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To the Graduate Council:

I am submitting herewith a dissertation written by Richard Charles Legendre entitled "Metal-Metal Ion Exchange of Mercury and Some Amalgams." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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METAL-METAL ION EXCHANGE OF MERCURY AND SOME AMALGAMS

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

---

by

Richard Charles Legendre

June 1960

To my Mother and Father

Without whose support, encouragement and perseverance

this would never have been.

457887

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CHAPTER I

INTRODUCTION

A. Exchange Processes

1. General Statement

An exchange process is one in which atoms of an element are interchanged among two or more chemical states of that element.[1] Rates of such processes may range from very short times such as the 10^{-3} sec. required for chloride ion to exchange completely with chlorine gas[2] to very long times (years) necessary to detect any appreciable exchange such as in the case of phosphate ion exchanging with phosphite ion.[3]

2. Methods of Detection and Estimation

Early investigators were unable to follow the course of true exchange. This process was approximated, however, by following by traditional chemical methods the behavior of a chemical entity different from that whose exchange is to be approximated but which would be expected to behave similarly to it.

The classical true exchange work, which will be discussed more fully below, was begun by von Hevesy[4,5] in 1912 using a few of the then available radioactive species as tracers. The superiority of the tracer technique for following exchange reactions was quickly recognized, a superiority demonstrated by the fact that practically all modern exchange studies utilize this method.

The desirability of radiotracers is based primarily on two main characteristics. The first is that before its radioactive decay, a radiotracer behaves in essentially the same way as the other atoms isotopic with it. The second is that the presence of these radiotracer atoms is easily and conveniently detected by their emitted radiations. The technique of following the course of an exchange is thus facilitated since all that is required is the following of the appearance or disappearance of emitted radiations in a given specie (after separation of the various species by suitable analytical procedures). In addition to the matter of convenience, the use of the array of radiotracers now available in high degrees of radiochemical purity greatly extends the sensitivity, lowers the concentration limit of possible study, and allows quantitative estimation without destruction of the sample.

Common methods for the quantitative expression of the exchange rate are by use of kinetic rate constants and half-time periods. This latter refers to the time necessary for one half of the total possible exchange to have occurred. The amount of exchange occurring is commonly expressed simply in units of per cent (of total possible exchange) or of atomic layers. This latter term, often used in the case where one phase is a solid, and especially when that solid is a metal, refers to a theoretical thickness of the solid to which the total number of exchanged atoms would be equivalent. This, of course, is merely a formal expression and does not purport to represent the actual distribution of the exchanged atoms.

3. Homogeneous Exchange Reactions

A homogeneous exchange is one in which the reactants entering into exchange are uniformly distributed in only one phase. On investigation of the behavior of homogeneous exchanges, one finds that a simple exponential rate law has been followed regardless of the exchange mechanism, the number of exchange sites per specie, or the concentration of the tracer. This process has been treated amply in the literature.[1] The mathematical expression derived and experimentally shown to apply has the form

$$\frac{dA}{dT} = K_1 \exp(-K_2 t) \qquad \text{Eq. 1}$$

where K_1 and K_2 are constants, t is the time and A is the concentration of the radioactive specie at time t.

4. Heterogeneous Exchange Reactions

A heterogeneous exchange reaction is defined similarly to the preceding case except that the materials undergoing exchange are located in more than one phase. The mechanisms and therefore the mathematics of this situation are complicated by the fact that the exchange is dependent not only on the rate of actual exchange between the reactants, but also on the rate at which there may occur an incorporation of the surface-deposited material into the interior of the bulk material. It may be noted that in the special case of fluid-fluid exchange there may be an approximate following of the previously stated (homogeneous) rate law as illustrated by Eq. 1. This is attributed to the relatively rapid diffusion in fluids, especially when they are agitated.

A theoretical work by Zimens[6] treats the system of heterogeneous exchange with solids. This author assumed the slow steps to be the diffusion

across the interface, exchange at the interface, and diffusion into the solid. If one considers the passing of an atom of the solid into the solution and of a solution phase ion into the solid as two independent processes, one may arrive at the relation

$$\frac{-dx}{dt} = \frac{d}{dt}(m-x) = \frac{k(r-x)}{s} \qquad \text{Eq. 2}$$

where m is the total number tagged atoms and ions; r is the ratio m/c, c being the number of untagged ions in solution (this ratio will normally be constant due to the small per cent of exchange over short periods); s is a constant which is determined by the surface area of the solid phase; k is a constant reflecting the influence of the total amount of solute; and x is the amount exchanged.

Integrating Eq. 2 one obtains

$$\ln (rs - x) = \frac{kt}{s} + C. \qquad \text{Eq. 3}$$

But x = 0 at t = 0, therefore

$$\ln \left(1 - \frac{x}{rs}\right) = -k_1 t \ , \qquad \text{Eq. 4}$$

or

$$\ln (rs - x) = k_1 t + k_2 \ . \qquad \text{Eq. 5}$$

This result, then, is to be compared to the actual relation followed as found by Haissinsky[7] in his extensive work. His relation takes the form

$$\ln x = a \ln t + \ln b \qquad \text{Eq. 6}$$

or

$$x = bt^a \qquad \text{Eq. 7}$$

where x is the amount of exchange, t is the time, and a and b are constants.

A second relation which was found by Haissinsky[8] to hold but only over shorter time periods, and which allows easier handling of the experimental data is

$$\ln (1 - F) = -kt \qquad \text{Eq. 8}$$

where F is the fraction of exchange, t is the time, and k is an experimental rate constant.

Many exchange studies by the above investigator over periods up to about two hours in length have demonstrated the validity of these latter two relations. Reflection upon and comparison of the theoretically derived and the experimentally observed equation forms demonstrates a considerable lack of agreement. This is usually attributed to the fact that in actual exchanges the surface of the solid in contact with an exchanging medium cannot be considered as remaining constant as was assumed by Zimens.[6]

In most time-exchange studies there has been noted an initial rapid uptake of the tracer material. This was seen to be due to adsorption phenomena at the interface. During this very brief time interval, the "exchange", or rather the observed decrease in radioactivity, is directly proportional to time. The problem of adsorption to the surface before exchange is treated by King.[9] Following this, the subsequent processes come into play and the above equations are followed.[10]

B. Metal Exchange Reactions

1. Solid-solid Exchange Reactions

The interdiffusion of solid materials was observed qualitatively in 1894 by Spring,[11] and these observations were followed by a quantitative

study by Roberts-Austen[12] on the diffusion of lead through gold.

This type of diffusion, as well as the true exchange process involving only one type of atom, is followed by a variety of rather specialized methods. Generally, such methods depend on the analysis of successive thin layers of the metal after subjecting it to exchange. Various techniques have been devised to accomplish these analyses, among them being chemical, x-ray, spectroscopic and radiotracer methods.

Good compilations of metal-metal exchanges and mixed metal diffusions are available in Barrer[13] and Wahl and Bonner.[1] These sources report exchange and diffusion rates which for many systems follow the relation

$$D = D_0 \exp(-E/RT) \qquad \text{Eq. 9}$$

where D is the observed diffusion, D_0 is the diffusion coefficient, E is a diffusion activation energy, R is the gas constant, and T is the absolute temperature. Some values for D_0 are 4×10^{-10} cm.^{2}/sec. for copper at 940°, and 2×10^{-12} cm.^{2}/sec. for iron at 970°. Corresponding values of E are 60 kcal./mole and 74 kcal./mole, respectively.

2. Solid-liquid Exchange Reactions

The first and classic experiments on metal-solution exchange were carried out by von Hevesy.[4] In the process of studying the electrochemical potentials of radioactive metal ions, he noted that each of the metal ions used could be deposited spontaneously to some extent onto a variety of metals regardless of the relative electrochemical potentials involved. Investigating this unexpected phenomenon further, he studied[5] solutions of lead ions as the nitrate and chloride and containing some thorium-B

(radiolead) in their exchanges with strips of lead metal. A rapid exchange was noted, as demonstrated by the loss of thorium-B from the solution. In addition to the obvious variables of time, temperature and concentration, it was soon noted[14] that the condition of the surface at the time of exchange had a profound effect on the extent and rate of exchange.

Following these early studies, many experimenters have worked in the field using naturally occurring, and more recently, the ever-widening selection of artificially produced radionuclides. Table I lists the systems that have been investigated. The heading "Form" is meant to indicate only the oxidation number of the metal under investigation, and would include any complexed form of the metal as well as the simpler aquated forms. Additional detail as to temperature, ionic specie, pH, etc. may be obtained from a similar tabulation in Wahl and Bonner[1] or from the references cited.

A study of this mass of data has pointed out the following generalities:

a. The amount and rate of exchange varied widely, reflecting the effect of the previously mentioned variables, but for salts of many metals in about 10^{-3} M. solutions tens of atomic layers, and in 10^{-1} M. solutions hundreds of atomic layers, were exchanged in about ten minutes. After a rapid initial exchange the process is considerably slowed and the experimental data became somewhat irregular.

b. The kinetics of exchange followed a form other than that found so commonly for other exchanges. The relation found applicable for times

TABLE I

SUMMARY OF METAL-METAL ION EXCHANGE SYSTEMS

Metal	Form	References
Antimony	III	7, 15
Arsenic	III	15
Bismuth	III	7, 16
Cadmium	II	17, 18
Chromium	III	20
Cobalt	II	21, 22
Copper	II	7, 9, 23, 24, 25
Gold	III	7, 16
Lanthanum	III	7
Lead	II	5, 16, 26, 27
	IV	28
Manganese	II	7
Mercury	I, II	8
Selenium	a	29
Silver	I	9, 10, 30, 31, 32, 33, 34, 35, 36 37, 38, 39, 40, 41
Tantalum	V	22
Tellurium	IV	7, 42
Zinc	II	18, 19, 23, 31, 43, 44

[a]Polyselenide.

up to about two hours was $x = bt^a$ where a and b are constants dependent on the system.[7]

c. The nature of the anion exerted a considerable influence on the exchange. The sequence of exchangeability rates within a set of anions varied according to the metal ion used, and there may even be a transposition in the series at different concentrations or temperatures. Generally, a high exchange was found when using anions which are likely to have a chemical effect on the metal, or which may form a complex ion with the ion of the metal when in solution.[7]

d. The exchange rate generally increased with solution acidity.[45] However, von Hevesy and Biltz[5] demonstrated that corrosion of the metal is not an essential condition for exchange to occur, but that it is thus facilitated due to chemical disintegration of the surface.

e. Exchange usually increased with an increase in temperature. By assuming a linear increase in exchange rate over small temperature intervals, one may determine an initial activation energy for the exchange. This value is obtained from the slope of a plot of ln k versus 1/T. Inspection of the results of ten exchange systems indicated values of about 4 kcal./mole for metal chlorides and about 7.5 kcal./mole for metal nitrates.

f. The exchange was not related in a simple manner to the electrochemical potential values. For instance, with the same anion and at equal concentrations, ions of copper (E_{ox} = -0.34 v.) and manganese (E_{ox} = +1.05 v.) had similar exchange rates with their respective metals.[16] Other workers[46,47,48] have shown that spontaneous deposition of ions occurs even onto metals more noble than themselves. Thus we find that zinc ions

plated out spontaneously to some extent onto silver, copper and iron. However, for a given ion the extent of the pickup by a sample of metal was determined by the position of that metal in the electrochemical series.[16,48]

g. The exchange evidenced by a given metal was greatly dependent on the condition of the surface, with circumstances such as mode of preparation, fabrication, and physical treatment prior to the exchange being of importance.

Exchange experienced by a sample of metal regardless of its prior history was usually different from an identical sample which had been previously immersed in a solution like that to which it was to be subjected for exchange but which contained no tracer ions. Erbacher[26] showed that after such a treatment the extent of exchange was usually reduced, but in some cases an increase was noted. Moreover, for the same system there may be either an increase or a decrease dependent on the pH or the length of time of immersion.[7]

Electropolishing of the metal surfaces likewise affected the results of exchange studies. Generally there was found a decreased exchange rate and extent, and an increased difficulty in obtaining reproducible data.[22]

To illustrate some of these effects the following results for the same system are listed. Chemically etched silver exchanged ten atomic layers with 0.1 M. silver nitrate solution and the exchange was complete in a few seconds. If, however, the metal sample was first mechanically polished, the exchange amounted to 100 atomic layers, but was only 90 per cent complete after twenty-four hours.[30] An electrolytically prepared

silver powder exchanged 30 atomic layers with 0.2 M. silver nitrate solution in twenty hours, but a sample of silver from chemical reduction resulted in the exchange of 7500 atomic layers under the same conditions. This chemically prepared powder was found via x-ray studies to have recrystallized during the exchange, thus modifying the surface.[35]

Early notice was taken[5] of the fact that an initial heterogeneity of the surface and a consequent formation of local cells seemed to play an important part in exchange phenomena. An estimation of the current of such cells has been made[21] for cobalt. This study reports a current of 3.9×10^{-8} coulomb/sec./cm.^{2}, and the authors concluded that it is this current between the anodic and cathodic areas that causes ions to be plated. Autoradiographic studies were presented to substantiate these claims. Further, it was presumed that these cells become "shorted out" by immersion of the metals into solutions of their ions prior to exchange. Nevertheless, autoradiographs indicated the presence of a few active centers on silver foil even after immersion in silver nitrate for five months.[9]

The presence of oxygen in the system was found to have a varied effect on the exchange, depending on the nature of the film formed at the surface. If the oxide film was unprotective in nature it acted as a depolarizing agent and thus increased the exchange. If, on the other hand, the film was protective, then it covered the active centers and thereby reduced exchange.[21] In the above case of cobalt, the value of 3.9×10^{-8} coulomb/sec./cm.^{2} was reduced to 1.3×10^{-8} coulomb/sec./cm.^{2} if the oxygen were removed prior to exchange.

Also affecting exchange were processes such as cold-rolling, tempering, annealing, electroplating, and method of cleaning the metal before exchange. All of these are found to affect in some way the metal surface presented for exchange.

In the overall process of exchange, the important individual processes occurring seem to be the diffusion of the ion through the solution to the metal, the discharge of the ion by the electronic transfer, and the incorporation of the newly formed metal atom into the bulk metal. The first of these might be rendered unimportant by the use of reasonably high concentrations and by agitation of the solution. The second has been measured directly for a few reactions and has been found to be quite fast, and usually reversible.[7,34,49] The third process has generally been found to be the rate-determining step.[44] It is necessary to note at this point that the sometimes high rate of exchange cannot be attributed to self-diffusion alone at temperatures not too near the melting point of the metal. For silver ion onto silver metal at 25°, exchange was about 10^5 times greater than the self-diffusion at this temperature. In addition, the exchange activation energy was about one-fifth that for self-diffusion.[10] Generally, it seems that the metal surfaces do not remain unchanged when in contact with their ions in solution. Even in the absence of corrosion in the normal sense of the word, exchange disorganizes the structure of the superficial layers by the constant processes of dissolution and precipitation, thereby making the metals more permeable to ions.

The total uptake of the ion from solution may be broken down into two quantities: that adsorbed as an ionic double layer at the interface,

and that incorporated into the bulk of the metal (actually exchanged). The rapid initial "exchange" is due to such adsorption, and then the slower uptake of ions is due to true exchange by passage of the ion through the ionic double layer and subsequent diffusion into the lattice.[20] Since the overall measured rate is dependent upon this latter process, it is found that exchange rates are dependent on the ability of the metal to alter itself when in contact with a solution of its ions. This, in turn, is a function of the structural properties of the metal and its cohesion energy. In this respect, Haissinsky[16] recognizes three classes of metals: those (lead, mercury and thallium) which have weak cohesive forces, large atomic volumes, rather high coefficients of self-diffusion, strong tendency to recrystallize and weak mechanical strength; those (iron, cobalt, other transition metals) which are more compact and have higher cohesive energies; and an intermediate group (bismuth, antimony, gold and copper). The exchange undergone by a metal with its ion in solution seems to be roughly dependent on its classification in the above manner.

3. Liquid-liquid Exchange Reactions

Examples of this type of exchange are considerably limited in scope since one is confined to the lower melting alloys and metals. In this discussion particular emphasis will be placed on systems involving mercury or amalgams as the metal phase.

Groh[50] has demonstrated that a rapid exchange occurred between bismuth and lead(II) ions in solution with their respective amalgams. Kayas[51] found essentially the same behavior in the case of copper(II) ions and

copper amalgam, and reported a kinetic equation of a form identical to that reported by Haissinsky for solid metal-metal ion heterogeneous exchanges.

Haissinsky and Cottin[7,8] likewise reported a rapid exchange of mercury(I) and (II) ions with mercury. A very slight dependence of exchange on temperature and anion were found for this system, although its study was restricted by the insolubility and ease of hydrolysis of most mercury(I) salts, and complications involved in the reduction of mercury(II) ions to mercury(I) when in contact with metallic mercury.

