SILVER-SILVER ION EXCHANGE REACTIONS

A Thesis

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by

Abraham Paul Baerg

McGill University
Montreal, Canada.

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INTRODUCTION

HETEROGENEOUS EXCHANGE REACTIONS

It has long been assumed that when a metal is placed into a solution of its ions an equilibrium is rapidly established in which a reversible interchange of atoms and ions takes place. If one of the components of the system contains a radioactive isotope of the metal, it is possible to follow this exchange by observing the distribution of the active isotope among the atoms and ions present.

The general scheme of such a heterogeneous exchange may be represented by the equation,

where M^{n+} and M represent the metal ions and atoms respectively, and the asterisk is used to denote the radioactive isotope.

It is evident from the reversible nature of the reaction that the rates in the two directions are equal (once equilibrium is established) and consequently the relative amounts of the respective components remain unaltered. It also follows that the reaction, as shown, has an associated equilibrium constant equal to unity and is therefore not accompanied by a change in free energy. The process is simply one involving the statistical distribution of the isotopes among the atoms and ions participating in the

exchange.

Although a particular kind of exchange has been portrayed here, many other heterogeneous systems exhibit similar characteristics. For example, besides studies of metal-ion exchange, the literature contains numerous reports on such equilibrium inter-phase reactions as that between an insoluble salt and its saturated solution, or of a gas between an adsorbed and a gaseous phase.

Recently, the mathematics of heterogeneous exchange reactions have been developed, notably by Zimens (1,29) and Duffield and Calvin (2), which permit the quantitative interpretation of experimental data. It seems appropriate to consider first some of the fundamental relations governing the distribution of the radioactivity, upon which most of the pertinent investigations are based.

To simplify the mathematical presentation, a solid-solution system will be considered and it will be assumed that, initially, the radioactivity is all in the solution phase. Subject to this condition then, the equilibrium distribution of the active isotope among the total amount of exchangeable material, b , in the solution and the total amount of exchangeable material, a , in the solid, is given by,

$$\frac{x_{\infty}}{y_{\infty}} = \frac{a}{b} \text{ - - - - - (1)}$$

where x and y designate the radioactivity in the solid and solution phases

respectively. The subscript (∞) indicates that the activities are determined at statistical equilibrium (time, $t = \infty$). With a knowledge of b and determinations of x and y , this equation has been used to determine the total amount of solid material participating in the exchange. Thus, in the absence of pronounced diffusion of the isotope into the solid, a may, under certain conditions, be associated with exposed surface atoms and, therefore, provide a measure of the true surface (3).

A similar equation may be used to define a quantity, a_t :

$$\frac{x_t}{y_t} = \frac{a_t}{b} \text{ - - - - - (2)}$$

where the distribution of the active isotopes is measured at any time, t , after commencement of the exchange reaction. Accordingly, a_t is that amount of solid material which has come into equilibrium with the isotopes in the solution, at the specified time. Since a_t , x and y vary with the time, equation (2) may be regarded as representing a continuum of "quasi-equilibrium" states for the system, which becomes identical with equation (1) at infinite time.

Equations have also been derived which indicate that the reaction must obey a first order rate law with respect to the radioactivity. If R be the rate at which atoms and ions interchange, both active and inactive, then the rate of appearance of the radioactivity in the initially inactive solid phase will be:

$$\frac{dx}{dt} = R\left(\frac{y}{b} - \frac{x}{a}\right) \text{ - - - - - (3)}$$

However, y is given by

$$y = x_{\infty} + y_{\infty} - x \text{ --- (4)}$$

whence, by equation (1),

$$y = x_{\infty} + \frac{b}{a} x_{\infty} - x \text{ --- (4a)}$$

Substituting this expression for y in (3) and rearranging,

$$\frac{dx}{dt} = R \frac{a+b}{ab} (x_{\infty} - x) \text{ --- (5)}$$

Integration of equation (5), with the condition that $x = 0$ at $t = 0$ gives:

$$2.3 \log\left(\frac{x_{\infty} - x}{x_{\infty}}\right) = -kt \text{ --- (6)}$$

where

$$k = R\left(\frac{a+b}{ab}\right)$$

Similar equations may be derived for the condition that, initially, the radioactivity is all in the solid phase. It is emphasized, however, that the simple first order rate law (equation (6)) will not be applicable unless the exchangeable atoms within each phase are all equivalent with respect to exchange. For example, if diffusion into the solid is rapid, the rate of exchange may not be governed solely by reaction at the surface. Zimens (1) has treated such a process and finds that under certain conditions the rate expression becomes,

$$2.3 \log \frac{x_{\infty} - x}{x_{\infty}} = -kt + \text{constant} \text{ --- (7)}$$

where k is a function of the coefficient of auto-diffusion, D , within the initially inactive (solid) phase, and is given by:

$$k = \frac{\pi^2 D}{4d^2} \text{ - - - - - (8)}$$

where d is the thickness of the exchanging solid specimen. These equations will be valid if the amount of material in solution is much greater than that in the solid. Although the effect of diffusion into the interior of solid metals may be negligible over the ordinary duration of experiments, diffusion into liquid metals may well become rate controlling in exchange reactions.

