, 924 (1955)

5. A. Lodding, A. Lunden and H. von Ubisch, "The Temperature Dependence of the Isotope Effect of Current Passage in Molten Indium", Z. Naturforschung, 11a, 139 (1956).

6. A. Lunden, A. Lodding and W. Fischer, "The Isotope Effect of a Current Passage in Molten Lithium Metal", Z. Naturforschung, 12a, 268 (1957).

7. A. Lodding, "Isotope Separation in Molten Rubidium at Different Temperatures", Z. Naturforschung, 14a, 7 (1959).

8. A. Lodding, "Haeffner Effect in Tin, Cadmium, and Zinc", Z. Naturforschung, 12a, 569 (1957)

9. I. V. Bogoiavlenskii, V. N. Grigor'ev, N. S. Rudenko, and D. G. Dolgopolov, "Variations in the Isotopic Composition of Mercury in a D. C. Electric Field", J. Exptl. Theoret. Phys., U. S. S. R., 33, 581 (1957).

10. A. Lodding, "Isotope Transport Phenomina in Liquid Metals" p17 (1961).

11. M. Goldman, G. Nief and E. Roth, "The influence of Temperature on Isotopic Separation Under the Effect of Direct Current in Molten Gallium", C. R. Acad. Sci., Paris, 243, 1414 (1956).

12. H. B. Huntington and A. R. Grone, "Current-Induced Marker Motion in Gold Wires", J. Phys. Chem. Solids, 20, 76 (1961).

13. A. R. Grone, "Current-Induced Marker Motion in Copper", J. Phys. Chem. Solids, 20, 88 (1961).

14. H. B. Huntington and Siu-Chung Ho, "Electromigration in Metals", J. Phys. Society of Japan, 18, 202 (1963)

15. A. Klemm, "Isotopenuberfuhrung and Sebstuberfuhrung in Metallen", Z. Naturforschung, 9a, 1031 (1954)

16. R. P. Johnson, "Construction of Filament Surfaces", Phy. Rev., 54, 459 (1938).

17. H. Wever and W. Seith, "Uber Einen Neuen Effekt der Electrolytischen Uberfuhrung in Festen Legierungen", Z. Elektrochem., 59, 942 (1955).

18. S. E. Bresler and C. E. Pikus, "Separation of Ions According to their Mobilities", J. Exptl. Theoret. Phys., U. S. S. R., 1, 102 (1956).

19. P. G. de Gennes, "The Separation of Isotopes by the Passage of a Current in a Liquid Metal", J. Phys. and Rad., 17, 343 (1956).

20. D. C. Jacobs, "A Theoretical Study of the Mechanism for the Haeffner Effect", Master of Science Thesis, Univ. of Missouri School of Mines and Metallurgy (1962).

21. A. Lodding, "Das Temperaturverhalten des Isotopieeffektes bei Stromdurchgang in Flussigen Alkalimetallen", Z. Naturforschung, 14a, 934 (1959).

Appendix I

Experimental data used to determine the effects of temperature on the Haeffner Effect in mercury.

$30^\circ C$ one centimeter from the negative electrode

Time in hours	Counting Rate in counts/100 seconds		Counting Ratio
	Uncorrected	Corrected for Half-life	$\dfrac{C_x - C_o}{C_o} \times 10^{-3}$
0	15643	-----	----
2	15931	15951	13.3
4	15971	16010	23.5
6	16041	16097	29.0
8	16032	16112	30.0
10	16013	16112	30.0

$30^\circ C$ one centimeter from the positive electrode

Time in hours	Counting Rate in counts/100 seconds		Counting Ratio
	Uncorrected	Corrected for Half-life	$\dfrac{C_x - C_o}{C_o} \times 10^{-3}$
0	15400	-----	-----
2	15285	15304	- 6.3
4	15104	15141	-16.8
6	14954	15009	-25.4
8	14937	15011	-25.3
10	14919	15011	-25.3