These authors interpreted the processes in an agitated system of mercury ions and mercury metal as a rapid exchange at the mercury surface, with the process being sustained by the self-diffusion of the mercury. Thus they feel that the experimental activation energy obtained for such a system would be related to the process of self-diffusion itself. These conclusions will be discussed in Chapter III.

Randles[52] presented a series of publications dealing with the processes occurring at an amalgam electrode as studied by the electrical impedance of a dropping-amalgam electrode to an alternating potential while the electrode is dripping amalgam into a solution of the ions of the amalgamated metal. The authors visualized the ion deposition as occurring in two stages: the initial discharge of the ion with deposition, then a subsequent migration of the deposited specie. Their experimental arrangements caused the measurements to be concerned with only the initial deposit of the ion, and the rate determined is ascribed to that of the electron ex-

change itself. Since this present research will be concerned with the overall exchange reactions and rates, these results will be of interest only inasmuch as they help to elucidate one step of the overall process. A critical review of the method and results of Randles is available.[53] Gerischer[18] has also carried out some measurements with the same method as above.

Miller and Pleskov[54] have investigated by tracer methods the exchange of bismuth, lead and zinc ions with their amalgams. They reversed the usual attack by tagging the metal initially, a method found to be altogether equivalent to the converse.[33,35] Their rate equation took the form

$$\ln\left[\frac{x_{\infty}}{x_{\infty} - x}\right] = \frac{A + B}{AB} srt \qquad \text{Eq. 10}$$

where x_{∞} is the solution activity after total exchange, x is the solution activity after time t, s is the surface area, r is the exchange current, A is the amount of metal in the amalgam, and B is the amount of metal in the solution. This equation was found to be valid over a range of stirring rates, and failed only when the stirring was so vigorous that the surface of the amalgam was broken. This equation is easily transformed into the form previously reported, $\ln (1 - F) = -kt$ (Eq. 8).

Fronaeus[17] has investigated the behavior of cadmium ions in contact with cadmium amalgams, both with and without complexing agent in the aqueous phase. He visualized an equilibrium process

$$M^{+n} + ne \rightleftharpoons M$$

with the total process comprising the loosening and coordinating of the

ligands (water or intentionally added complexing agents), transport of the metal ions in the solution and of the atoms in the amalgam, and the transfer of the electrons. The conclusions drawn from these studies are that for exchange of cadmium ions without intentionally added complexing agents (i.e., aquated), and of cadmium ions with complexing agents of intermediate strength (bromide or chloride ion, ammonia) with cadmium amalgams the rate-determining step is the diffusion of the ion through the Nernst diffusion layer. Systems involving strongly complexed cadmium ions (e.g., in cyanide solution) no longer seemed to be diffusion-controlled, but, rather, dependent on the energetically difficult removal of the cyanide ligands from the cadmium. The earlier work of Gerischer[18] was reinvestigated by Fronaeus and compared with the above mentioned data and conclusions. A very favorable agreement was found.

C. Proposed Problem

The object of this research was to investigate the behavior of metal ions in aqueous solution in their exchange with atoms of the same metal, but where the metallic phase would be in the liquid state.

Research along these lines but involving solid metallic phases has demonstrated that the exchangeability of an ion with a solid metal probably depends on the ability of the metal to re-form its surfaces when in contact with these solutions. A preceding section has reported on the sensitivity of exchange to any of the various processes that can affect the nature of the surface of the metal. With this in mind, it was felt that if the metallic phase to be subjected to exchange were to be in the liquid state,

then many of the problems ("hot spots", variation in crystal size or orientation, channeling in cracks or faults) arising from use of solid phases could be eliminated or minimized.

CHAPTER II

EXPERIMENTAL PROCEDURES

A. Apparatus

1. Stirring and Temperature

After the desired experimental system had been assembled in a 25-ml. glass-stoppered Erlenmeyer flask provided with a 2-cm. length of glass-enclosed iron wire, stirring was accomplished by means of a magnetic stirring device equipped with a thermostatically controlled water supply. This device was constructed such that magnets were mounted in a vertical position beneath and very close to a stainless steel tray. Water from a constant temperature bath was circulated through this tray by means of a pump and siphon arrangement. The magnets were rotated by a belt and pulley system connected to a low r.p.m. motor. This arrangement allowed the magnets to be rotated at from zero to about 450 r.p.m., dependent on the setting of a rheostat connected to the motor. The device contained twelve magnets, but due to slight differences in construction not all rotated at the same rate. For this reason the same stirring position was used in all exchanges.

It was found that even with the agitation of the air from the rotation of the magnets at full speed, the temperature of the bath could be maintained within 0.5° at all times. The control was somewhat better at temperatures close to room temperature. The temperature of the solutions in the exchange flasks was found to vary to about the same extent,

but the readings averaged about 0.1° lower than the corresponding bath temperature.

2. Radioactivity Measurements

All radioactivity measurements were carried out with a Tracerlab "Thousand Scaler" which utilized a Nuclear G-M tube having an end-window thickness of 1.4 mg./cm.^{2}.

In these as in all determinations involving the detection of radiations from radioactive decay, an inherent randomness is involved. Traditional statistical treatment[55] yields the relation that the standard deviation (σ) is equal to the square root of the total number of counts recorded (N). A frequently used quantity, probable error (p), is shown to be 0.67σ or its equivalent, $0.67N^{\frac{1}{2}}$. Thus, for a determination of 5000 total counts, p is 47 counts. This is to say that a repetition of the determination is just as likely to yield a value within 5000 ± 47 as not.

It was intended that normally a total of at least 5000 counts would be recorded for each sample. In this way, the probable error due to counting variations would be held to within 1 per cent.

3. pH Measurements

All pH measurements were made with either a Beckman Model H2 or Model G pH meter. In either case, the same set of miniature saturated calomel and glass electrodes was used. Standardization of the instruments was against a buffer solution of pH of 7.05 or 4.01, depending on the pH range of the solutions to be determined.

4. Glassware

In an attempt to preserve as fully as possible the chemical purity of the system, all cleaning of glassware was accomplished in the following way. The article was allowed to stand in chromic acid cleaning solution, usually overnight. It was then removed, drained, and rinsed vigorously ten times with tap water. This was followed by three rinses each with distilled water and with specially prepared deionized water (see below).

B. Reagents

1. Deionized Water

All water to be used in exchange systems was first subjected to the following pre-treatment. Ordinary distilled water from a copper still was allowed to drip slowly through a 60-cm. long column of Amberlite MB-3 resin. This precaution was taken to prevent deleterious effects due to possible trace contaminants in ordinary distilled water, especially chloride ion.

2. Radionuclides

All radionuclides for this research were obtained from Oak Ridge National Laboratory, and, except in the case of zinc, were used without further treatment, except dilution.

a. Mercury-203 was obtained as the nitrate in dilute nitric acid solution, and had a specific activity of 34.5 millicuries per gram (mc./g.).

b. Cadmium-115 was obtained as the nitrate in dilute nitric acid solution, and had a specific activity of 13.8 mc./g.

c. Zinc-65 was obtained as the chloride in dilute hydrochloric acid solution, and had a specific activity of 342 mc./g. The presence of the chloride ion in the solution required one series of experiments to determine whether or not this small concentration of complexing ion needed to be removed before experiments on uncomplexed systems could be accomplished. The removal was brought about by heating with concentrated nitric acid.

d. Silver-110 was obtained as the nitrate in dilute nitric acid solution, and had a specific activity of 394 mc./g.

3. Mercury

Mercury metal for exchange work and for amalgam preparation was treated as follows. Reagent grade metal was stored in a stoppered flask under dilute nitric acid to prevent reaction with laboratory gases. A tube was provided which extended through the acid solution and into the mercury. This allowed direct access to the mercury as well as its easy removal by means of a pipette. This access tube was kept stoppered at all times except when actually withdrawing mercury. The container described above was equipped with a stirring bar, and was stored over one of the stirring positions of the stirring apparatus. This provided a supply of clean, thermally-equilibrated mercury at all times.

For the preparation of amalgams, appropriate amounts of the mercury were withdrawn and used as described under preparation of amalgams. In the series of studies on mercury itself, the metal phase was handled in

two different ways. In one type of experiment, sufficient metal was used to fill small cylindrical reservoirs of known orifice areas. One of these was a 1-cm. high cup with an inside diameter of 11.5 mm., a second was a 1-cm. high cup with an inside diameter of 4 mm., and a third was a capillary of 1-cm. length and an inside diameter of 1.68 mm. The diameters of the first and second containers were determined by careful measurement, while that of the third was determined by calculation from the amount of mercury contained in a given length of thread within the capillary. A second type of experiment was carried out using known weights of mercury injected directly into the solutions. The weights used were those delivered by a 0.05-ml. (50 lambda) or a 0.005-ml. (5 lambda) micro-pipette. The average weights found to be delivered by these were 674 mg. and 69 mg., respectively. It was desired to study the effect of the lowering of the amount of mercury by still another factor of ten, so a technique was worked out to allow a reproducible delivery of mercury metal in this low weight range, about 7 mg. A reproducible sample of 7 mg. of mercury was obtained as follows. A 3.80-ml. sample of 5×10^{-3} M. mercury(I) perchlorate was heated in a boiling water bath for about five minutes, after which time about 15 drops of 88 per cent formic acid were added. The mercury(I) ions were reduced quickly to the metal, but it appeared grey and lusterless and did not coalesce into a drop. To the above solution was added about 1 to 2 milliliters of concentrated hydrochloric acid, and the mixture was then returned to the boiling water bath for about five minutes. The now clean and coalesced mercury was collected on a fritted glass filter, washed thoroughly with dilute nitric

acid and water, and dried on filter paper. The weights of mercury obtained by this method were found to be quite reproducible, the majority of the samples falling between 6.9 mg. and 7.1 mg.

4. Amalgams

The exact method used to prepare the various amalgams for exchange varied somewhat from case to case.

The granular silver prepared from the spontaneous deposition from silver nitrate solution onto copper was assimilated instantly into the clean mercury.

Granular zinc, although acid-washed and stored in a desiccator until used, resisted quick dissolution by the mercury. It was then accomplished by placing the metal along with the mercury under a layer of water acidified slightly with perchloric acid. Gentle warming, then, usually brought about dissolution without discernable chemical effects. An identical procedure was followed for cadmium.

Desired concentrations of the metal in the amalgam were accomplished by dissolving a weighed amount of the metal in the mercury where feasible, but further dilutions were often necessary before use. After the desired concentration had been obtained, a measured aliquot was removed, washed thoroughly with water, placed in a small beaker, covered with water and placed in the water bath for thermal equilibration. Due to the recognized "ageing" effects of amalgams,[17,49] they were usually used within ten minutes of their preparation, and always within twenty minutes.

5. Other Chemicals

All other chemicals, including the various metals, acids, and salts were of reagent grade.

C. Methods for Exchanges

1. Preparation of Solutions

Normally a concentrated stock solution was prepared for each material to be used in quantity. In the case of the metal ions under study, the ultimate aim was to have each metal ion in solution as the perchlorate. This was accomplished by dissolving the respective metal perchlorate in water, or the oxide, carbonate or hydroxide in perchloric acid.

The stock mercury(I) solution presented some difficulty in its preparation. A common preparation for solutions of mercury(I) salts is to prepare accurately a solution of the corresponding mercury(II) salt and to reduce it with metallic mercury according to the reaction

$$Hg^{+2} + Hg \rightleftharpoons Hg_2^{+2} ,$$

for which a value for the equilibrium constant at 25° of 2×10^8 has been reported.[56] It is this very reaction of mercury that prevents any extensive study of exchanges between mercury(II) and the metal. Thus, a weighed quantity of mercury(II) oxide was dissolved in a slight excess of perchloric acid in a volumetric flask and diluted to volume. Mercury was then added, and the solution and the metal were stirred overnight. Due to the uncertainties involved, it was decided that the stock solution so prepared should be standardized, and the method of Kolthoff and Lar-

son[57] was chosen. This consisted of the titration of the mercury(I) ion with standard potassium bromide using a bromophenol blue indicator. This adsorption-type indicator is lilac color in excess mercury(I) ion and yellow in excess bromide ion, and furnishes an extremely reproducible end-point for this titration.

Many of the solutions used contained additional solute beside the salt of the metal ion under study. The original plan of maintaining stock solutions of these materials so that appropriate aliquots could be added along with those of the metal ion stocks was abandoned. This was due to the fact that some of these stocks, bromides and iodides for instance, were found to be unstable on standing. Weighed quantities of the dry salts were then substituted for the unstable solutions.

2. Sampling

Sampling was accomplished by means of a 0.01-ml. (10 lambda) micropipette attached to a syringe pipette filler. This desired volume of solution was delivered to a planchet which consisted of a 25-mm. diameter watch glass. Reproducible delivery was accomplished by filling to the mark twice with distilled water and adding this to the same planchet.

Samples thus prepared were dried under a heat lamp and reserved for counting.

3. Equilibration and Exchange

After the proper solution had been prepared, a 10-ml. portion was withdrawn, tracer added, its pH adjusted when required, then delivered to a 25-ml. glass-stoppered Erlenmeyer flask provided with a glass-enclosed

stirring bar. This flask, then, was placed in position in the water bath over a magnet and allowed to become thermally equilibrated with slow stirring. In those cases where noted, the entry of nitrogen gas was started at this point. The time required for this thermal equilibration before the exchange could be started was found to vary with the difference between the water and ambient temperatures.

After thermal equilibration had been obtained, the stirring speed was increased to the operating range, and a "zero time" reference sample was taken from the solution as described above. The metal phase was then added while simultaneously starting an electric timer. Additional samples were extracted over appropriate, noted, time intervals dependent on the rate of the individual exchange. These were placed on individual planchets for subsequent drying and counting. The total volume removed by sampling never exceeded 0.1 ml. so that the error incurred from this source would not be greater than 1 per cent.

4. Treatment of Data

After the samples had been prepared, the activity, A_t, of each was determined and recorded. The loss in activity with respect to a "zero time" sample, A_o, was determined according to the relation

$$F' = \frac{A_o - A_t}{A_o} . \qquad \text{Eq. 11}$$

Since the total loss in activity is dependent on the relative amounts of the metallic specie in the aqueous and metal forms, these fractions were "normalized" by dividing by the maximum value of F' obtained. This gives for the various times the fraction of the total possible exchange, F, since

$$F_t = \frac{F_t'}{F_\infty'} \qquad \text{Eq. 12}$$

where F_t is the normalized fraction of exchange at time t, F_t' is the un-normalized fraction of exchange at time t, F_∞' is the un-normalized fraction of exchange at "infinite" time. Since the exchange data were found to follow the equation: $\ln(1 - F) = -kt$, plots of $\ln(1 - F)$ versus t were constructed to obtain values for the experimental exchange rate constant, k. The curves so obtained were linear and passed through or near the origin. To make the placement of these curves more reproducible and less subject to personal prejudices, the method of least squares was usually applied.

One might summarize the method of least squares as follows: choose as the best approximation of the unknown that value which minimizes the sum of the squares of the differences between the observed values and that predicted by the above-approximated unknown. This difference is given by $y_o - y_p$ where the subscripts o and p indicate the observed and predicted values, respectively. For the case of a straight line, this may be represented as

$$s = y_o - y_p = y_o - (mx_o + b). \qquad \text{Eq. 13}$$

The quantity to be minimized is the sum of the squares of all of the deviations as calculated from the values $x_1, x_2, \ldots x_n$ of x and $y_1, y_2, \ldots y_n$ of y. This sum, then, is

$$S = \left[y_1 - (mx_1 + b)\right]^2 + \left[y_2 - (mx_2 + b)\right]^2 + \ldots + \left[y_n - (mx_n + b)\right]^2, \qquad \text{Eq. 14}$$

where S is a function of the two variables m and b. In order to minimize

the quantity S, we set its two partial derivatives equal to zero

$$\frac{\partial S}{\partial m} = -2x_1 \left[y_1 - (mx_1 + b)\right] - 2x_2 \left[y_2 - (mx_2 + b)\right] - \ldots - 2x_n \left[y_n - (mx_n + b)\right] = 0, \qquad \text{Eq. 15}$$

and

$$\frac{\partial S}{\partial b} = -2 \left[y_1 - (mx_1 + b)\right] - 2 \left[y_2 - (mx_2 + b)\right] - \ldots - 2 \left[y_n - (mx_n + b)\right] = 0. \qquad \text{Eq. 16}$$

From these we obtain

$$nb + (\sum x)m = \sum y, \qquad \text{Eq. 17}$$

and

$$(\sum x)b + (\sum x^2)m = \sum xy. \qquad \text{Eq. 18}$$

Solving these equations for m and b, we have that

$$m = \frac{\begin{vmatrix} n & \sum y \\ \sum x & \sum xy \end{vmatrix}}{\begin{vmatrix} n & \sum x \\ \sum x & \sum x^2 \end{vmatrix}} = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2}, \qquad \text{Eq. 19}$$

and

$$b = \frac{\sum y - m(\sum x)}{n}. \qquad \text{Eq. 20}$$

For this particular case, $y = \ln (1 - F)$ and $x = t$. Hence Eqs. 19 and 20 become

$$m = \frac{n \sum \left[\ln (1 - F)t\right] - \sum \left[\ln (1 - F)\right] \sum t}{n \sum t^2 - (\sum t)^2} \qquad \text{Eq. 21}$$

and

$$b = \frac{\sum \left[\ln (1 - F)\right] - m \sum t}{n}. \qquad \text{Eq. 22}$$

Thus k is given by -m, and b is the intercept for the curve. In this manner k values for various exchanges have been determined, and are tab-

ulated in Chapter III. A representative calculation of this type may be found in Appendix I.