Control of exchange rate by diffusion of ions to the surface has also been considered (1). The kinetics of the reaction, however, retain the first order form given by equation (6), where k will now be a function of the diffusion coefficient through a solution layer at the interface.

Since this thesis is concerned with the exchange between a solid metal and its ions in solution, no attempt will be made to review in detail all of the studies which have been made on other heterogeneous systems. Instead, only that information which is considered relevant will follow the main historical account of the former reactions.

Exchange Reaction with Solid Metals

Early investigations of heterogeneous exchanges revealed that generally the kinetics of reaction were not amenable to a simple treatment because of non-equivalence of atoms, or as a result of complicating side reactions. It is probably for this reason that much of the work reported in the literature has treated with the extent of exchange during a given

period of time, using either equation (1) or (2). Thus, Hevesy (4), in his classical exchange experiments with thorium B in 1915, reports that lead foils in a lead nitrate solution exchanged to as much as 625 superficial atomic layers of the metal during one hour.

Hevesy found that the exchange during the one-hour period was roughly proportional to the concentration of lead ions in solution. To show that the reaction was reversible, in the sense that the relative amounts of the atoms and ions remained unaltered, he repeated the experiments with active lead foils and initially inactive solutions. It was concluded that diffusion within the metal was not sufficiently rapid to account for the great apparent depth of exchange. Instead, the results were explained on the basis of "local solubility elements", which appear as more or less easily dissolved regions on the surface. This, in fact, implied that the reaction was irreversible, not in the sense that the exchange was accompanied by a change of free energy, but that a spontaneous electrochemical reaction on the surface resulted in the incorporation of ions from the solution into the metal.

In 1929 Hevesy and Blitz (5) repeated these experiments with similar results and conclusions. In addition, exchange between lead sols and lead ions was studied. They found that, when the sol was initially inactive, the solution lost activity corresponding to exchange several times greater than was possible on the basis of the total amount of lead present in the sol. Only about one-tenth this extent of exchange was observed when the sol was initially active and the solution inactive. The purely

qualitative observation was also made that the sol exchanged much more slowly than did foils. These surprising results were explained by postulating a high degree of lead ion adsorption on the sol particles. Their slower rate of exchange appears to correspond to Zimons' process of diffusion through an adhering or adsorbed layer (1).

Erbacher (6) has made an extensive study of the local elements referred to by Hevesy (4,5) largely in connection with electrochemical deposition of monolayers of radioactive lead on less noble metal surfaces. In exchange experiments with lead or bismuth he found that mechanical abrasion of the surfaces always resulted in multiple atomic layer exchange, due to local cells which depended on the reactivity of individual points on the surface. Through corrosion of the metal in question these local solubility cells became inactive and the exchange was concluded to follow in a monatomic layer. Thus, lead foils were exchanged with lead ions in acid solutions sufficiently strong to give observable dissolution of the metal during the experiment. Under these conditions the activity distribution between the two phases soon reached an equilibrium value which was taken to be representative of the true extent of the metal surface. An interesting aspect of area measurement is presented here but the method has been criticized (7) for the procedure adopted by Erbacher.

Earlier experiments were, of course, necessarily restricted to systems for which naturally radioactive isotopes existed. However, many other metals have been studied since artificially produced radioelements became readily available. The most remarkable fact about these exchange

studies is that the number of apparent monatomic layers affected has always been relatively high although diffusion into the solid metal is probably negligible. Consequently the results have generally been explained on the basis of surface transformations or local cell action postulated earlier by Hevesy.

Rollin (8) has investigated the exchange between a polished sheet of metallic silver and a silver nitrate solution. Assuming again that the actual surface of the metal is the same as the apparent area, 150 atomic layers participated in the exchange with active solution during 24 hours. Similarly, a silver mirror, formed on the inside of a glass flask, exchanged to a depth of 20 atomic layers. On the other hand, an initially radioactive mirror in contact with inactive solution for 2 hours showed an exchange equivalent to 10 atomic layers. Anomalous results were obtained by preliminary treatment of the mirror with a solution of sodium nitrate. The initially inactive silver solution then gained activity corresponding to 150 monolayers of the metal.

The exchange of silver with 0.1N silver nitrate has also been studied by Coffin and Tingley (9) with particular emphasis on the influence of the method of preparation of the metal foils. A marked difference in the apparent depth of exchange was observed between etched and polished surfaces - 10 and 100 atomic layers respectively for the annealed metal. More profound, perhaps, was the effect on the rate of exchange. Etched foils picked up their maximum activity in a matter of seconds, but under the same conditions polished surfaces acquired only 90% of their equilibrium

activity in 24 hours. About 25% of the activity on polished surfaces was shown to be removable in an inactive solution.