40°C one centimeter from the negative electrode

| Time in hours | Counting Rate in counts/100 seconds | | Counting Ratio |
	Uncorrected	Corrected for Half-life	$\frac{C_x-C_o}{C_o}$ X 10^{-3}
0	14450	-----	-----
4	14435	14473	1.6
8	14683	14755	21.1
12	14756	14865	28.7
16	14824	14970	36.0
20	14789	14967	35.8
24	14752	14968	35.9

40°C one centimeter from the positive electrode

| Time in hours | Counting Rate in counts/100 seconds | | Counting Ratio |
	Uncorrected	Corrected for Half-life	$\frac{C_x-C_o}{C_o}$ X 10^{-3}
0	14400	-----	-----
4	14073	14108	-20.3
8	13951	14024	-26.1
12	13707	13808	-41.1
16	13671	13805	-41.3
20	13639	13807	-41.2
24	13607	13808	-41.1

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50°C one centimeter from the negative electrode

| Time in hours | Counting Rate in counts/100 seconds | | Counting Ratio |
	Uncorrected	Corrected for Half-life	$\frac{C_x - C_o}{C_o} \times 10^{-3}$
0	14763	-----	-----
4	15064	15101	22.9
8	15468	15562	54.1
12	15735	15851	73.7
16	15875	16031	85.9
20	15883	16078	89.1
24	15842	16076	89.0

50°C one centimeter from the positive electrode

| Time in hours | Counting Rate in counts/100 seconds | | Counting Ratio |
	Uncorrected	Corrected for Half-life	$\frac{C_x - C_o}{C_o} \times 10^{-3}$
0	14050	-----	-----
4	13679	13713	-24.0
8	13311	13331	-51.2
12	13017	13113	-73.8
16	12797	12914	-80.9
20	12755	12912	-81.0
24	12724	12912	-81.0

60°C one centimeter from the negative electrode

| Time in hours | Counting Rate in counts/100 seconds | | Counting Ratio |
	Uncorrected	Corrected for Half-life	$\frac{C_x - C_o}{C_o}$ X 10^{-3}
0	11654	-----	----
3	11773	11795	12.1
6	11876	11922	22.9
9	12238	12306	55.9
12	12246	12341	58.9
15	12226	12339	58.8

60°C one centimeter from the positive electrode

| Time in hours | Counting Rate in counts/100 seconds | | Counting Ratio |
	Uncorrected	Corrected for Half-life	$\frac{C_x - C_o}{C_o}$ X 10^{-3}
0	11318	-----	-----
3	11152	11173	-12.8
6	10794	10835	-42.7
9	10756	10815	-44.4
12	10732	10811	-44.8
15	10713	10812	-44.6

65°C one centimeter from the negative electrode

| Time in hours | Counting Rate in counts/100 seconds | | Counting Ratio |
	Uncorrected	Corrected for Half-life	$\frac{c_x - c_o}{c_o} \times 10^{-3}$
0	13042	------	----
2	13391	13394	27.0
4	13426	13459	32.0
6	13404	13453	31.5
8	13383	13449	31.2
10	13376	13458	31.9

65°C one centimeter from the positive electrode

| Time in hours | Counting Rate in counts/100 seconds | | Counting Ratio |
	Uncorrected	Corrected for Half-life	$\frac{c_x - c_o}{c_o} \times 10^{-3}$
0	14113	------	------
2	13849	13866	-17.5
4	13583	13616	-35.2
6	13565	13615	-35.3
8	13555	13621	-34.9
10	13536	13619	-35.0

Appendix II

Data obtained from the two runs that were made to check the temperature dependence of the Haeffner Effect.