Some studies on the effect of temperature on the rate of exchange were performed. The equation that had been demonstrated as being followed is

$$k = k_o \exp \left(- E/RT\right) \qquad \text{Eq. 23}$$

where E is the experimental exchange activation energy, R is the gas constant, and T is the absolute temperature. Alternately, we have $\ln k = \ln k_o - E/RT$. Thus, a plot of ln k *versus* 1/T should be linear, at least over small temperature intervals, and the curve would have a slope equal to -E/R. In this research, values for E were determined after accumulating a series of values of k over a 30° temperature interval. The method of least squares was again applied to obtain the best values for the slope and intercept.

CHAPTER III

RESULTS AND DISCUSSION

A. Steps Within the Overall Exchange Process

One might visualize a number of possible processes as contributing to the overall process of chemical exchange in systems involving metals in contact with their ions in solution. Among these are the diffusion of the ion through the solution to the metal, the discharge of the ion by the transfer of electrons, and the diffusion of the metal atom within the metal phase. The experimental rate constant for the exchange will be determined by the slowest of these individual processes. Zimens[6] has applied the theoretical diffusion equations of Duenwald and Wagner[58] to the process of solid-solution heterogeneous exchange. This treatment has furnished equations which should relate an observed reaction (exchange) rate constant with: first, the ionic diffusion coefficient, assuming the diffusion of the ions to be the slow step of the reaction; second, the autodiffusion coefficient within the second phase, assuming this type of diffusion as the slow step.

1. Ionic Diffusion

An equation developed by Zimens to show the relation between ionic diffusion coefficient and the observed rate constant is

$$k = \frac{D_i c a}{\sigma n(1-s)} \qquad \text{Eq. 24}$$

where D_i is the diffusion coefficient of the ion in solution, c is the

concentration of this ion in the solution (gram ions/ml.), a is the surface area of the solid phase, n is the number of gram atoms of the solid, σ is the thickness of the diffusion layer, and s is the ratio $\frac{n_s}{n_s + n_l}$ (where n_s is the number of atoms of the diffusing specie in the solid form, and n_l is the number of ions of the same specie in the solution). The general form of this equation remains the same when the second (non-solution) phase is liquid.

2. Electron Transfer

A method has been developed by Randles[52] by which he was able to demonstrate that the rate of electron transfer at an inert electrode in equilibrium with a solution containing the oxidized and reduced form of the components of a redox reaction should be approximately proportional to $(C_oC_r)^{\frac{1}{2}}$ where C_o and C_r refer to the concentrations of these oxidized and reduced forms, respectively. Hence, for such a system one has the relation

$$k = K(C_oC_r)^{\frac{1}{2}} \qquad \text{Eq. 25}$$

where K is a proportionality constant. For the case of exchange where the reaction is between the ions in an aqueous solution and a metal in an amalgam, the relation may be rewritten as

$$k = K(C_sC_m)^{\frac{1}{2}} \qquad \text{Eq. 26}$$

where C_s and C_m refer to the concentrations of the ion in solution and the metal in the amalgam, respectively.

To be thorough, though, one must realize that this "electron transfer" step will encompass more than the mere neutralization of the ionic charge. When the ionic specie migrates up to the metal surface it carries

with it a number of attached ligands, e.g., water, anions, etc. Thus, this step should actually include the loosening of these ligands from the ion to be discharged, and the coordinating of the ligands to the "bare" ion as it enters the solution.

Reports[7,34,49,52] on the rate of the electron transfer indicate that it is extremely high, in many cases immeasurably so. In applications of the present type, it is usually conceded that the process would be reversible and with a rate so high that it need not be considered. However, a decrease in the rate of electron transfer has been noted[52] on adding complexing agents which become strongly bound to the ion, so the above simplification is not necessarily always possible.

3. Metal Phase Diffusion

The previously mentioned work by Zimens develops also an expression that would relate self-diffusion coefficients with observed rate constants. This equation takes the form

$$D = \frac{4h^2k}{\pi^2} \qquad \text{Eq. 27}$$

where h is the thickness of a sample of metal. If the metal particles are spherical in shape with radius r, the equation becomes

$$D = \frac{r^2k}{\pi^2} \quad . \qquad \text{Eq. 28}$$

If the sphere contacts the solution with only one-half of its area, then

$$D = \frac{4r^2k}{\pi^2} \qquad \text{Eq. 29}$$

B. Results of Exchange Reactions

All of the experiments of this investigation were of the type where a metal ion in solution was allowed to exchange with a liquid form of the metal (in one case pure mercury metal; in all others, amalgams of the metals). In order to identify more completely each exchange system studied, additional information will be given concerning: the identity and concentration of all solutes in the solution phase; the identity, concentration and/or amount of the metal phase (the orifice area in the case of the controlled area studies on mercury, the amount of metal in the cases where mercury was agitated with the solution, or the amount and concentration in the case of amalgams); pH; and temperature. In the following resumé of experimental results, this information will be abbreviated in the following manner. A solution of 5×10^{-3} M. mercury(I) perchlorate at a pH of 2 in contact with a mercury surface controlled at 104 $mm.^2$, both at a temperature of 30° is written: 5×10^{-3} M. Hg(I)/104 $mm.^2$ Hg^o, pH 2, 30°. When any of these specifications is not mentioned in the title of a study, it will be found to be varied within the study. Also, when not stated to the contrary, it is to be assumed that no attempt was made to remove atmospheric gases prior to exchange.

In the following listings of exchange results, the starred (*) values indicate the best single value as determined by the method of least squares to represent all of the data on exchange of a given type. Following this figure in most instances (in parentheses) will be the half-time of exchange in minutes calculated from the relation: $k = 0.693/t_{\frac{1}{2}}$.

1. Mercury System Results

The information obtained on the exchange of mercury(I) ion with mercury metal may be summarized as follows.

a. Study 1, the effect of the variation of solution concentration and amount of mercury on the system: $Hg(I)/Hg^{o}$, pH 2, 30°.

Mercury(I) Ion Concentration	Rate Constant		
	674 mg. of Hg^{o}	69 mg. of Hg^{o}	7 mg. of Hg^{o}
5×10^{-4} M.	0.314 $min.^{-1}$	0.062 $min.^{-1}$	0.009 $min.^{-1}$
	0.298	0.053	0.014
	0.396	0.067	0.014
	0.335 (2.1)*	0.058 (12)*	0.012 (58)**
5×10^{-3} M.	0.306 $min.^{-1}$	0.082 $min.^{-1}$	0.063 $min.^{-1}$
	0.204	0.064	0.035
	0.267	0.069	0.031
	0.265 (2.6)*	0.070 (10)*	0.043 (16)*
5×10^{-2} M.	0.487 $min.^{-1}$	0.114 $min.^{-1}$	0.161 $min.^{-1}$
	0.398	0.086	0.216
	0.497	0.127	0.073
	0.460	0.118 (5.9)*	0.066
	0.471 (1.5)*		0.177
			0.128 (5.4)*

**Arithmetic average

b. Study 2, the effect of controlled surface area of mercury on the system: 5×10^{-3} M. $Hg(I)/Hg^{o}$, pH 2, 30°.

Area of Mercury Surface	Rate Constant
2.2 $mm.^{2}$	0.11×10^{-3} $min.^{-1}$
	0.19×10^{-3}
	0.15×10^{-3}
	0.15×10^{-3} (4600)**
13 $mm.^{2}$	0.76×10^{-3} $min.^{-1}$
	1.24×10^{-3}
	1.23×10^{-3}
	1.14×10^{-3} (608)*

**Arithmetic average

Area of Mercury Surface	Rate Constant
104 mm.^{2}	9.33×10^{-3} min.$^{-1}$
	10.9×10^{-3}
	8.13×10^{-3}
	9.50×10^{-3} (73)*

c. Study 3, the effect of temperature on the system: 5×10^{-3} M. Hg(I)/104 mm.^{2} Hg^o, pH 2.

Temperature	Rate Constant
0.2°	0.397×10^{-2} min.$^{-1}$
	0.306×10^{-2}
	0.351×10^{-2}
	0.308×10^{-2} (230)*
30°	0.933×10^{-2} min.$^{-1}$
	1.09×10^{-2}
	0.813×10^{-2}
	0.950×10^{-2} (73)*
40°	0.993×10^{-2} min.$^{-1}$
	0.974×10^{-2}
	1.19×10^{-2}
	1.11×10^{-2} (62)*
50°	1.53×10^{-2} min.$^{-1}$
	1.74×10^{-2}
	1.22×10^{-2}
	1.45×10^{-2} (48)*
98°	2.40×10^{-2} min.$^{-1}$
	2.53×10^{-2}
	3.85×10^{-2}
	2.92×10^{-2} (24)*

d. Study 4, the effect of addition of surface-active substances on the system: 5×10^{-3} M. Hg(I)/674 mm. of Hg^o, pH 2, 30°. (1) Gelatin added in varying amounts from 0.006 to 0.02 per cent caused a definite, though erratic, lowering of the observed exchange rate, and the normally linear plot of ln(1-F) *versus* t was concave upward. (2) Similar experiments were carried out using dodecyl sodium sulfate as the surface-

active additive. This material also gave the curved plots indicated for gelatin unless the mercury to be used in the exchange was previously equilibrated several times with dodecyl sodium sulfate of the concentrated to be used subsequently in the solution of the mercury(I) ion. The following shows the effect of variation of the amount of dodecyl sodium sulfate on the system: 5×10^{-3} M. Hg(I)/674 mm. of pre-equilibrated Hg^{o}, pH 2, 30°.

Concentration of Dodecyl Sodium Sulfate (Per Cent x 10^5)	Rate Constant
0.0	0.27 $min.^{-1}$
3.8	0.22
5.0	0.20
7.5	0.07
10.0	0.04
12.5	0.01

2. Mercury System Discussion

Some of these data might be inspected in the light of the relations presented in part A of this chapter. If the diffusion of the ions through the diffusion layer is to be the slow step, then Eq. 24 should allow one to estimate a value for the diffusion coefficient for the mercury(I) ion. From the data at hand, seven values of D_i can be calculated. The results are summarized as follows (a representative calculation may be found in Appendix II):

Area of Mercury Surface	D_i/σ in cm./sec. 0.05 M. Hg(I)	0.05 M. Hg(I)
7 cm.^{2}**	9×10^{-3}	6×10^{-3}
0.7 cm.^{2}***	7×10^{-3}	13×10^{-3}
1 cm.^{2}	- - - -	3.2×10^{-3}
0.1 cm.^{2}	- - - -	2.1×10^{-3}
0.02 cm.^{2}	- - - -	1.2×10^{-3}

**Area estimated for 674 mg. of agitated mercury.

***Area estimated for 69 mg. of agitated mercury.

The average value for D_i/σ was 5.9×10^{-3} cm./sec. To be able to calculate an absolute value for the diffusion coefficient, a value for the diffusion layer thickness must be known.

The extent of this layer has been studied, and has been shown to be dependent on the intensity of the agitation of the system.[59] The usual form for the relation between the rate of a diffusion-controlled process and the speed of agitation is

$$k \propto (\text{r.p.m.})^b \qquad \text{Eq. 30}$$

where b depends on the individual system, but usually falls between 0.4 and 1.0. The argument here is that the thickness of the diffusion layer decreases with increased agitation and thus so does the rate constant. This correlation between diffusion layer thickness and speed of revolution of a stirrer is easily established for a given apparatus, but the actual size of the layer for a given agitation speed will, of course, depend greatly on the shape and size of the stirrer and container. Investigation of the literature, however, did indicate a range of 10^{-2} to 10^{-4} cm., depending on the extent of agitation and the type of surface in contact with the solution. For a system somewhat similar to that

used in the present studies, a value of 3×10^{-3} cm. was found.[60] Considering the physical arrangement used by the author from which it was obtained, the agitation of the solution was probably somewhat greater than that in the present studies, so the figure selected above is probably too low. Using this figure, though, one could estimate some values for the diffusion coefficient of the mercury(I) ion. Since the average value of D_i/σ given above was 5.9×10^{-3} cm./sec., the diffusion coefficient can be calculated to be 1.8×10^{-5} cm.^{2}/sec. No value for the diffusion coefficient of the mercury(I) ion dimer was located in the literature, but the range of values reported for other cations at about the same temperature is from about 1×10^{-5} to 2×10^{-5} cm.^{2}/sec. It must be remembered that this calculation depends quite strongly on a value for the diffusion layer thickness for which only an estimation was available. Also, it had been found[49] advisable to design systems such that the ratio s of Eq. 24 will be in the range of 0.1 to 0.5, while that in this research was with one exception 0.7 to 0.9.

The previously-mentioned work of Haissinsky and Cottin[49] presented calculations similar to the above, and concluded from the range of values obtained, 10^{-8} to 10^{-7} cm.^{2}/sec., that ionic diffusion could not be responsible for the determination of the overall rate. These low values for diffusion coefficient can be traced to low experimentally-determined exchange rate constants. These rates had been criticized previously as too low with the suggestion offered that the reaction had been retarded by the unsuspected presence of contaminants on the mercury surface.[54] Nonetheless, once Haissinsky and Cottin had discarded ionic diffusion as

the slow step in the exchange, they named the metal phase diffusion as the rate-determining step. In this connection they calculated by Eqs. 27 and 29 an average value for the "autodiffusion constant" of mercury of 8×10^{-8} cm.^{2}/sec. Hoffman[61] has determined this constant by a more direct method of capillary diffusion and found it to be 1.8×10^{-6} cm.^{2}/sec. A better agreement with Hoffman's results are obtained if the faster rate constants of this research are substituted for those of Haissinsky and Cottin. Representative values for the autodiffusion constant obtained using the present results in Eqs. 27 and 29 were 8×10^{-6} cm.^{2}/sec. and 3×10^{-6} cm.^{2}/sec., but these calculations are quite approximate due to uncertainties in the shape and dimensions of the mercury droplets. It is not probable that arguments of this type alone could allow a definite selection of a rate-determining process due to the uncertainties in calculations mentioned above, and to the fact that the indicated magnitudes of the two constants are so close, about 2×10^{-5} cm.^{2}/sec. for ionic diffusion and 2×10^{-6} cm.^{2}/sec. for autodiffusion.

A somewhat different approach to the study of the processes occurring during exchange was made by Fronaeus.[17] This approach may be adapted such that the type of data of the present research may be utilized and investigated. In a system composed of a solution of concentration C_i in inactive metal ion and C_a in the radioactive form of the ion in contact with its metal, the individual processes occurring will be:

1.) $\overset{*}{M}^{+n} + M^{o} \longrightarrow \overset{*}{M}^{o} + M^{+n}$

2.) $M^{+n} + M^{o} \longrightarrow M^{o} + M^{+n}$

3.) $M^{+n} + \overset{*}{M}^{o} \longrightarrow M^{o} + \overset{*}{M}^{+n}$

4.) $\overset{*}{M}^{+n} + \overset{*}{M}^{o} \longrightarrow \overset{*}{M}^{o} + \overset{*}{M}^{+n}$

where M^{+n} and M^{o} refer to the ionic and atomic forms, respectively, of the metal, and the star (*) indicates that the specie named is radioactive. Each of these processes will occur at a rate reflected in the rate constants h_1, h_2, h_3, and h_4. The overall rate is given by

$$h = \sum_{j=1}^{4} h_j \qquad \text{Eq. 31}$$

If $\bar{q}_a$ is the average concentration of $\overset{*}{M}^{o}$ calculated in moles of $\overset{*}{M}^{o}$ per gram of the metal, then the rate of increase in $\bar{q}_a$ is

$$m_o \frac{d\bar{q}_a}{dt} = s_o (h_1 - h_3) \qquad \text{Eq. 32}$$

where m_o is the mass of an amalgam droplet of surface area s_o. These latter terms should remain approximately constant within one type of exchange system, so for the ratio s_o/m_o one can substitute a constant, K_1, and arrive at

$$\frac{d\bar{q}_a}{dt} = K_1 (h_1 - h_3) \ . \qquad \text{Eq. 33}$$

Before exchange has started $\bar{q}_a = h_3 = 0$, so

$$\lim_{t \to 0} \frac{d\bar{q}_a}{dt} = K_1 h_1 \ . \qquad \text{Eq. 34}$$

Also

$$\lim_{t \to 0} \frac{d}{dt} \left[\frac{\bar{q}_a}{C_a} \right] = \frac{K_1 h_1}{C_{a(o)}} \qquad \text{Eq. 35}$$

where $C_{a(o)}$ is the concentration of the radioactive specie at time zero.