Etched surfaces of unannealed or of annealed, cold worked foils showed visually distinct patterns of crystalline and "non-crystalline" (amorphous Bielby layer) metal. Such "mixed" surfaces picked up activities commensurate with those acquired by highly polished sheets, and gave autoradiographs which showed that the activity was largely confined to the crystalline areas.

Coffin suggests that an electrochemical mechanism is responsible for the activity acquired by the crystalline areas of a mixed surface, while a kinetic process is responsible for the activity picked up by polished foils and the anodic non-crystalline areas of cold worked specimens.

The mechanism of exchange on metal surfaces has very recently been studied by Simnad and Ruder (10) and viewed as a process of local cell action. Radioactive cobalt was used as indicator in all of their experiments and the activity acquired by various metals and alloys from cobalt solutions, in the presence and absence of oxygen, was observed. Autoradiographs of the surfaces after exchange showed that on alloys no activity was present on regions where visible corrosion had occurred. Similarly, for pure metals the activity was largely confined to specific regions. It was concluded that exchange is governed by the distribution of local anodes and cathodes which result in deposition of the cation on cathodic areas.

Exchange of zinc metal with its ions was observed by Haenny and Mivelaz (11) and also by Rollin (8). The former workers found that films of oxide or basic salt were formed on the surface before an exchange equilibrium was reached.

A close scrutiny has been given the kinetics of exchange reactions on metal surfaces by several recent workers. Quintin and his co-workers (12) have examined the exchange between radioactive copper and cupric sulfate solutions. In all of their experiments they were able to express the increase of activity in the solution by the theoretical equation ((6), page 4). The equilibrium extent of exchange varied from 500 to 17000 apparent atomic layers, depending on the pre-treatment of the surfaces (cold rolling, electrolytic polishing and washing with different solvents). Although the reaction obeyed a first order rate law, the multi-atomic layer exchange again suggests a non-equilibrium reaction on the surface.

It is probably reasonable to expect the rates of exchange, among different metals, to be related to their normal electrochemical potentials. An extensive study along these lines has been made by Haissinsky and his collaborators (13). The metals examined were emery-surfaced sheets of lead, bismuth, copper, manganese, gold, antimony, tellurium and lanthanum. Their overall results may be summarized as follows:

1. Most metals showed exchange of ten or more apparent atomic layers after about ten minutes in 0.001M solutions of the corresponding ions. This was increased to hundreds of layers when the concentration of the solution was increased by a

factor of a hundred. After one or two hours the exchange slowed down considerably but the results became quite irregular.

2. Kinetically, the exchange was not found to obey the first order rate law as observed by Quintin (12). Instead, over a period of several hours, it was possible to express the results by the empirical relation:

$$x = bt^a$$

where a and b are constants which, however, varied from one system to another.

3. The anion was observed to exercise considerable influence on the exchange but the effect depended on the nature of the metal. In fact it was found to vary for the same metal with concentration of the solution and the time of exchange. The extent of exchange was increased in the presence of anions which are susceptible to reaction with the metal.
4. Generally the rate of exchange increased with increasing acidity; that is, with conditions favoring attack of the metal.
5. Rates of reaction were obtained by assuming that, for time, t, near zero, the exchange was proportional to the time. From the temperature coefficient of these rates, activation energies were calculated. These energies were found to depend on the nature of the anion - 7 to 8 kcal./mole for nitrates and 3 to 6 kcal./mole for chlorides.

6. Contrary to some observations made by Erbacher (6), preliminary immersion of the metals in inactive solutions did not particularly reduce the extent of exchange with active solutions. In fact the exchange was found to be increased for bismuth.
7. No relation was observed (14) between the electrochemical potentials and the rates of exchange. Thus, with the same anion and concentration of metal ion, manganese ($E_H^0 = -1.05$ volt) showed a rate of exchange approximately equal to that for copper ($E_H^0 = +0.34$ volt).

Haissinsky (14) suggests that a transformation of the metal surfaces takes place on contact with the solution. The surface lattice structure is thought to become disorganized, rendered loose and more permeable to the penetration of ions. On the other hand, the solution may provoke virtual corrosion or recrystallization, in line with the views expressed by Hevesy (4,5). In addition, it is postulated that the elementary process of electron transfer ($M^{n+} \rightleftharpoons M$) between a metal and its ions is reversible, rapid and independent of the nature of the metal. Audubert (14), however, feels that an electrical double layer at the interphase must play a prominent role in the exchange process and that such an effect is possibly manifested in the influence of various anions.