45°C one centimeter from the negative electrode

Time in hours	Counting Rate in counts/100 seconds		Counting Ratio
	Uncorrected	Corrected for Half-life	$\dfrac{c_x-c_o}{c_o}$ X 10^{-3}
0	15001	------	----
12	15710	15826	55.0
14	15825	15961	64.0
16	15969	16126	75.0
18	16023	16201	80.0
20	16003	16200	80.0
24	15974	16201	80.0

45°C one centimeter from the positive electrode

Time in hours	Counting Rate in counts/100 seconds		Counting Ratio
	Uncorrected	Corrected for Half-life	$\dfrac{c_x-c_o}{c_o}$ X 10^{-3}
0	15051	-----	-----
10	14191	14278	-52.0
12	14018	14140	-61.0
14	13841	13998	-70.0
16	13824	13983	-70.1
24	13641	13998	-70.0

55°C one centimeter from the negative electrode

Time in hours	Counting Rate in counts/100 seconds		Counting Ratio
	Uncorrected	Corrected for Half-life	$\dfrac{c_x - c_o}{c_o} \times 10^{-3}$
0	12061	-----	----
12	12703	12796	61.0
14	12834	12945	70.0
16	12875	13002	78.0
18	12883	13026	80.0
20	12879	13025	80.0
24	12834	13024	79.9

55°C one centimeter from the positive electrode

Time in hours	Counting Rate in counts/100 seconds		Counting Ratio
	Uncorrected	Corrected for Half-life	$\dfrac{c_x - c_o}{c_o} \times 10^{-3}$
0	12130	-----	-----
10	11393	11463	-55.0
12	11271	11354	-64.0
14	11173	11269	-71.0
16	11160	11270	-70.9
24	11105	11269	-71.0

Appendix III

Statistical Treatment of Data

In this section the data from the experiment performed at $30^{\circ}C$ will be treated to obtain ins standard deviation. Since the change of isotopic abundance is followed by the change in counting rate the accuracy of this change will be determined and reported in the table in this appendix. It is felt that it is necessary to treat the data from only one experiment statistically as the accuracy of the other data will be similarl

Each datum point in this investigation was obtained by taking 50 readings of the number of seconds necessary to record 1000 counts. The standard deviation of a given count is equal to the square root of the count, thus each count will have a precision of $\pm$ 312 counts or $\pm$ 3.12% of the count. At $30^{\circ}C$ and zero time, at the location near the negative electrode, it took an average of 6.4 seconds to record 1000 counts. The precision of each time measurement is .05 second. When converting a given count to a counting rate the standard deviation is equal to the sum of the squares of the components, or in this case:

$$1000 \pm 312 = 1000 \pm 3.12\%$$

$$6.4 \pm .05 = 6.4 \pm .782\%$$

$$S.D. = \pm [(3.12)^2 + (.782)^2]^{\frac{1}{2}} = \pm 3.257 \text{ counts/second}$$

Since there are 50 readings per datum point, the standard deviation of the average counting rate will be:

$$S.D._{t_o} = \pm .734 \text{ count/second}$$

In this work the interest is in the change in counting rate with time. For two hours the accuracy of the change in

counting rate will be:

$$(159.31 \pm .734 \ \frac{counts}{second}) - (1.56.43 \pm .721 \ \frac{counts}{second}) =$$

2.88 ± 1.028 counts/second

or 35.7% of the change in counting rate.

Using the same method the following table can be obtained.

Time in hours	Position	Accuracy of the change in counting rate (%)
2	NE	35.7
2	PE	86.2
4	NE	31.4
4	PE	33.5
6	NE	25.9
6	PE	22.1
8	NE	25.9
8	PE	21.4
10	NE	25.9
10	PE	20.5

NE is one centimeter from the negative electrode

PE is one centimeter from the positive electrode

The graphs in this investigation were plotted by drawing a line through the points in a manner which seemed to fit them best and no attempt was made to treat them statistically or to obtain their equations. The time to reach equilibrium for each run is somewhat in question since the curves were drawn in a more or less arbitrary manner

Although the accuracy of the results, as calculated by the standard deviation of the counts, is not very good, the author is confident in them as they are reproducible and can be predicted from Figures 16 and 17, (eg.- check temperatures).

VITA

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