According to Fronaeus' method, it is desirable to investigate the nature of the left side of Eq. 35. To do so, a plot of $\bar{q}_a/C_a$ <u>versus</u> t

for a series of mercury exchanges is constructed. Here, unfortunately, the data of this research are somewhat inadequate. Basically, the important region of this curve is that where time approaches zero, and therefore the curve in this region should be well established. To accomplish this, one ideally should have exchange data over quite small time increments near zero time, but in the experimental method used here the shortest feasible time increment was 0.5 minute and more normally was 1.0 minute. If, however, this type plot is constructed* for a series of mercury exchanges, it will be seen that the curves obtained all seem to approach the origin in a similar manner (Figure 1). For each of the curves there was assigned a "limiting slope" which, for the purposes of this discussion, was defined as the slope of the line drawn from the origin to the point on the curve at a time of 0.3 minute. These slopes ranged from 2.4 to 3.4 ml./gm./min., with an average of 2.9 ml./gm./min. or 4.8×10^{-2} ml./gm./sec.

Rewriting Eq. 35, substituting K_2, the constant obtained above, for the left side of the equation, one has that

$$K_2 = \frac{K_1 h_1}{C_{a(o)}} \qquad \text{Eq. 36}$$

and from this,

$$(h_1)_{t=0} = \frac{K_2 C_{a(o)}}{K_1} \quad . \qquad \text{Eq. 37}$$

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*For these plots, $\bar{q}_a$ can be obtained from the relation, $\bar{q}_a = \frac{vC_a'}{m}$ where C_a' is the concentration in gram ions/ml. of the radioactive ion in the solution formed by dissolving m grams of mercury in a total volume of v milliliters. One may replace the actual concentration C_a' with the activity recorded for some aliquot of the solution since the two should be proportional. Similarly, a concentration of radioactive ion in the bulk of solution with the metal is to enter into exchange (C_a) may be replaced with an activity determined in the same manner as the above.

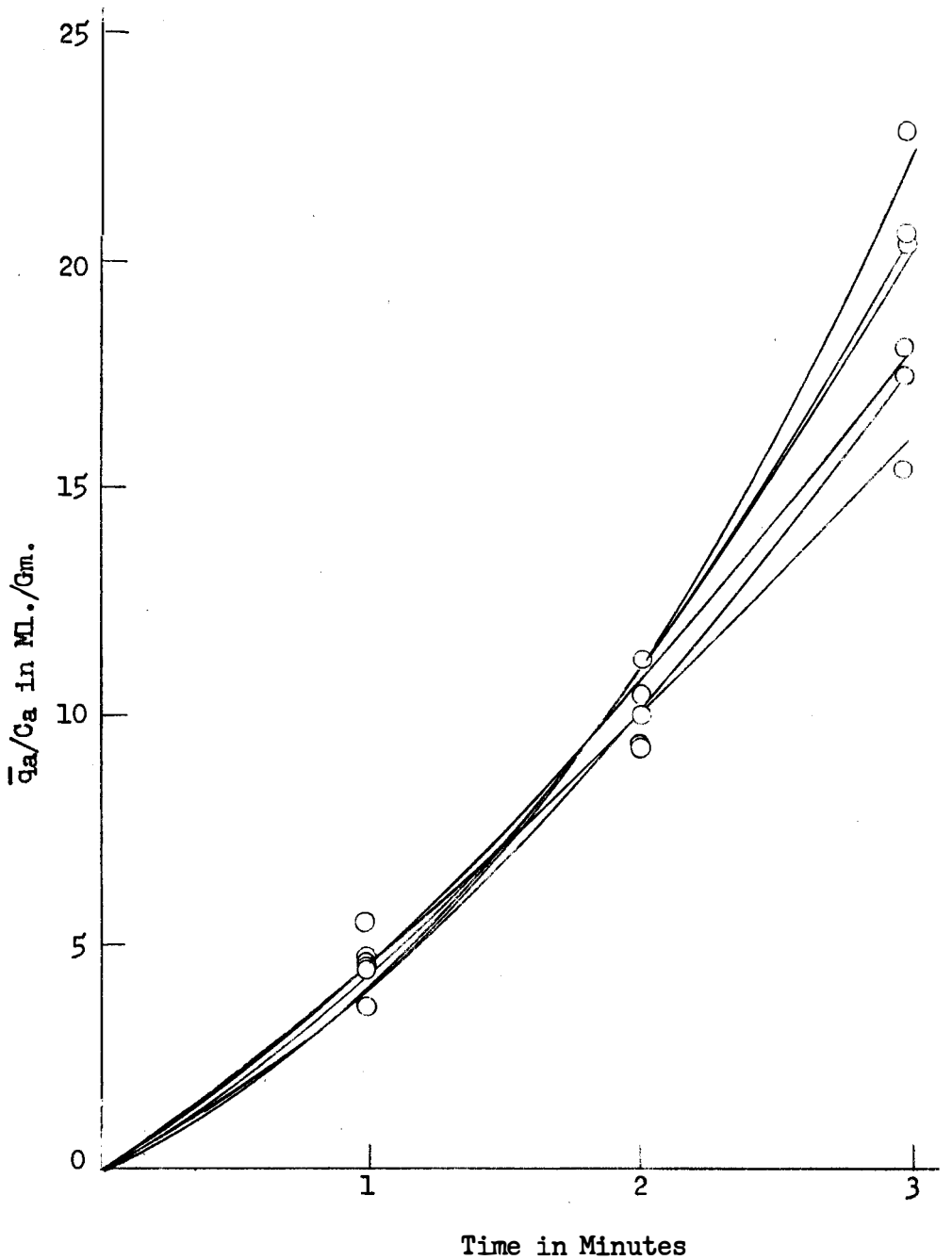

Figure 1. Plot of $\bar{q}_a/C_a$ versus Time for the Exchange of Mercury Metal With Mercury(I) Perchlorate Solution.

Since M^o and M^{+n} are assumed to have properties identical with $\overset{*}{M}{}^o$ and $\overset{*}{M}{}^{+n}$, one would expect that the rate of process number two would follow a parallel relation of the form

$$(h_2)_{t=0} = \frac{K_2 C_i(o)}{K_1} \quad . \qquad \text{Eq. 38}$$

Under the selected conditions of t approaching zero, the mercury has not yet become radioactive so processes number three and four cannot occur, and $h_3 = h_4 = 0$. Applying Eq. 31,

$$h = \sum_{j=1}^{4} h_j = \frac{K_2 C_a(o)}{K_1} + \frac{K_2 C_i(o)}{K_1} \quad , \qquad \text{Eq. 39}$$

and

$$h = \frac{K_2}{K_1} \left[C_a(o) + C_i(o) \right] . \qquad \text{Eq. 40}$$

It is to be noted that although the relation is derived for the case of time approaching zero, it is not dependent with time, so it should be valid for all time values.

Comparison of this form (Eq. 40) with that noted for cases where the electron transfer is the slow step (Eq. 26) indicates that such a process is probably not rate-determining in these exchanges. Further, the diffusion of the metal is not indicated as the slow step since the rate would not have been found to be dependent on the solution phase concentration. If these are discarded as possible slow steps, then Eq. 40 should describe a rate that is determined by diffusion of the ionic specie within the solution phase.

Under the condition of time approaching zero, none of the radioactive form of the metal would be leaving the metal phase, and the ions of the metal arriving there should be discharged immediately by the elec-

tron transfer. Thus the concentration of ion at the metal-solution interface can be set equal to zero. On the outside of the Nernst diffusion layer of thickness σ there is an essentially-constant concentration of the radioactive ion due to the intense stirring of the solution. The rate of the net transfer of the radioactive ion across the concentration gradient of $C_{a(o)}/\sigma$ will be

$$h_1 = \frac{DC_{a(o)}}{\sigma} \qquad \text{Eq. 41}$$

where D is the ionic diffusion coefficient. Applying Eq. 31 once more, one arrives at

$$h = \frac{D}{\sigma} \left[C_{a(o)} + C_{i(o)} \right]. \qquad \text{Eq. 42}$$

Substituting the value of h from Eq. 40 into Eq. 42, one obtains the relation

$$D = \frac{\sigma K_2}{K_1} \qquad \text{Eq. 43}$$

where σ is the thickness of the Nernst diffusion layer, K_1 is a constant dependent on the ratio of the area to mass of the mercury droplet, and K_2 is a constant, which for the mercury exchange system had an average value of 2.9 ml./gm./min. or 4.8×10^{-2} ml./gm./sec.

One might test these equations by calculating a value for the diffusion coefficient from Eq. 43. A value for K_2 may be approximated with sufficient accuracy for this calculation since it is found that the ratio of the surface area of a mercury droplet to its weight is relatively insensitive to the size, and consequently the number, of the mercury droplets making up the metal phase. If the mercury is assumed to be dispersed into, firstly, 10^2, then 10^3, then 10^4 equal-sized droplets, then the corresponding area to weight ratios are 4.5, 9.6 and 21 cm.^{2}/gm. The value

of 10 $cm.^2/gm.$ was selected as best representing the experimental condition in these exchanges. Referring to Eq. 43, the diffusion coefficient will be $4.8 \times 10^{-3}\ \sigma\ cm.^2/sec.$ Using the same estimated value for σ used previously, the calculated ionic diffusion coefficient is $1.4 \times 10^{-5}\ cm.^2/sec.$ This calculation suffers from the same uncertainty in the size of the diffusion layer, but indicates at least a proper order of magnitude.

If the rate of exchange is determined by the rate of diffusion of the ion in solution, then the differences in exchange rate for a given solution concentration shown by the data in studies 1 and 2 should be due to the difference in surface area presented for exchange. The rate constants for 2.2, 13 and 104 $mm.^2$ of mercury surface in contact with 5×10^{-3} M. mercury(I) perchlorate solution are $1.5 \times 10^{-4}\ min.^{-1}$, $1.1 \times 10^{-3}\ min.^{-1}$ and $9.5 \times 10^{-3}\ min.^{-1}$, respectively. The corresponding rate constants per unit of surface are $6.9 \times 10^{-5}\ min.^{-1}\ cm.^{-2}$, $8.5 \times 10^{-5}\ min.^{-1}\ cm.^{-2}$ and $9.1 \times 10^{-5}\ min.^{-1}\ cm.^{-2}$. Similar figures for the stirred mercury phase experiments are not presented due to the difficulty in obtaining reliable values for the surface area presented for exchange. In addition, since in all probability the diffusion layer thickness would not be the same size in the controlled area and stirred mercury experiments, the rate constants per unit area would not be directly comparable.

The data reported under study 3 allow the determination of an experimental activation energy of exchange. If a plot of ln k <u>versus</u> 1/T is constructed, the slope of the straight line so obtained can be used to calculate the activation energy. The relation being used is the Arrhenius equation; $k = k_o \exp(-E/RT)$, or its equivalent $\ln k = \ln k_o -$

E/RT. Hence the slope is -E/R, and the experimental activation energy is -R times the slope. Figure 2 shows this plot for 5×10^{-3} M. mercury(I) ion in contact with 104 mm.^{2} of mercury surface, the curve being placed by the method of least squares. The slope was -2.47×10^3 °A and the intercept was -0.67. Using these values, one may represent this system by the relation

$$\ln k = -0.67 - 2470/T \qquad \text{Eq. 44}$$

or

$$k = 5.1 \times 10^{-1} \exp(-4940/RT) \; . \qquad \text{Eq. 45}$$

Equation 45 above might be compared to that for autodiffusion of mercury found by Hoffman,[61] $D = 1.26 \times 10^{-4} \exp(-1160/RT)$, and that found by Nachtreib and Petit,[62] $D = 8.5 \times 10^{-5} \exp(-1005/RT)$. The rather wide divergence displayed is further evidence against the process of autodiffusion being the rate-determining step as was claimed by Haissinsky and Cottin. The divergence is particularly accented when the values for the activation energy are compared. The process of autodiffusion of mercury had been found to have an activation energy of 1.0 to 1.2 kcal./mole while that for the process of exchange was 3.1 kcal./mole according to Haissinsky, and 4.9 kcal./mole according to this research. It may be noted here that, although information on the temperature coefficients of ionic diffusions is rather limited, reported experimental activation energies are commonly in the range of 3 to 5 kcal./mole.[63,64]

The studies on the effect of adding surface-active substances to the exchange medium showed, generally, the expected slowing of the exchange rate. The shapes of the exchange curves obtained deviated con-

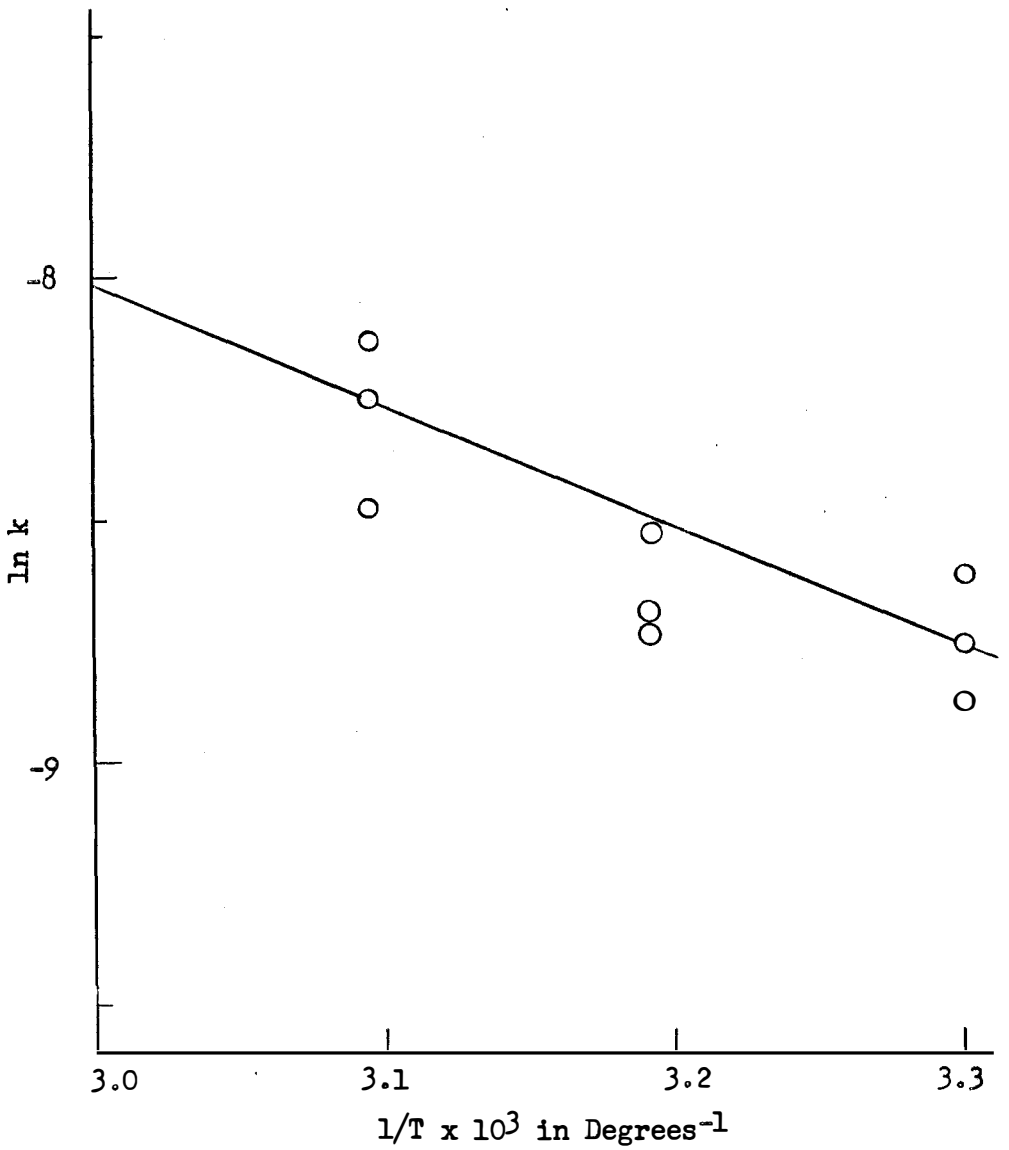

Figure 2. Plot of ln k versus 1/T for the Exchange of 674 Mg. of Mercury With 5 x 10^{-3} Mercury(I) Perchlorate.

siderably from the straight lines obtained in previous studies. These curves were concave upward suggesting a possible competition of rates in the overall process. This behavior was studied further in the systems containing dodecyl sodium sulfate as the additive. Examination of the literature revealed[65] a time element in the establishment of the maximum lowering of the surface tension on adding dodecyl sodium sulfate to water, especially in the low range of concentrations used in this research, so a series of experiments was performed after allowing sufficient time for the establishment of equilibrium with respect to the surface-active substance. The results of these experiments were that the exchange curves obtained now showed one major discontinuity and two slopes. Investigation indicated the possibility of a time variable in the establishment of equilibrium adsorption to the mercury surface. Another series of experiments was designed in which the mercury to be used for exchange was pre-equilibrated several times with water containing dodecyl sodium sulfate of the concentration to be used subsequently during exchange. In this way the coverage of the mercury was established before the start of the exchange reaction, so one more time-dependent process might be eliminated. Results of these experiments showed that the exchange curves obtained were now essentially linear, with a gradual decrease in exchange rate constant with increasing concentration of the dodecyl sodium sulfate. The rate is seen to have dropped off sharply at an equilibrium concentration of dodecyl sodium sulfate of about 5×10^{-5} per cent, and was found to reach an extrapolated "zero rate" at a concentration of 1.3×10^{-4} per cent. Attempts to correlate this concentration for a zero rate with

complete coverage of the mercury surface were unsuccessful. The primary difficulty was that the above-indicated concentration was lower than that reported for the critical concentration for micelle formation.[66,67] In such a situation it had been noted[66] that adsorption became quite unpredictable, following neither a Langmuir nor Freundlich type isotherm.