These studies by Haissinsky were later extended to include the amphoteric element, selenium (15). A hydro-chloric acid solution, 0.1M in selenium dioxide, was used in the exchange. A rapid reaction was ob-

served, provided the normality of the acid was 5.5 or greater. The rate of exchange increased with acid strength, reaching a maximum value of 40% in one hour when the acid was 10N. Measurements at 1, 16 and 33°C. indicated a temperature coefficient corresponding to an activation energy of 6 kcal./mole. During the exchange, red amorphous selenium changed gradually to the black crystalline form.

The behavior of cobalt and tantalum has been examined recently by Cottin (16). The rate of exchange of cobalt with its ions was found to be much slower than those of other metals (13), which, however, depended again on the nature of the anion. Tantalum was slowly attacked in the solutions, which rendered the results inconclusive.

The Behavior of Mercury and Amalgams

Following the interpretation given to the results of exchange with solid metals, Haissinsky and Cottin (17) have studied the reaction between pure mercury and its ions in solution. The rate of exchange was shown to obey the first order rate law (equation (6), page 4) but graphically the logarithmic plot did not pass through the origin. This was interpreted on the basis of a rapid initial exchange between the surface atoms and the ions, followed by a slower process of diffusion to the interior of the mercury. An activation energy of 3200 cal./mole gave support to this conclusion. Later (18) the coefficient of auto-diffusion for mercury was determined by this exchange method, using Zimens' equations (pages 4 and 5).*

* Mention must be made of a recent work to determine the diffusion coefficient of sulfur by this method (19).

An activation energy of 3100 cal./mole was obtained for the diffusion process and this was found to be independent of the nature of the anion in solution (nitrate or chlorate). These observations are taken in evidence (20) to support the earlier interpretations of the results for solid metals.

The exchange of amalgams with the corresponding metal ions was first studied by Groh in 1927 using lead or bismuth. In his procedure he dropped small amalgam globules through a radioactive solution (0.1N) to give a transitory contact of the two phases. By this method he obtained a value of 1.7×10^{18} atoms/cm² sec. for the rate at which lead atoms and ions exchanged. This value seems extraordinarily high since pure lead (lattice constant, $a = 4.94 \times 10^{-8}$ cm.) exhibits only about 0.8×10^{15} atoms per cm² of surface. Groh has extrapolated the rate for the amalgams to the pure metals to establish the solution pressures of the latter. (21)

Measurements of exchange currents across amalgam solution interfaces have also been made by Miller and Pleskov (22) for mercury solutions of radioactive lead, bismuth and zinc with the corresponding ions. The radioactivity, x , of the initially inactive solution was given as a function of time, t , by:

$$\ln \frac{x_{\infty}}{x_{\infty} - x} = \left(\frac{A + B}{AB} \right) Str$$

where A and B are the amounts of metal in the amalgam and solution respectively, r the exchange current and S the rate of stirring. Exchange rates, r , as high as 0.1 ampere/cm² were observed. These values are considerably

greater than those observed by other workers (17,18) for pure mercury and the discrepancy is presumably due to surface active impurities in the systems studied by the latter.

Exchange with Insoluble Salts

A method of determining the specific surface of a lead salt in equilibrium with its saturated solution, by using thorium B as a radioactive indicator, was introduced in 1922 by Paneth (3). In principle, the method is identical with exchange between a metal and its ions in solution. According to Paneth's results, however, there appears to be an essential difference in behavior in that, not only does a rapid diminution of the activity in solution take place, but the process stops almost completely after a few minutes. In addition, the distribution of the isotopes is far from complete throughout the solid salt at this "quasi-equilibrium" state. Paneth assumed that the rapid exchange involved surface atoms only. On this basis, the area, calculated by assuming a cubic structure for the salt molecule in the solid, was found to agree very satisfactorily with that measured by dye adsorption or microscopic determination of the surface.

Later investigations of such exchange reactions have furnished much information concerning their mechanisms. Some of the more important results are given here because they seem to be closely related to the reaction between a metal and its ions.

It may be recognized that two conditions must be satisfied for the radioactive method to be valid as a surface area measurement:

- (a) The exchange must involve only surface atoms.
- (b) All of the surface atoms must exchange.

A series of investigations made by Kolthoff and his co-workers between 1933 and 1939 has contributed much to a clarification of whether the first condition may be satisfied. It was shown (23) that the extent of exchange depends markedly on the age of the crystals. A fresh precipitate of lead sulfate, for example, required only 5 minutes for complete distribution of the isotopes throughout the solid. An extremely rapid aging process occurred, however, and after standing for one hour the exchange decreased by a factor of 20 to 40; but the final state of recrystallization was reached very slowly. Even after a few days of standing, a further decrease in the specific activity of the solution was observed. Microscopic examination of the crystals showed no distinct changes of average size during the first hour of aging but distinct growth of the particles was noticed over longer times.