3. Cadmium System Results

The information obtained on the exchange of cadmium(II) ions with cadmium amalgams may be summarized as follows. All amalgam phases were prepared by adding the proper amount of cadmium metal to 674 mg. of mercury.

a. Study 5, the effect of prior sweeping of solutions with nitrogen gas on the system: 1×10^{-3} M. Cd(II)/2 per cent amalgam, pH 4, 30°.

Rate Constant	
Containing Air	Nitrogen-swept
0.256 $min.^{-1}$	0.221 $min.^{-1}$
0.238	0.219
0.224	0.183
0.225 (3.1)*	0.217 (3.2)*

b. Study 6, the effect of pH on the system: 1×10^{-3} M. Cd(II)/1 per cent amalgam, 30°, nitrogen-swept.

Rate Constant	
pH 4	pH 6
0.295 $min.^{-1}$	0.347 $min.^{-1}$
0.279	0.305
0.298	0.360
0.289 (2.4)*	0.366 (1.9)*

c. Study 7, the effect of the variation of cadmium ion and amalgam concentration on the system: Cd(II)/amalgam, pH 4, 30°, nitrogen-swept.

Cd(II) Ion Concentration	Rate Constant 1 Per Cent Amalgam	2 Per Cent Amalgam	4 Per Cent Amalgam
2×10^{-4} M.	0.341 $min.^{-1}$	0.232 $min.^{-1}$	0.303 $min.^{-1}$
	0.272	0.277	0.353
	0.281	0.236	0.256
	0.298 (2.3)*	0.268	0.311 (2.2)*
		0.259 (2.7)*	
1×10^{-3} M.	0.295 $min.^{-1}$	0.256 $min.^{-1}$	0.250 $min.^{-1}$
	0.253	0.238	0.200
	0.306	0.224	0.224
	0.286 (2.4)*	0.225 (3.1)*	0.225 (3.1)*
2×10^{-3} M.	- - -	0.292 $min.^{-1}$	- - -
		0.279	
		0.298	
		0.289 (2.4)*	

d. Study 8, the effect of temperature on the system: Cd(II)/2 per cent amalgam, pH 4, nitrogen-swept.

Temperature	Rate Constant 2×10^{-3} M. Cd(II)	1×10^{-3} M. Cd(II)	1×10^{-3} M. Cd(II) with 1×10^{-3} M. Bromide
30°	0.292 $min.^{-1}$	0.256 $min.^{-1}$	0.153 $min.^{-1}$
	0.279	0.238	0.185
	0.298	0.224	0.167
	0.289 (2.4)*	0.225 (3.1)*	0.141
			0.161 (4.3)*
40°	0.388 $min.^{-1}$	0.365 $min.^{-1}$	0.212 $min.^{-1}$
	0.444	0.329	0.244
	0.439	0.374	0.174
	0.426 (1.6)*	0.357 (1.9)*	0.210 (3.3)*
50°	0.528 $min.^{-1}$	0.403 $min.^{-1}$	0.253 $min.^{-1}$
	0.575	0.570	0.262
	0.439	0.413	0.385
	0.541	0.426	0.276 (2.5)*
	0.507 (1.4)*	0.425 (1.6)*	

e. Study 9, the effect of inert electrolytes in the cadmium ion solution for the system: 1×10^{-3} M. Cd(II)/2 per cent amalgam, pH 4, 30°, nitrogen-swept.

Rate Constant	
No Additional Electrolyte Added	Solution Saturated in $KClO_4$
0.256 $min.^{-1}$	0.285 $min.^{-1}$
0.238	0.299
0.224	0.268
0.225 (3.1)*	0.284 (2.4)*

f. Study 10, the effect of added complexing agents, showing also the effect of some concentration combinations for the system: Cd(II)/ amalgam, 30°, nitrogen-swept. These results are summarized in Table II. For comparison, results on the uncomplexed system are repeated.

4. Cadmium System Discussion

In the systems involving amalgams it was noted that the surface of the metal lost the characteristic appearance of mercury soon after the start of an attempted exchange reaction. The results from such determinations where the surface of the amalgam had been visibly attacked were extremely erratic, so a method was sought to circumvent this difficulty. Two approaches were possible: one, to remove atmospheric gases from the exchange medium by sweeping with an inert gas; second, to prevent the formation of what is probably an oxide of the cadmium by increasing the acidity of the solution sufficiently. A series of experiments was proposed where a given exchange reaction would be carried out with and without prior flushing of the system with nitrogen. The pH chosen for this

TABLE II

SUMMARY OF RATE CONSTANTS FOR THE EXCHANGE OF CADMIUM AMALGAM WITH COMPLEXED CADMIUM ION SOLUTIONS[a]

Cd(II) Ion Concentration	Agent Added	Amalgam Per Cent	Individual Rate Constants (Min.$^{-1}$)	Least Squares Single Values (Min.$^{-1}$)
1×10^{-3} M.	None	2	0.256, 0.238, 0.224	0.225 (3.1)
2×10^{-4} M.	None	2	0.232, 0.277, 0.236, 0.268	0.259 (2.7)
1×10^{-3} M.	0.1 M. Chloride	4	0.229, 0.172, 0.195	0.198 (3.5)
	0.1 M Chloride	2	0.181, 0.218, 0.123, 0.163, 0.232, 0.178	0.184 (4.3)
	0.05 M. Chloride	2	0.335, 0.270, 0.301	0.289 (2.4)
2×10^{-4} M.	0.1 M. Chloride	1	0.295, 0.329, 0.300	0.288 (2.4)
	0.1 M. Chloride	0.5	0.294, 0.423, 0.596	0.347 (2.0)
	0.1 M. Chloride	0.1	0.513, 0.524, 0.427, 0.464, 0.878, 0.593, 0.573	0.596 (1.2)
	0.1 M. Chloride	0.05	0.365, 0.450, 0.602	0.402 (1.7)
1×10^{-3} M.	0.1 M. Bromide	2	0.153, 0.185, 0.167, 0.141	0.161 (4.3)
1×10^{-3} M.	0.1 M. Iodide	2	0.283, 0.389, 0.320, 0.327	0.331 (2.1)
1×10^{-3} M.	0.1 M. EDTA[b]	2	Long[c]	- - - - -
	0.01 M. EDTA	2	Long[d]	- - - - -
	0.001 M. EDTA	4	0.135, 0.131, 0.174	0.140 (5.0)
	0.001 M. EDTA	2	0.101, 0.110, 0.117	0.103 (6.7)

TABLE II

SUMMARY OF RATE CONSTANTS FOR THE EXCHANGE OF CADMIUM AMALGAM WITH COMPLEXED CADMIUM ION SOLUTIONS[a]
(Continued)

Cd(II) Ion Concentration	Agent Added	Amalgam Per Cent	Individual Rate Constants (Min.$^{-1}$)	Least Squares Single Values (Min.$^{-1}$)
1×10^{-3} M.	0.1 M. Cyanide	2	Long[e]	- - - - -
	0.01 M. Cyanide	2	0.0787, 0.0543, 0.0594	0.0601 (12)

[a]The pH at the start of the exchanges was 4, except those involving cyanide where the pH was 8.

[b]The ethylenediaminetetraacetate ion.

[c]About 8 per cent exchange in 1.5 hours.

[d]About 10 per cent exchange in 1.5 hours.

[e]No exchange detected in 2 hours.

study (number 5) was 4, the highest pH which would allow reasonably reliable exchange curves where unflushed solutions were used. Even at this pH the surface of the amalgam was slightly clouded by the end of the determination, and the scatter in the points from which the exchange curve was to be plotted was more than would be desirable. When an identical solution was swept with nitrogen gas prior to exchange, the surface of the amalgam remained unattacked as far as could be detected, and the points for the individual exchange curves showed considerably less scatter. Listed under study 5 are the results obtained by means of such an experimental arrangement. The sweeping of the solutions with nitrogen, besides making each exchange curve more ideal, seemed to lower the exchange rate slightly. If the small difference in exchange rate indicated above is real, then it would seem to be in accord with the results of solid metal-solution exchanges as summarized in Chapter I. It was noted then that the exchange rate observed in a system involving a solid metal and a solution in equilibrium with atmospheric gases could be either larger or smaller than that observed when the solution had been swept with nitrogen. When the oxide film formed was protective in nature, the exchange was reduced but when the film was unprotective the exchange was enhanced.

Further investigation was made into the effect of the pH of the exchanging solution on the exchange rate, and these results are shown under study 6. The rate constant was seen to be higher at the higher pH, an effect the opposite of what was observed in the case where a solid metal was used. The proposed explanation in the case of solid metals is

that the exchange is greatly dependent of the penetration of deposited atoms into the metal, and that the chemical disintegration of the surface aids this penetration. In the present case of a "liquid metal", however, the chemical attack could serve only to stabilize the ionic form of the metal and thus lower the observed exchange rate.

A pH of 4 was arbitrarily chosen for use in further studies since it seemed low enough to prevent, in conjunction with sweeping by nitrogen gas, attack of the cadmium in the amalgam by traces of atmospheric gases, but not too low that it would dissolve the cadmium. This pH was used in study 7 which shows the effect of variation of amalgam and solution concentrations on the rate of exchange. This study parallels study 1 on the mercury system, and arguments similar to those presented during discussion of the results of the mercury system may be applied.

If this cadmium exchange is to be diffusion-controlled, then a knowledge of experimental rates of reaction should allow the calculation of diffusion coefficient values for the cadmium ion by Eq. 24. In this application the terms n and s will take the following meanings: s will refer to the ratio of the amount of exchanging metal in the amalgam to the total amount of that substance in the system, and n will be the number of gram atoms of the metal dissolved in the amalgam. The results of these calculations are summarized as follows:

Concentration of Cd(II) Ion Solution	D_i/σ in Cm./Sec. 1 Per Cent Amalgam**	2 Per Cent Amalgam**	4 Per Cent Amalgam**
2×10^{-4} M.	6.9×10^{-3}	6.3×10^{-3}	8.9×10^{-3}
1×10^{-3} M.	6.0×10^{-3}	4.3×10^{-3}	4.9×10^{-3}
2×10^{-3} M.	- - - - -	5.2×10^{-3}	- - - - -

**674 mg. of amalgam used; estimated area of 7 $cm.^2$

The average value for D_i/σ from the above seven was 6.1×10^{-3} cm./sec. Using the same estimated value for the diffusion layer thickness, the average diffusion coefficient can be calculated to be 1.8×10^{-5} cm.^{2}/sec., once more of the magnitude to be expected.

The approach of Fronaeus that was applied to the mercury exchange system (page 39, et. seq.) may be extended to systems involving amalgams. The "limit" term of Eq. 35 is still to be investigated by means of a plot of $\bar{q}_a/C_a$ versus t. The relation given in the footnote on page 41 is still helpful in the preparation of these plots, but m now refers to a weight in grams of amalgam. Six such plots for the cadmium exchange system (see Figure 3) gave an average limiting slope (defined as in the mercury system discussion) of 1.9 ml./gm./min. or 3.1×10^{-2} ml./gm./sec. Applying Eq. 43 and using the same value estimated for K_1 of 10 cm.^{2}/gm., one has a value for the diffusion coefficient of cadmium ion of $3.1 \times 10^{-3}\ \sigma$ cm.^{2}/sec. If the same value for diffusion layer thickness is assumed, the ionic diffusion coefficient would be 0.9×10^{-5} cm.^{2}/sec.

Study 8 shows the effect of temperature on the exchange rate in the cadmium system. A plot of ln k versus 1/T gave a slope of -3.39×10^3 ^oA when the solution was 1×10^{-3} M. in Cd(II) ion, and -3.25×10^3 ^oA when the Cd(II) ion concentration was 2×10^{-3} M. (Figure 4. The third curve in this figure will be discussed later.). The corresponding activation energies of exchange are 6.7 and 6.5 kcal./mole, respectively. As mentioned previously, data on the temperature dependence of ionic diffusion coefficients are rather limited. The indicated behavior, however, is for the activation energy to decrease with decreasing concentration

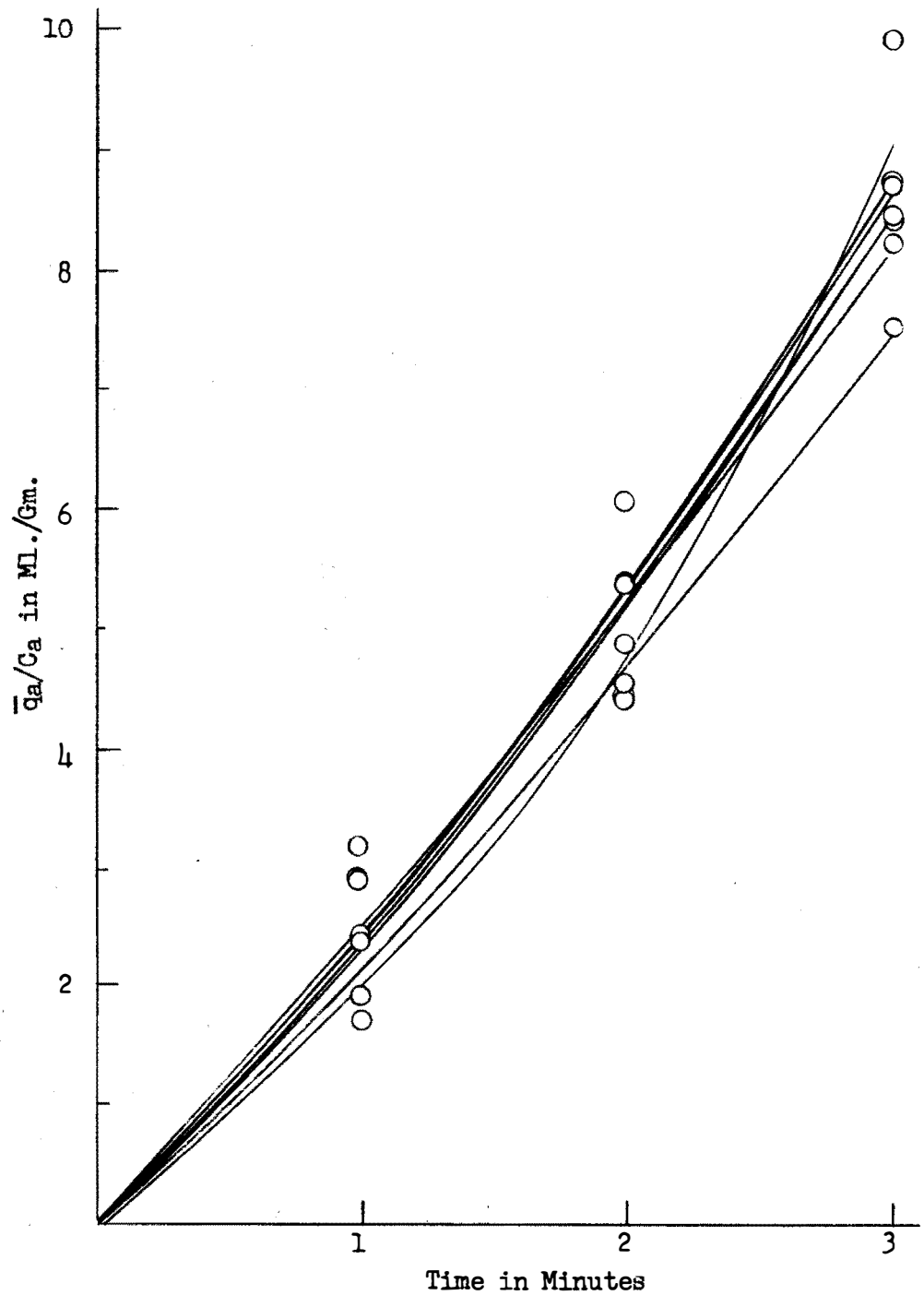

Figure 3. Plot of $\bar{q}_a/C_a$ versus Time for the Exchange of Cadmium Amalgam With Cadmium Perchlorate Solution.