It is interesting to note that recrystallization of lead sulfate crystals could be virtually prevented by preliminary adsorption of certain dyes. Thus, in the presence of wool violet dye, the exchange with radioactive lead was evidently limited to the surface layer only (24). Similarly, good agreement was found between the results of area measurement by dye adsorption and the radioactive method in the presence of dyes, with either fresh or aged silver bromide crystals (25).

Qualitative observations on the kinetics of the exchange on lead sulfate indicated that a large excess of lead nitrate in the supernatant liquid actually diminished the rate of exchange (26). This seems to be in harmony with the observations on lead sols made by Hevesy (5). Similarly, adsorption of dyes inhibited the speed of exchange at the interface (24). Kinetically this behavior must correspond to Zimons' process (page 5) of rate control by diffusion through an adhering solution layer.

Kolthoff has concluded that fresh crystals must be entirely porous and all atoms in open communication with the exterior. The rapid aging involves a perfection of the crystals first separated while the slower process evidently concerns the spontaneous growth of the larger particles at the expense of the smaller ones. Perhaps this process corresponds to the local cell action observed in the exchange on metals. It appears, then, that only under very limited conditions will the exchange be restricted only to surface atoms.

The question of exchange with the entire surface (condition b) has received special attention from Paneth (27). It was observed that, for crystalline fusion products of lead sulfide, area measurements made by the radioactive method were consistently inferior to those furnished by microscopic evaluation. This discrepancy became still more pronounced when natural lead sulfide (galanite) was studied. X-ray examination of the crystals, however, showed no essential difference in the lattice structures, but a greater angle of reflection for the artificial crystals

indicated a less regular lattice. In addition, they were not as brilliant visually as the natural lead sulfide. It was also observed that the rate of solution in water was about six times greater for the fused products.

Autoradiographs of exchanged crystals of natural lead chromate indicated that the active thorium B was deposited largely on the edges of the crystals. Similar photographs of large crystal faces showed the activity confined to scratches and edges on an otherwise flat face. A non-exchanging surface of stibinite readily acquired activity after polishing with pumice. It therefore appears that, the more nearly perfect a crystal is, the less easily it exchanges with ions in solution.

Paneth has explained these various observations on the basis of the theories of crystal growth developed by Volmer, Kossel and Stranski (28). These theories predict a marked difference in the energy required to remove an atom from a crystal face, depending on the number of other atoms surrounding the given one. Exchange of atoms and ions is, therefore, expected to occur most easily at the apices and flaws of crystal lattices. It follows, then, that natural crystals, comparatively void of flaws and dislocations because of slow growth and aging, will exchange at best very slowly.

As an integral part of these theories on crystal structures, no crystal at a temperature above absolute zero can be perfect and the number of flaws and lattice vacancies must increase with temperature. Paneth argued that it should be possible to produce imperfections in natural lead sulfide crystals by heating, and then to preserve these by rapid cooling,

thus inducing the property of rapid exchange with lead ions. Experiments with galanite were in complete agreement with this line of reasoning. Heating the crystals to 850°C . (fusion point 1112°C .) enhanced subsequent exchange and in fact gave results comparable with those on artificial lead sulfide.

Zimens (7) has also considered in some detail the probable mechanism of these exchange reactions on the basis of the theories developed for crystal growth. An average crystal surface is visualized as consisting of a series of steps or incompleated layers of atoms. At the absolute zero of temperature the edges of these steps will be perfectly straight but at higher temperatures they will consist of a number of "Frenkel kinks" (30), holes, and protruding atoms "adsorbed" on the steps. It is also recognized that a crystal in equilibrium with its solution (or vapor) will have a number of atoms adsorbed singly on the plane surfaces. It is easy to see that these atoms are least strongly bound and that the greatest energy is liberated by adsorption at the steps. Over the range of temperatures for which atoms are firmly held at a step, those on the main surface are readily desorbed. The surface atoms, however, travel considerable distances by surface flow before they evaporate, and, therefore, it is to be expected that some of these will hit step positions. By a reverse process those atoms in the step positions "evaporate" onto the flat surface and eventually into the solution or vapor.

Accordingly, exchange of atoms and ions is considered to occur by a two-way process: (1) exchange of ions with relatively few adsorbed

atoms on the flat surfaces, and (2) exchange of the latter with atoms adsorbed at the steps. Furthermore, by statistical fluctuations of the Frenkel kinks, some of the originally adsorbed atoms are incorporated into the "two dimensional" lattice of the monolayers. Considerations of the energy required to remove an atom from within a flat surface essentially exclude the possibility of significant exchange by such a direct process.

Although Paneth and Zimens have made use of the theories of crystal growth specifically to explain the results of exchange reactions on insoluble salts, the principles must apply equally well to exchange between a metal surface and its ions in solution.

Summary

The results of the investigations on various heterogeneous exchange reactions may be summarized as follows:

1. Multi-atomic layer exchange is generally observed with solid metals. Since diffusion into the metal is probably negligibly slow, the deep exchange has usually been attributed to local cell action, recrystallization or other surface structural transformations.
2. The method of preparing the surfaces (polishing, mechanical abrasion, etching, etc.) has a profound influence on the apparent depth and rate of exchange.
3. The rate of exchange depends in an unpredictable manner on:

- (a) the initial surface structure
 - (b) the anion in the solution
 - (c) the metal in question
 - (d) the concentration of the exchange solution.
4. Kinetically the exchange reaction rarely obeys the theoretical first order rate law.
 5. The rate of exchange of mercury or amalgams with the corresponding ions is controlled by diffusion into the metal.
 6. The radioactive exchange method of area measurement, when applied to "aged" precipitates of insoluble salts, gives results in agreement with other methods. No such agreement is, however, found when applied to natural crystals of these salts. This may be explained on the basis of recent theories of crystal structure and growth.

THE PROBLEM

The primary purpose of this investigation was to study the influence of surface structure on an exchange reaction, in an attempt to differentiate between a reversible kinetic exchange and the irreversible local reactions on the surface which have been observed. The study was, therefore, to centre first on the influence of surface preparation and ultimately on the kinetics of reversible exchange and the influence of crystal orientation on the latter.

It is a characteristic of most of the previous work on ion-

solid metal exchange reactions that no account has been taken of the true surface area of the metal specimens. Instead, the exchange has usually been expressed in terms of the superficial area. It is, however, well recognized that, depending on the method of preparation, metals may exhibit a true surface many times the planar value. To what extent local cell action does, in fact, enter into exchange reactions of this type, therefore, becomes questionable. This factor, however, has not been wholly ignored by previous workers. In fact, Erbacher (6), in particular, has sought to determine the absolute surface of metals, specifically by means of exchange reactions. Independent measures of actual surface have been very useful in the studies on insoluble salts, and it is obvious that such information would be valuable in studies on exchange with metals.

It therefore seemed advisable, in this study, to obtain some measure of the roughness of the surfaces used for exchange reaction. A method introduced by Bowden and Rideal (31) has received wide use (32,33,34) and seemed particularly well adapted to the present study. The general principles involved in this measurement are as follows:

The rate at which an electrode in an acid solution attains its hydrogen overvoltage potential, immediately after switching on a cathodic current, has been followed by photographing the movement of a string galvanometer, or by means of an oscillograph. Both of these instruments are capable of following rapid changes of potential. Bowden and Rideal (31) found that, by careful elimination of impurities, and particularly all traces of oxygen, from a sulfuric acid electrolyte, the potential increased

in a linear manner with the quantity of electricity passed. This constant rate of potential growth implies that the buildup of the hydrogen over-voltage is due to the establishment of an electrical double layer, acting virtually as a condenser across which there is no transfer of charge.

The capacity of the condenser at the electrode surface is equal to dQ/dE so that it can be obtained from the slope of the linear plot of the quantity, Q , of electricity passed against the potential, E , or against the over-voltage.

By careful precautions to exclude all extraneous substances, a capacity of 20 mfd. per cm^2 was obtained for a mercury cathode. The magnitude of this capacity appeared to be the same for all electrode materials, since platinum on mercury and silver amalgams both gave the same capacity as pure mercury. Assuming that the mercury surface is planar, the capacity of any other electrode may then be compared with that for mercury and used as a measure of its true surface area. Such capacitance measurements were, therefore, made in conjunction with the exchange experiments.

The exchange system, silver-silver nitrate, using the radioactive isotope of atomic weight 110, was selected in this study for several desirable characteristics:

1. The simple nature of the ion precluded the possibility of complications due to reduction of the ion to lower valence states.
2. Owing to the long half life (270 days (35)) of the isotope, radioactive decay is insignificant during normal periods of experimentation.

3. The relatively high energy gamma radiation obtained from this isotope is easily detected with standard counting equipment.

It is obvious that metal-solution exchange involves principally those atoms of the solid which are in the vicinity of the surface. To make full use of the radioactive isotope it is therefore advisable to study the reaction with the metal initially inactive. The exchange reaction may then be followed by determination of the radioactivity acquired by the metal surface or that lost by the initially active solution. The maximum change in specific activity of the solution is proportional to the number of exchanging atoms on the surface. However, since the amount of material exposed at the surface is relatively small (generally about 2.5×10^{-9} g. atom per absolute cm^2 for silver), the working concentration of exchange solution will be limited to very low values if the exchange is to be measured by determination of the radioactivity remaining in solution.