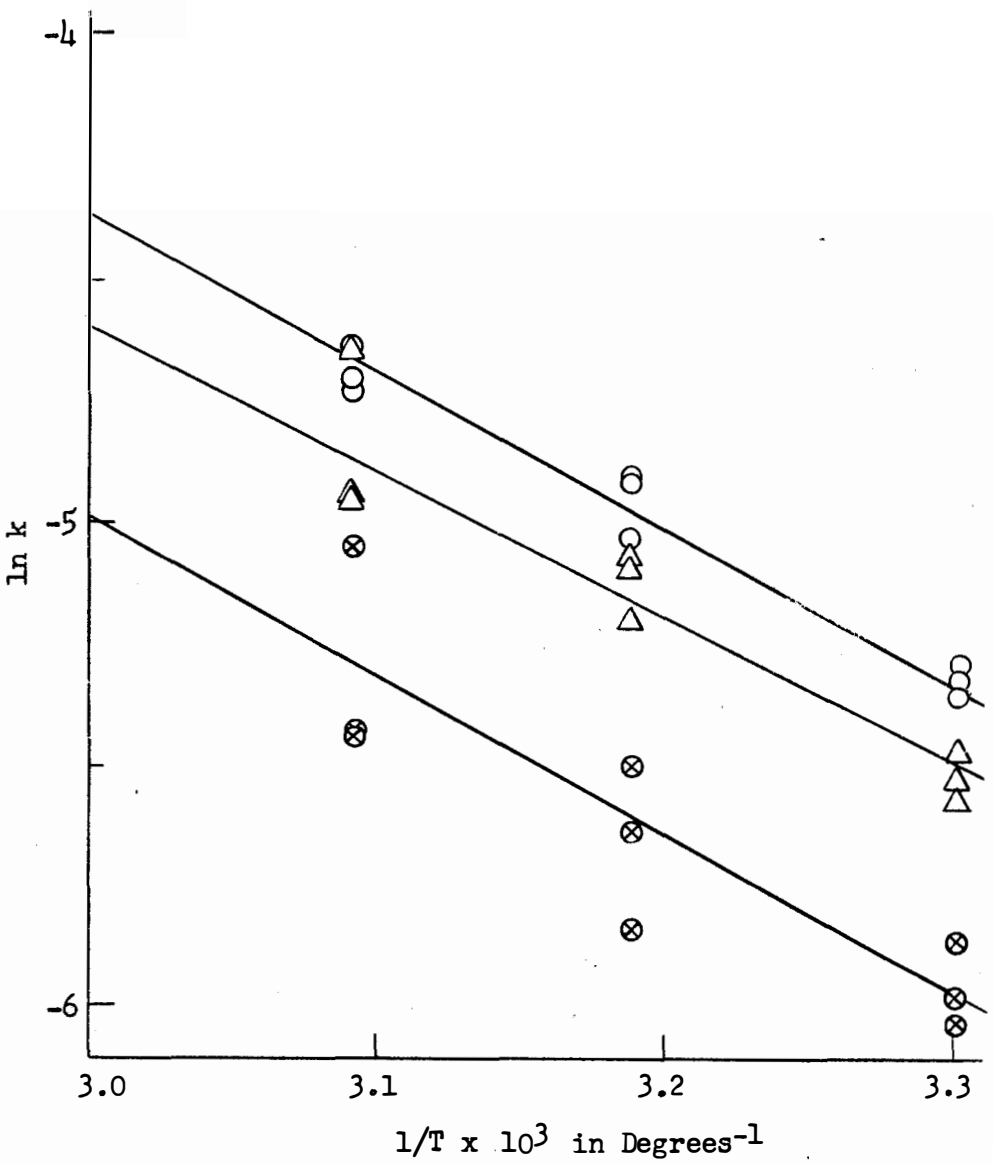

Figure 4. Plot of ln k *versus* 1/T for the Exchange of 2 Per Cent Cadmium Amalgam With 1×10^{-3} M. (Δ) and 2×10^{-3} M (○) Cadmium Perchlorate and With 1×10^{-3} M. Cadmium Perchlorate Plus 1×10^{-1} M. Chloride (⊗).

of the solution,[63] a behavior that would seem to be in disagreement with the results of this research. It would be difficult, with the present data, to decide whether an actual contradiction exists. One reason for this is the very slight indicated increase in the activation energy of ionic diffusion with decreasing concentration, about 2 per cent for a tenfold increase in concentration. A second reason is the questionable reliability for the activation energy of exchange indicated by the single determination of this research. Still a third is the marked scarcity of directly determined values of activation energies of ionic diffusion, therefore the uncertainty of "expected" behavior.

A series of experiments was planned in which a complexing agent would be added to the Cd(II) ion solution prior to exchange. In order to obtain an indication as to whether any difference in exchange rate observed by the above was due to the solute acting in its complexing role or simply due to alterations in the properties of the solution caused by the presence of the additional solute, study 9 was carried out. In it are contrasted the rate constants obtained for a given exchange reaction with those obtained when the solution phase was saturated with potassium perchlorate. The exchange rate was found, somewhat surprisingly, to be slightly higher in the presence of the potassium perchlorate. Since this reaction is thought to be diffusion-controlled, then the above difference in rate should be attributable to some change affecting the diffusion of the ion in solution brought about by the addition of the additional solute. Stackelberg, Pilgram and Toome[68] have studied the effect of additional electrolyte on the diffusion coefficient of Cd(II) and a number

of other ions. This diffusion coefficient was seen to decrease rather rapidly on adding the "inert" salt potassium nitrate, to remain fairly stable at this decreased value over a considerable increase in concentration of the salt, but then to start increasing at still higher concentrations. In view of the ability of the diffusion coefficient to behave in such a manner, it is not at all impossible that the exchange results obtained in study 9 could be obtained.

Study 10 was undertaken to investigate the effect on exchange rate of addition of complexing agents to the exchanging medium. Unfortunately, interpretation of the results will be rather limited due to the scarcity of pertinent information in the literature on the many processes that come into play during such exchanges. The overall process of exchange was discussed previously under the individual steps of diffusion of the exchanging specie within the solution up to the exchange site, the discharge or "electron transfer", and diffusion within the metal phase. It was mentioned at that time that normally either the first or third process would be rate-determining since the discharge step was generally very rapid. Further, it was mentioned that it would not necessarily always be so rapid that it could be eliminated from consideration. Glasstone, Laidler and Eyring[69] suggest that the discharge of an ion at a static electrode as used here would involve the removal of all of the ligands in the coordination sphere, the transfer of the "stripped" ion to the exchange surface, the electron transfer, and the deposition of the atom at the surface. In previous cases of aquated ions none of these latter processes came under consideration since all occurred quite rapidly.

Now, however, on the addition of agents that can become coordinated to the ion more strongly than can water, the possibility exists that the de-coordinating step can become increasingly important as the strength of the metal-to-ligand bond increases.

On adding to the system agents which become weakly or only moderately strongly complexed with the cadmium ion (e.g., chloride, bromide or iodide ions), there was noted only a slight alteration of the exchange rate. The addition of a hundredfold excess of the halide ions to 1 x 10^{-3} M. cadmium ion solution enhanced the exchange when the halide was iodide, but retarded it when the halide was chloride or bromide. In either case, though, the alteration of exchange rate is only slight. Fronaeus[17] reported similar behavior with respect to iodide, but he found that the bromide likewise increased the reaction rate. Fronaeus' exchange data for cadmium systems involving the bromide ion, iodide ion or ammonia demonstrated the constancy of the "limit" term of Eq. 35, so these exchanges, too, are thought to be diffusion-controlled. If this is so, then the variations produced in the reaction rates must be attributable to the change in diffusibility of the cadmium specie. This would be caused by the displacement of the water ligands by the intentionally-added complexing agent.

The work of Stackelberg and co-workers[68] mentioned previously showed the effect on the diffusion coefficient of the addition of chloride ion to cadmium-ion solutions. The observed diffusion coefficient was seen to show either an increase or a decrease depending on the concentration of the chloride ion. In other words, the diffusibility of the cad-

mium specie was found to be dependent on its size and structure which, in turn, would be dependent on the relative amounts of cadmium and chloride ions. This type of effect might well be the cause for the behavior demonstrated on progressively increasing the chloride ion concentration. When the chloride concentration was raised from zero to 0.05 M., an increase in exchange rate was noted, but when the chloride concentration reached 0.1 M. the exchange rate was lower than that obtained in the absence of chloride.

On comparison of the rates of cadmium exchange with and without added halide ion, it was found that the rate was decreased in the presence of 0.1 M. chloride or bromide, but was increased in the presence of 0.1 M. iodide. Unfortunately, even the scant information on the diffusibility of cadmium in a chloride medium was not matched for the cases of bromide and iodide. Therefore, the only statement that may be made with regard to these exchanges is the generalization permitted for any diffusion-controlled process: the rate of the process is dependent on the diffusibility of the reacting specie. At a given metal ion and complexing agent concentration, this diffusibility would be dependent on the strength of the metal-ligand coordination and the size of the ligand (versus the water that it replaces).

One might reflect briefly upon the results obtained where exchanges were carried out with identical solutions of chloride-complexed cadmium ion and progressively more dilute amalgams. On lowering the amalgam concentration from 1.0 to 0.5 to 0.1 per cent, there was a gradual increase in the reaction rate. The direction of this trend is understood easily

enough even if the magnitude of the increase is slightly surprising. It is thought that the increased rate is caused by a greater dispersion of the amalgam droplets due to a decrease in viscosity and/or surface tension at a lower concentrations. A further decrease in amalgam concentration to 0.05 per cent produced a rate that was still higher than that with 0.5 per cent but lower than that with 0.1 per cent. This behavior might be due to a maximum in the aforementioned properties of the amalgam affecting its dispersion (a behavior that has been noted in aqueous solutions), or perhaps to the fact that metal phase diffusion might be becoming of importance at these lower concentrations. Further studies at still lower concentrations were unproductive due to the very small decreases in solution activity that one is required to follow. This prohibits a reliable determination of reaction rate with the present techniques.

Under study 8 were presented the data showing the effect of temperature on the rate of exchange in a bromide-complexed cadmium ion system. Treatment of these data by the least squares method indicated a slope of -3.4×10^3 °A (Figure 4) from which the activation of exchange may be calculated to be 6.8 kcal./mole (compared to 6.7 kcal./mole with uncomplexed cadmium ion of the same concentration). The relative magnitudes of these activation energies is what might be expected if both processes are diffusion-controlled, and would seem to be in agreement with the generalization that large diffusion coefficients invariably infers a small temperature coefficient (and therefore activation energy).[69]

Prior discussion in this section made mention of the possible increasing importance of the step involving the de-coordination of the metal in the determination of the overall rate as the metal-ligand bond strength increases. Study 10 presents results of a few exchange reactions carried out in the presence of the stronger complexing agents, cyanide and ethylenediaminetetraacetate ions. These results indicate that much slower exchange rates were obtained when either of the above ions was substituted for the weaker complexing agents, chloride, bromide or iodide ion. The rates were retarded so much, in fact, that it would be very improbable that the difference could be attributed to differences in diffusion coefficient, and thus the exchange would not seem to be diffusion-controlled.

A derivation has been performed[17] assuming that the de-coordination step is rate-determining in the exchange of cadmium in an excess of sodium cyanide (at which almost all of the metal ion exists as the saturated complex). The form of the equation obtained indicated a dependence of exchange rate in this system on the concentration of the amalgam, cadmium ion, and cyanide ion, and the number of cyanide ligands on the rate-determining specie. From the dependence of observed exchange rates on the concentrations mentioned above, it was possible to evaluate this number of ligands on the rate-determining cadmium specie. This number was found to be 2.2 ± 0.1, indicating that under the conditions studied where practically all of the cadmium was bound as the saturated complex $Cd(CN)_4^{-2}$, the rate of the exchange was controlled almost totally by the

discharge of the specie** $Cd(CN)_2$. This effect would seem to be due to the low probability of the simultaneous loosening of three of four cyanides from these more abundant species on one hand, and the very low concentrations of the hydrated cadmium ion and first complex on the other. It has been claimed[18] that at even higher excesses of cyanide ion the rate is determined by the discharge of the third complex**, $Cd(CN)_3^{-1}$.

5. Zinc System Results

The information obtained on the exchange of zinc(II) ions with zinc amalgams may be summarized as follows. All amalgam phases were prepared by adding the proper amount of zinc metal to 674 mg. of mercury.

a. Study 11, the effect of the removal of trace amounts of chloride ion from tracer stock solution prior to exchange for the system: 1×10^{-3} M. Zn(II)/1 per cent amalgam, pH 6, 30°, nitrogen-swept.

Rate Constant	
No Pretreatment	Chloride Ion Expelled From Tracer Stock
0.403 min.$^{-1}$	0.305 min.$^{-1}$
0.394	0.379
0.365	0.339
0.395 (1.8)*	0.340 (2.0)*

b. Study 12, the effect of pH on the system: 1×10^{-2} M. Zn(II)/1 per cent amalgam, 30°, nitrogen-swept. The exchange curves obtained at pH 13 were non-linear, therefore a rate constant as defined by a slope could not be determined in the usual manner. Consequently the re-

**The water ligands are omitted in these unsaturated complexes for simplicity.

action rates in this study are presented, first, as an experimentally-determined half-time of exchange, and second as a formal rate constant as calculated by the relation: $k = 0.693/t_{\frac{1}{2}}$.

Half-time of Exchange pH 6	pH 13	Rate Constant pH 6	pH 13
1.0 min.	7.6 min.	0.970 min.$^{-1}$	0.0912 min.$^{-1}$
0.8	8.0	1.02	0.0866
1.0	7.2	0.894	0.0962
0.9*	7.6**	1.00*	0.0912**

**Arithmetic average.

c. Study 13, the effect of variation of amalgam and solution concentrations on the system: Zn(II)/amalgam, pH 6, 30°, nitrogen-swept.

Zn(II) Ion Concentration	Rate Constant 1 Per Cent Amalgam	0.1 Per Cent Amalgam
1 x 10^{-2} M.	0.970 min.$^{-1}$	- - -
	1.02	
	0.894	
	1.00 (0.7)*	
1 x 10^{-3} M.	0.403 min.$^{-1}$	0.533 min.$^{-1}$
	0.394	0.522
	0.365	0.500
	0.395 (1.8)*	0.507 (1.4)*

d. Study 14, the effect of temperature on the system: 1 x 10^{-3} M. Zn(II)/1 per cent amalgam, pH 6, nitrogen-swept.

Temperature	Rate Constant
30°	0.403 min.$^{-1}$
	0.394
	0.365
	0.395 (1.8)*
40°	0.414 min.$^{-1}$
	0.408
	0.349
	0.391 (1.8)*

Temperature	Rate Constant
50°	0.488 min.$^{-1}$
	0.450
	0.482
	0.480 (1.4)*

e. Study 15, the effect of pretreatment of the amalgam with Zn(II) ion solution on the system: 1 x 10^{-3} M. Zn(II)/l per cent amalgam, pH 6, 30°, nitrogen-swept.

Rate Constant	
No Pretreatment	Pretreated with Zn(II) Ion Solution
0.403 min.$^{-1}$	0.233 min.$^{-1}$
0.394	0.296
0.365	0.358
0.395 (1.8)*	0.258 (2.7)*

f. Study 16, the effect of added complexing agents of the system: 1 x 10^{-3} M. Zn(II)/l per cent amalgam, 30°, nitrogen-swept. These results are summarized in Table III.

6. Zinc System Discussion

An attempt was made in these experiments on the zinc exchange system to investigate, in a manner similar to the cadmium system, the effect of sweeping the solutions with nitrogen gas prior to the exchange. Actually, no formal comparison is presented because the results obtained from exchange reactions performed without removal of atmospheric gases were so erratic as to be meaningless. Consequently, all exchange reactions involving this zinc system were carried out using solutions that were nitrogen-swept. Even then it was found that consistent experimental results were considerably more difficult to obtain than in either of the preceding systems (cadmium or mercury).