On the other hand, the activity acquired by the metal is not dependent on the concentration of the solution, but rather on the ratio of active to inactive isotopes. Counting the radioactivity on the metal, therefore, becomes a more reliable means of following the reaction and this method was used in the present studies.

EXPERIMENTAL

In line with the development in the introduction, several exchange experiments were made in conjunction with surface area measurements by the Bowden-Rideal method. A detailed description of the apparatus and procedures follows. Subsequently, however, a more detailed kinetic study of the reaction necessitated a complete revision of technique. The apparatus used will be described later, in the appropriate section.

The Exchange Experiments

1. Radioactive silver

The silver isotope, Ag 110, was obtained as solid silver nitrate from the National Research Council, Atomic Energy Project. About 0.04 gram of silver nitrate was irradiated to the one millicurie level in the atomic pile at Chalk River. This quantity of silver nitrate was dissolved in concentrated nitric acid (to dissolve any reduced silver), the solution was evaporated to dryness and the residue taken up in 250 ml. of twice distilled water. The concentration of this active stock solution was accurately determined by titrating an aliquot with standard potassium iodide, using eosin as indicator (36).

2. The Electrodes

Metallic silver for the electrodes was obtained as pure silver foil, 0.004 inch in thickness, from Johnson, Matthey and Mallory Ltd. Silver discs of 2.5 cm.² superficial area were cut from this foil with a hollow punch.

The electrodes were designed so that exchange experiments could be made with the same surface for which the area was measured by the Bowden-Rideal method. A 24-40 standard taper re-entrant joint was fitted at each end with a lucite plug. A silver foil disc was cemented to the face of the plug at the re-entrant end of the joint, by wetting the flat lucite face with chloroform. A silver spring pressing against the back of the foil, through a hole in the centre of the plug, served as an electrical contact to a brass rod running through the middle of the taper joint.

3. The Exchange Cell

This cell was a 500-ml. round bottom flask with six 24-40 standard taper inlets to accommodate the electrodes. A 29-42 standard taper female at the top centre of the flask provided an inlet for a stirrer and a nitrogen bubbler. The flask was covered with black tygon paint to exclude light. It was mounted in a thermostat maintained at $25 \pm 0.2^\circ\text{C}$.

The radioactive exchange solution used in this cell was made up from the standardized stock solution, using twice distilled water. The ratio of active to inactive silver was suitably adjusted by adding inactive silver nitrate. The final concentration, unless otherwise indicated,

was 3×10^{-4} N in silver nitrate, and the 400 ml. of this solution in the cell contained about 0.3 millicurie active silver. Nitrogen, purified over hot copper ($450^{\circ}\text{C}.$), was bubbled through the solution continuously to sweep out dissolved oxygen and to maintain an inert atmosphere in the cell.

4. Counting the Activity on the Electrodes

The assembly for counting consisted of a horizontally mounted end-window Geiger tube with a female 24-40 standard taper joint fitted to hold the electrode opposite the end-window. The electrode holder assembly was made adjustable for various counting rates.

The remainder of the counting assembly consisted of a pre-amplifier in a lead castle, a high tension source with a voltage regulator, a scalar, a timer and a register.

A power pack was constructed to supply the regulated high tension D.C. to the Geiger tube. The unit operated on 110 volts, 60 cycles A.C. input and delivered a well regulated D.C. voltage variable from 500 to 1500 volts. The circuit of this unit is shown in Fig. 1.

The scalar was an Atomic Instruments Co. scale of 64, the output of which operated a mechanical register through a relay controlled by an interval timer.

Counting the activity on the electrode was done by placing the electrode in the holder described above. Positioning of the surface

Figure 1

Power Pack Circuit Diagram

relative to the Geiger tube was found to be sufficiently reproducible to give the same counting rate, within the errors of statistical fluctuations, for repeated determinations on the same electrode. The maximum deviation in positioning among the different electrodes used was less than 0.5 mm. The activity determinations were, therefore, strictly comparable with a common standard, the construction of which was identical with that of the electrodes.

The possible errors due to statistical fluctuations in the rate of radioactive disintegration have been shown (37) to be equal to the square root of the number of disintegrations recorded. Accordingly, the counting interval was always selected to give at least 10^4 counts so as to reduce the error from this source to 1% or less.

The background count was below 100 counts per minute and the activity determinations were corrected accordingly. The count obtained from activity adsorbed on the glass and lucite of the electrode assembly was of the same order of magnitude as the background. No correction was applied for adsorbed activity in the preliminary experiments, but in later experiments, where the electrodes were used only once in exchange reactions, this correction was made by counting the electrode assembly after the active foil had been removed.