TABLE III

SUMMARY OF RATE CONSTANTS FOR THE EXCHANGE OF ZINC AMALGAM WITH COMPLEXED ZINC ION SOLUTIONS

Agent Added	pH	Individual Rate Constants (Min.$^{-1}$)	Least Squares Single Values (Min.$^{-1}$)
None	6	0.403, 0.394, 0.365	0.395 (1.8)
1×10^{-1} M. Chloride	6	0.410, 0.373, 0.241, 0.285	0.314 (2.2)
1×10^{-1} M. Iodide	6	0.352, 0.332, 0.348	0.342 (2.0)
1×10^{-1} M. Cyanide	10	Long[b]	- - - - - -
1×10^{-1} M. Ammonia	11	0.365, 0.333, 0.220	0.264 (2.6)
1×10^{-4} M. EDTA[a]	6	0.111, 0.165, 0.223, 0.192, 0.240	0.186 (3.7)

[a]The ethylenediaminetetraacetate ion.

[b]No exchange detected in 10 hours.

Since the stock tracer solution as received from Oak Ridge National Laboratory contained some chloride ion, study 11 was undertaken to determine if this chloride needed to be removed before exchanges with "uncomplexed" zinc ion could be effected. In this study a series of exchanges were carried out in which the solutions were tagged with the tracer solution as received, and another in which the tracer solution was heated with nitric acid to remove the chloride ion prior to being used to tag the zinc ion solution. A slightly slower exchange rate was obtained after this nitric acid treatment, but it could easily have been caused by the presence of salt in the solution from the neutralization of the excess acid with base. In any case, the change was not very large and the amount of chloride small, so further exchange reactions were effected without pretreatment of the tracer.

The effect of pH on the rate of the exchange was investigated, and the results appear under study 12. Acidic pH range values were limited by the attack on the metal in the amalgam at a pH of about 4, or by precipitation of the ion at a pH of about 6. Even then the chosen pH values were hard to maintain during the exchange, and many attempted reactions had to be voided due to precipitation during the course of the exchange. A series of reactions was carried out at a pH of 13 where the zinc in solution reportedly exists as the zincate. As mentioned at the time of the presentation of the results of study 12, the exchange curves obtained at a pH of 13 were non-linear, a fact that necessitated the calculation of formal rate constants from experimentally-determined half-times of exchange. The deviation in these curves was similar to that observed

in the mercury system when surface-active materials were added to the solution. This latter deviation was rationalized as being due to competing rates. If competing rates do exist in this exchange involving zinc as the zincate, it would be altogether compatible with the existence of the "zincate" not as a true ion, but as a dispersion of the solid hydroxide.[70]

Using the data in study 13 and Eq. 24, one can calculate values for the ionic diffusion coefficient for the zinc ion in the manner of the preceding systems, mercury and cadmium. These results are summarized as follows:

Zn(II) Ion Concentration	D_i/σ in Cm./Sec. 1 Per Cent Amalgam**	0.1 Per Cent Amalgam**
1×10^{-2} M.	1.3×10^{-2}	- - - - - -
1×10^{-3} M.	9.3×10^{-3}	6.7×10^{-3}

**674 mg. of amalgam used; estimated area of 7 cm.^{2}

The average for D_i/σ from these three values was 9.3×10^{-3} cm./sec. Using the same estimated value for σ, the average diffusion coefficient can be calculated to be 2.8×10^{-5} cm.^{2}/sec.

The same "alternate approach" that was presented in the discussion of the mercury system exchange, and extended to exchange in systems involving amalgams for the cadmium system may be reapplied here. Six values for the "limit" term of Eq. 35 were determined to be in the range 1.3 to 1.8 ml./gm./min. with an average at 1.6 ml./gm./min. (see Figure 5). Applying Eq. 43 in the same manner as previously, the calculated value for the ionic diffusion coefficient was 0.9×10^{-5} cm.^{2}/sec.

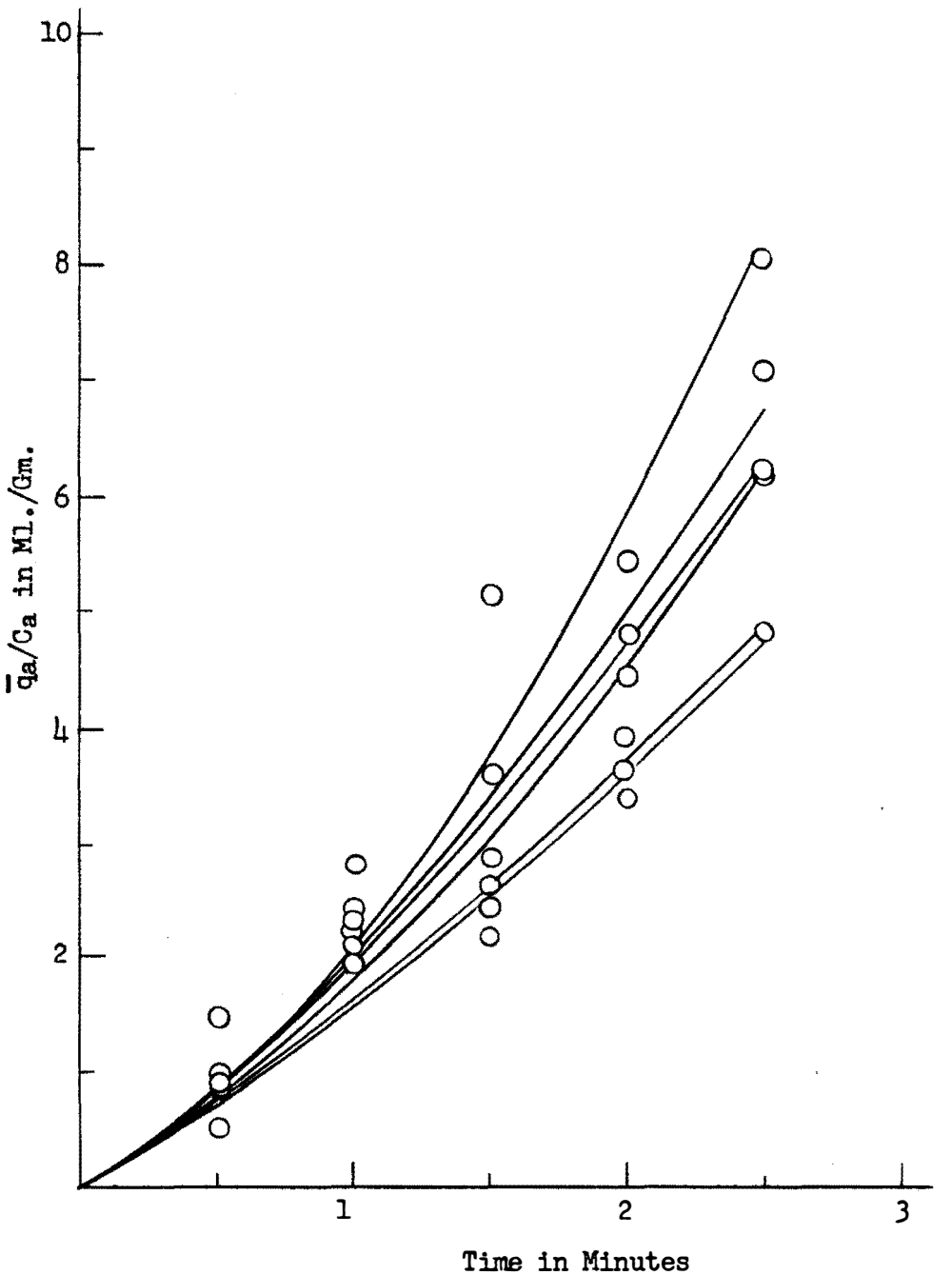

Figure 5. Plot of $\bar{q}_a/C_a$ versus Time for the Exch nge of Zinc Amalgam With Zinc Perchlorate Solution.

Under study 14 are listed the results of the study of the effect of temperature on the zinc system exchange. The slope obtained from a plot of ln k versus 1/T (Figure 6) was -1.13×10^3 °A from which the activation energy of exchange may be calculated as 2.3 kcal./mole.

Study 15 shows the effect on exchange rate due to the pretreatment on the amalgam with a zinc ion solution like that to be used in the exchange reaction, but not containing the tracer. Mention had been made in Chapter I in regard to the sometimes quite drastic difference in exchange rate that could be brought about by a treatment such as described above when the exchange concerns a solid metal. It was expected, moreover, that this would not be an important effect when using amalgams due to the assumed absence of the surface effects to which this phenomenon has been ascribed. This pretreatment was accomplished by agitating the freshly prepared amalgam under a nitrogen-swept solution of zinc ion identical with that to be used in the exchange. Since this treatment was carried out in the constant temperature water bath, the usual thermal equilibration of the amalgam could be eliminated, and the overall elapsed time before starting the exchange was essentially unchanged. There was, however, a considerable difference in the manner in which the amalgam was allowed to become thermally equilibrated. In the usual case, the amalgam was prepared, washed thoroughly, covered with a small amount of water in a beaker, and allowed to stand quietly in the water bath. The only agitation of the amalgam was that necessary to bring about the apparent dissolution of the metal. During the pretreatment described, however, the amalgam was agitated as strongly as in exchange, and it would not be

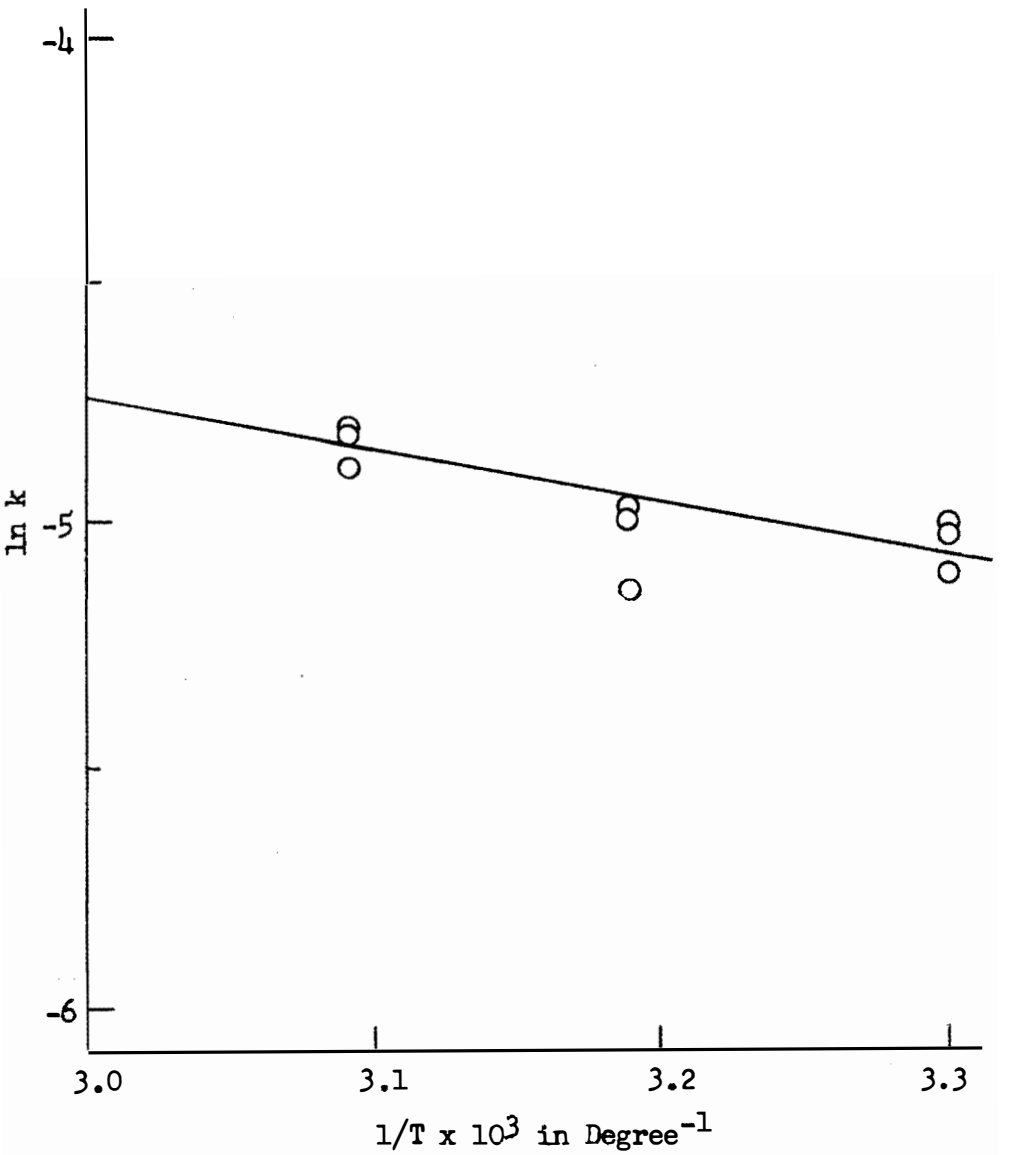

Figure 6. Plot of ln k *versus* 1/T for the Exchange of 1 Per Cent Zinc Amalgam With 1 x 10^{-3} M. Zinc Perchlorate.

too improbable that it could bring about a difference in the nature of the zinc as it exists in the amalgam. Further investigations along these lines should be both interesting and helpful in the understanding of the overall exchange occurring with amalgams.

Study 16 demonstrates the effect of added complexing agents on the zinc exchange rate. In general it is found that the effect produced on a given zinc exchange rate on addition of a complexing agent is very similar to that produced in the corresponding cadmium system, an effect that is not too surprising in view of the considerable similarity of the two in the chemistry of the simple and complex ions. Accordingly, much the same conclusions may be made here as were made during the discussion of the cadmium system. That is, the addition of complexing agents of moderate strength did not affect the exchange rate extensively as these reactions are still probably diffusion-controlled. In this series of exchanges the zinc ion solution was made 0.1 M. with respect to iodide ion, chloride ion and ammonia. In each case the exchange rate was reduced, the order of the reduction increasing in the order given. The alteration of the exchange rate is thought to reflect the change in the diffusion coefficient of the exchanging ionic specie, and this is dependent on the type and amount of complexing agent added. The similarity of these exchange results with those of the cadmium system extends to the exchanges carried out in the presence of the more strongly coordinating agents. The cyanide and ethylenediaminetetraacetate ions produced changes in reaction rate much greater than could be ascribed to changes in diffusibility of the reacting specie. It is proposed that here, too, it is probably the de-

coordination of the strongly bound ligands that is the slow step in the exchange.

7. Silver System Results and Discussion

Attempts were made to accomplish for the silver system studies paralleling those reported above for mercury, cadmium and zinc. Preliminary investigation showed, however, that the silver ion was lost to the metal phase even before any silver metal was dissolved in it. To prevent this premature removal of the silver, complexing agents were added to the aqueous phase. Although the ethylenediaminetetraacetate, iodide, and thiosulfate ions were unsuccessful in preventing the removal of the silver ion from the solution, the cyanide ion was able to accomplish the task. The next problem was to determine the stability of the silver amalgam to the cyanide ion solution. A few experiments where "tagged" silver amalgam was stirred with a solution containing cyanide ion showed that this agent did attack the silver metal. This dissolution was effectively stopped by removing atmospheric oxygen from the solutions by sweeping with nitrogen gas which had been purified by bubbling through an alkaline pyrogallate solution.

These precautions allowed the study of the system: 1×10^{-4} M. Ag(I), 1×10^{-1} M. CN^{-1}/amalgam, 30°, nitrogen-swept.

	Amalgam Concentration		
	"1 Per Cent"	0.04 Per Cent	0.004 Per Cent
Rate Constant	0.075 $min.^{-1}$	0.390 $min.^{-1}$	0.420 $min.^{-1}$ (1.7)*
	0.102	0.635	
	0.053	0.522	
	0.103	0.467 (1.5)*	

The first column shows the results of the exchange reactions involving a "1 per cent" amalgam. These were completed before the peculiar behavior of the amalgam spurred an investigation into the solubility of silver metal in mercury. This solubility is reported by Sidgwick[71] at 0.04 weight per cent of the metal in mercury at 20°. Sidgwick mentions the difficulty in obtaining values for the true solubility due to the fact that many metals, after having formed a saturated solution will continue to be "wet" by the mercury and will be held in suspension. That author's reported value for silver is an attempt at its true solubility, and was taken as that concentration of amalgam beyond which no further change is noted in the E.M.F. of a cell involving the silver ion in contact with silver amalgam. Silver, in particular, is capable of being suspended quite readily in a saturated amalgam. This was the case in the above results of this research reported as "1 per cent" amalgam which, evidently, was a saturated solution of silver in mercury with the remainder of the metal suspended in the amalgam. Reasonable-appearing exchange curves were obtained using these amalgams, and they reflected difficultly-reproduced rates that were slow compared to that obtained using a saturated 0.04 per cent amalgam. This is probably accounted for by the fact that these amalgams which contained about a twenty-five-fold excess of the solid metal dispersed within them, were sometimes noticeably difficult to disperse with the usual stirring arrangement. The reproducibility was not too much better when using 0.04 per cent amalgams, possibly still due to the above reason or to the formation of some silver-mercury intermetallic compound specie, many of which have been reported.[72]

Further difficulty was encountered in the series of experiments using 0.004 per cent amalgam, this time due to the fact that with such a dilute amalgam, only a small amount of silver was exchanged at "infinite" time, and small variations became quite important on a per cent basis. A considerable amount of scatter was noted in the few points obtained for each of the three individual exchange determinations, casting doubt as to the reliability of the exchange rates as determined by these points. For this reason it was thought best to report one exchange rate to represent collectively the data of all three determinations.

CHAPTER IV

SUMMARY

Studies of the rates of metal-metal ion exchange reactions at regulated temperatures were made using mercury or amalgams of cadmium, zinc or silver for the metal phase in contact with water solutions of the corresponding metal ions. Each metal ion was in solution either as the simple aquated specie, that is, as the perchlorate, or as some complexed specie according to the complexing agent added.

In most cases the course of the exchange was followed by the disappearance of the radioactive form of the metal in the solution. This disappearance was found to be representable by the equation, $\ln (1 - F) = -kt$ where F is the fraction of total possible exchange having occurred at time t, and k is an exchange reaction rate constant. The locus of points obtained by means of the experimental data and the above equation appeared approximately linear, and indicated a line that passed through or very near the origin. Curves were usually fitted to the data by the method of least squares, which yielded directly values for the slope of the curve and thus the exchange reaction rate constants.

The influence of temperature on these rate constants was studied in some cases. The behavior was found to be representable by the Arrhenius equation, $k = k_o \exp (-E/RT)$. Plots of ln k <u>versus</u> 1/T were linear over the temperature intervals used, and from treatment of these data by the least squares method were obtained values for the slopes of the curves. Since the slope is equal to -E/R, one may calculate a corresponding ex-

perimental activation energy as R (- slope).

The overall process referred to as exchange was inferred to consist of: the diffusion of the exchanging specie in the solution phase, the removal of all ligands from the coordination sphere of the ion, the transfer of the "stripped" ion to the exchange surface, the electron transfer, the deposition of the atom at the surface, and then the diffusion of the specie within the metal phase. The rate of the exchange will be determined by the slowest of these processes. Theoretically-derived relations were reported that indicate the form of the rate equations if diffusion in the solution or metal phase or ion discharge is to be rate-determining. In the absence of complexing agents that become strongly bound to the metal ions, the rate of the discharge of the ions is quite rapid and as such need not be considered in a discussion of rate determination.

The first system studied was the exchange of mercury(I) ion with mercury metal. The types of studies made included the effect on exchange rate of: variation of solution concentration and amount of agitated mercury; utilization of controlled surface areas of mercury; variation of temperature; and addition of surface-active substances.

The experimental data gave a value of ionic diffusion coefficient (D_i) of the proper order of magnitude ($\cong$ 1 to 2 x 10^{-5} cm.^{2}/sec.), although the calculation involves the estimation of a value for diffusion layer thickness. An alternate approach to the study of the exchange process was presented, and from the form of the relation obtained it was deduced that diffusion of the ionic specie must be the slow step. If this

is so, then the relations developed can be used to calculate D_i. The value was, once more, of the magnitude to be expected, although the calculation still depends on the estimated value of diffusion layer thickness.

The experimental activation energy of exchange was determined by means of the Arrhenius equation to be 4.9 kcal./mole. A comparison of this activation energy of exchange with that for ionic diffusion ($\cong$ 3 to 5 kcal./mole) and autodiffusion (1.0 to 1.2 kcal./mole), along with the seemingly successful calculation of values (although approximate) of D_i suggest that the rate of exchange of mercury(I) ion with metallic mercury under the experimental conditions is diffusion-controlled.

If the exchange reaction is diffusion-controlled, then differences in rate with varying amounts of mercury should be caused by the greater surface area available for reaction. A good correlation of exchange rate with surface area was obtained on conversion of these observed exchange rates to exchange rate per $cm.^2$.

The addition of surface-active substances to the exchange medium caused the expected slowing of the exchange rate, probably due to the lessening of the effective area available for exchange. An attempt at correlation of the concentration of the surfactant necessary to stop the reaction completely with complete coverage of the surface was unsuccessful, however.

Exchange studies similar to the above were performed in which amalgams of cadmium, zinc, and silver as the metal phase were allowed to enter into exchange with solutions of their respective ions. The types of inves-

tigations that were made included* the effect on the amalgamated metal-metal ion observed exchange rate of: prior sweeping of the solution with nitrogen gas; variation of the pH; variation of the metal ion and amalgam concentrations; variation of temperature; addition of "inert" electrolyte; pretreatment of the amalgam; and addition of complexing agents.

The effect of removal of atmospheric gases was to make the exchange curves from which the reaction rate constant is obtained more nearly linear, and to cause what appeared to be a slight decrease in rate. This decrease, if real, would seem to be in agreement with the results obtained when using solid metals in exchange reactions. To prevent the visibly obvious attack of the amalgams, all exchange reactions involving these rather reactive metallic phases were started only after sweeping of the system several minutes with a stream of nitrogen gas.

Studies on the effect of pH on exchange rate indicated that a higher rate was obtained as the acidity of the solution became lower, a behavior just the converse of that reported in the literature when solid phase metals were used. Exchange reactions were carried out in the zinc system at high pH where the zinc is said to exist as the zincate. The complex exchange behavior noted appears to be consistent with the existence, not of a true zincate ion, but of a dispersion of the hydroxide by the excess alkali.

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*Not every type of study listed was performed for each amalgamated metal-metal ion combination.

Generally, exchange reactions of a given type were carried out at different amalgam and solution concentrations. This allowed the calculation (*via* Eqs. 24 and 43) of values for D_i of the ions. Although the values are still dependent on the estimated size of the diffusion layer, they were all of the proper order of magnitude ($\cong$ 1 to 2 x 10^{-5} cm.^{2}/sec.).

From the studies on the effect of temperature on the exchange rates, values for the experimental activation energy of exchange were calculated. For 1 x 10^{-3} M. solutions, the activation energy was found to be 2.3 kcal./mole and 6.7 kcal./mole when the ion was Zn(II) and Cd(II), respectively. A slight decrease in activation energy (to 6.5 kcal./mole) was noted on doubling the concentration of the Cd(II) ion solution, in contradiction to the apparent trend in the scant supply of diffusion data in the literature.

It was found that the cadmium exchange rate was higher when the aqueous phase was saturated with the "inert" salt potassium perchlorate, an effect that, although not expected, was seen to be not inconsistent with demonstrated behavior of diffusion coefficients.

Stirring of the zinc amalgam with an inactive Zn(II) ion solution prior to exchange lowered the exchange rate. This type of behavior was seen to be common when solid metal phases were used, but it was thought that the use of the present liquid phase metals (amalgams) would eliminate such effects by the presumed absence of surface faults, cracks, "hot spots", *etc*.

Some exchange reactions were performed in the presence of complexing agents. Under the experimental conditions used, the agents that form only moderately strong complexes with the metal ions affected the exchange rate only slightly, an effect that would be expected for diffusion-controlled reactions. The addition of the cyanide or ethylenediaminetetraacetate ion, however, retarded the reaction much more than could be explained by a change in the diffusibility of the exchanging specie. It would seem probable that the energetically more difficult de-coordination of these ligands has made this step rate-determining.

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APPENDICES

APPENDIX I

Sample determination of the experimental exchange rate constant from exchange data for the system: 5×10^{-3} M. Hg(I)/69 mg. Hg^{o}, pH 2, 30°.

Time	c/m	Fraction Removed, F'	Fraction of Possible, F	ln(1-F)
0 Min.	5018	0.00	- - -	- - -
3	4934	0.02	0.03	-0.02
6	3855	0.23	0.30	-0.36
9	3371	0.33	0.43	-0.56
12	3297	0.34	0.45	-0.60
15	2819	0.46	0.60	-0.92
18	2366	0.53	0.70	-1.17
21	2176	0.56	0.74	-1.35
25	2163	0.57	0.75	-1.38
60	1191	0.76	1.00	- - -

A plot of ln(1-F) versus t is constructed, the best curve being placed by the method of least squares (Figure 7). For this treatment, the following data are useful:

Time	ln(1-F)	t[ln(1-F)]	t^2
3 Min.	-0.02	-0.06	9
6	-0.36	-2.16	36
9	-0.56	-5.04	81
12	-0.60	-7.20	144
15	-0.92	-13.80	255
18	-1.19	-21.05	324
21	-1.35	-28.35	441
25	-1.38	-34.45	625

From these data: $n = 8$, $\Sigma t = 109$ min.; $\Sigma [\ln(1-F)] = -6.36$; $\Sigma (t [\ln(1-F)]) = -112.11$ min.; $\Sigma t^2 = 1886$ min.^{2}. From Eqs. 21 and 22, one has that :

$$m = \frac{(8)(-112.11) - (-6.36)(109)}{(8)(1886) - (109)^2} = -0.0636 \text{ min.}^{-1}$$

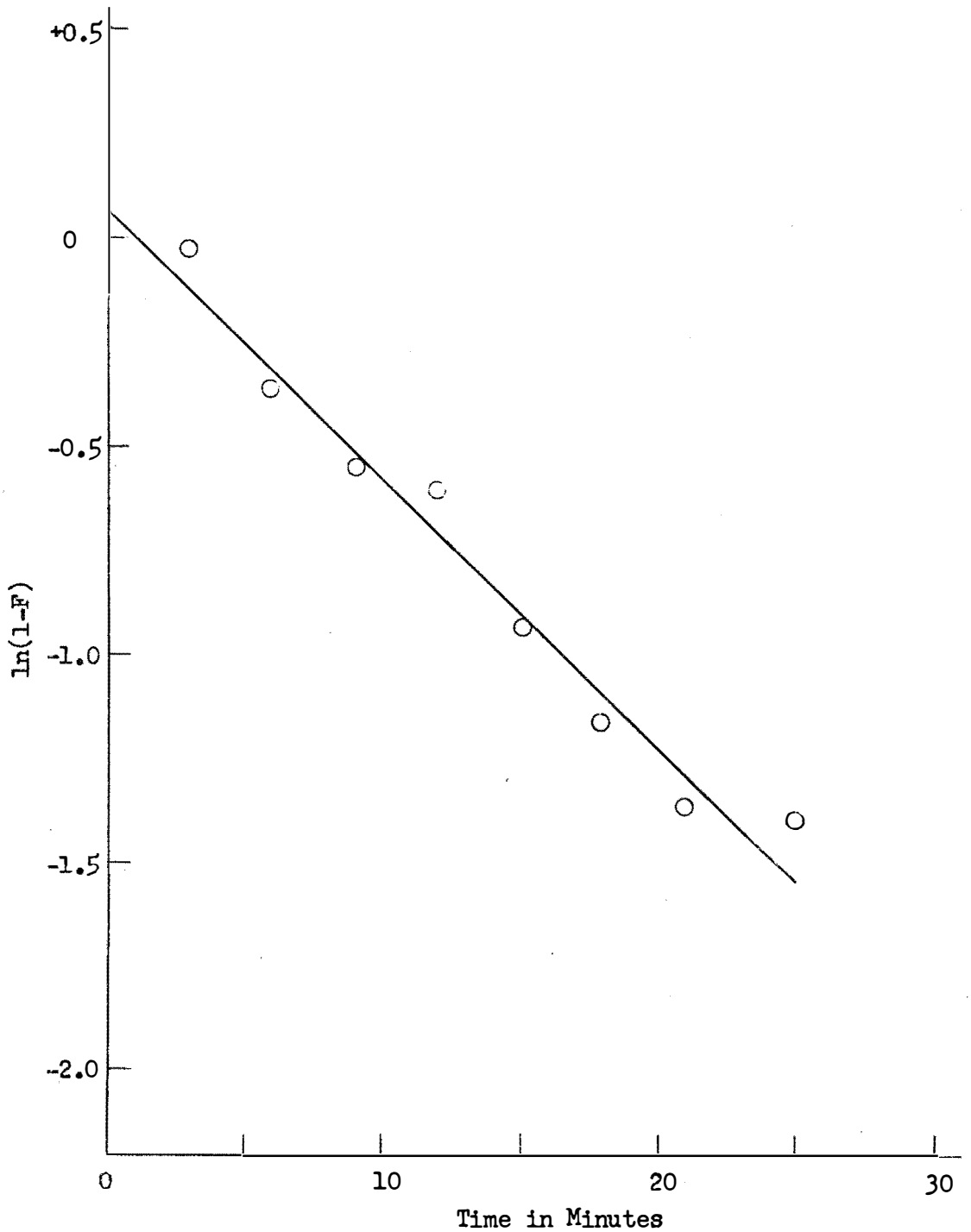

Figure 7. Representative Exchange Curve for the System: 5×10^{-3} M. Hg(I)/69 Mg. Hg^{o}, pH 2, 30°.

and

$$b = \frac{(-6.36) - (109)(-0.0636)}{8} = +0.08 \ .$$

In this same manner additional determinations for the same system were accomplished, and the values for m and b noted. Then the method of least squares was reapplied to all of the data collected for systems of a given type by determining the overall totals for n, Σ t, etc. as above and calculating for these a single value for m and b.

If it had been desired to tabulate a half-time of exchange in lieu of a rate constant, it could have been obtained in the following manner. The slope may be represented as

$$\text{slope} = \frac{\text{ordinate}_2 - \text{ordinate}_1}{\text{abscissa}_2 - \text{abscissa}_1} \ .$$

If it is desired to calculate $t_{\frac{1}{2}}$, one could substitute for ordinate_2 its value at 50 per cent exchange, ln(1-0.50), and for ordinate_1 its value at the point of intercept. Corresponding abscissa values are $t = t_{\frac{1}{2}}$ and $t = 0$. Then one has

$$\text{slope} = \frac{0.69 - b}{t_{\frac{1}{2}} - 0} = \frac{-0.69 - b}{t_{\frac{1}{2}}} \ ,$$

and

$$t_{\frac{1}{2}} = \frac{-0.69 - b}{\text{slope}} \ .$$

For the data presented above, $t_{\frac{1}{2}}$ is given by

$$t_{\frac{1}{2}} = \frac{-0.69 - 0.08}{-0.0636} = 12.1 \text{ minutes.}$$

It can be seen that for the ideal case where b is zero, this relation reduces to

$$t_{\frac{1}{2}} = \frac{-0.69}{\text{slope}} = \frac{0.69}{(-\text{slope})} = \frac{0.69}{k}$$

the form encountered in other first order processes.

APPENDIX II

Sample calculation of ionic diffusion coefficient by use of Eq. 24 for the system: 5×10^{-2} M. Hg(I)/69 mg. Hg^{o}, pH 2, 30°. Equation 24 is

$$k = \frac{D_i ca}{\sigma n(1-s)} ,$$

or

$$D_i/\sigma = \frac{kn(1-s)}{ca} .$$

The quantities needed for the calculation may be summarized as follows:

The rate constant, k: From the tabulation of mercury exchange system results, k equals 0.118 $min.^{-1}$ or 1.97×10^{-3} $sec.^{-1}$.

The number of gram atoms of mercury metal, n: 69 mg. is equivalent to 3.4×10^{-4} gram atoms of the metal.

The ratio of the amount of mercury in the metallic form to the total amount of mercury in all forms in the system, s: In 10 ml. of 0.05 M. Hg(I) solution there is 0.20 gm. of mercury. Therefore, s = 0.069/(0.069 + 0.20) = 0.26.

The concentration of the solution in gram ions/ml., c: A solution that is 0.05 M. in Hg(I) contains 1×10^{-4} gram ions/ml. of mercury (calculated as Hg^{+1}).

The surface of the mercury, a: This quantity had been estimated at 0.7 $cm.^{2}$.

Entering these values into the above equation, a value of D_i/σ may be determined as:

$$D_i/\sigma = \frac{(1.97 \times 10^{-3})(3.4 \times 10^{-4})(1-0.26)}{(1.0 \times 10^{-4})(0.7)} = 7 \times 10^{-3} \text{ cm./sec.}$$

VITA

Richard Charles Legendre was born in New Orleans, Louisiana, on August 11, 1931 and received his elementary education in the parochial schools of that city. In the fall of 1948 he entered Loyola University of the South at New Orleans from which he was graduated in 1952 with the degree of B. S. in Chemistry. He entered the University of Tennessee in June of that year to begin studies toward the M. S. degree which was obtained in March, 1954. Graduate studies toward the Ph.D. degree were resumed at the University of Tennessee in 1956 after a two-year term of induction into the Army. Financial aid during these periods at the University of Tennessee was provided by the following positions: Graduate Assistant, Research Assistant on an Atomic Energy Commission grant, Teaching Assistant, and Instructor in Chemistry.

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