An active silver electrode was used as a counting standard. It was calibrated in the following way: A given volume of active exchange solution was "diluted" with a much larger known amount of inactive silver nitrate. Silver from this diluted solution was electrodeposited on an

inactive electrode, using a known current for a given time. From Faraday's law the total amount of silver deposited was known. Since the relative amounts of active and inactive silver in the "diluted" electrolyte were known, the amount of active silver (from the exchange solution) deposited on the electrode could be calculated. The count on the electrode could, therefore, be directly related to this amount of active silver and, by comparison with the count on the standard, an active silver content was assigned to the latter.

Activity taken up by the inactive electrode, due to exchange with the electroplating solution, was reduced to insignificance by the high ratio of inactive to active silver. Self absorption of radiation from the electrode was negligible up to at least 10 micro-g.atoms since in this range a linear relation was obtained between count and amount of silver deposited. The amount of silver involved in any one exchange experiment was always much less than 10 micro-g.atoms. A representative calibration curve is shown in Fig. 2.

The extent of exchange on any electrode, in terms of the amount of silver involved, could be calculated from the activity determination. The exchange solution always contained at least 200 times more silver than was exchanged on any one electrode and, therefore, the ratio of active to inactive silver in solution remained essentially constant during a given experiment. Consequently, the extent of exchange, in terms of g.atoms, could be determined by direct comparison of the count on the electrode with that on the calibrated standard.

Figure 2

Calibration of Counting Standard

Whenever it was more convenient to express the exchange as the number of apparent atomic layers involved, the planar or apparent area was taken to be equivalent to 6.2×10^{-9} g.atom of silver. This value was obtained by assuming that the area occupied by one atom on the silver surface is equal to $(\text{g.atomic volume}/6.02 \times 10^{23})^{2/3} = 6.63 \times 10^{-16} \text{ cm.}^2$. This may be compared with $6.24 \times 10^{-16} \text{ cm.}^2$ per atom, taking the value of $1.44 \times 10^{-8} \text{ cm.}$ (38) for the radius of the silver atom and a coordination number of 12 for silver in the solid state.

The Area Measurements

The apparatus used for making the surface area measurements by the Bowden-Rideal method was similar to that described by Hutcheon (32), Roxborough (33) and Wiebe (39).

1. The Electrolytic (Overvoltage) Cell

The type of cell used is shown in Fig. 3. Two 200-ml. pyrex flasks were connected at the bottom through the stopcock S_1 and near the top through stopcock S_2 . Both compartments were fitted with hydrogen inlets so that the sulfuric acid electrolyte used could be cleared of dissolved gases. The anode compartment was fitted with a ground joint through which the platinum anode was inserted. Hydrogen escaped near the top of this fitting.

The calomel reference electrode made contact with the solution through a fine capillary fitted with a stopcock, S_3 . The capillary made

Figure 3

The Electrolytic (Overvoltage) Cell

connection with the probe which was drawn to a fine tip and positioned near the cathode surface. The whole assembly was mounted in a ground joint.

The silver electrodes (cathodes), described previously, fitted into the cathode compartment as indicated in Fig. 3.

2. The Electrical Circuit

A schematic diagram of the electrical circuit is shown in Fig.

4. The current for electrolysis was supplied from a 90-volt battery, B_1 , through large resistances, R_1 and R_2 , to the anode and cathode of the cell. The current was switched on with the switch, S_2 , or with the mercury switch, M , activated from the "single sweep circuit" in the lower right hand section of the diagram. The magnitude of the current was determined from the potential drop across a standard resistor, R_3 , measured with a "Queen" potentiometer (Gray Instrument Co.). The cathode to calomel potentials were measured with the same potentiometer through the switch, S_8 , with switches S_7 and S_9 open.

A Du Mont type 304-H oscillograph (CRO), containing sensitive D.C. amplifiers, was used for observation of rapid changes of the cathode-calomel potentials. Switch S_8 was then open to prevent pickup from the potentiometer circuit. The 1.5-volt battery, B_3 , was used to bias the potential to a suitable value.

The single sweep circuit was used to obtain a single sweep of the cathode ray trace and, when required, to switch on the electrolyzing

Figure 4

Electrical Circuit for Area Measurements

Parts List

R_1 - 10 Megohms	B_1 - 90 volts
R_2 - 10 Megohms	B_2 - 6 volts
R_3 - 1 K.ohm	B_3 - 1.5 volts
R_4 - 250 K.ohms	B_4 - 45 volts
R_5 - 500 K.ohms	C - 0.1 mfd.
R_6 - 25 K.ohms	M - Mercury Relay
R_7 - 10 K.ohms

current synchronously with the trace. The grid of the thyatron (6Q5G) in the CRO is biased to cutoff by charging the condenser, C, when S_3 is at the on position. With resistances R_5 and R_6 properly adjusted, the tube "fires" once, giving a single sweep. Switch S_3 also controls the mercury switch, M, in the input circuit and, since there is a slight time delay in this switch, the trace starts across the screen before the electrolyzing current is switched on. The speed of the lateral trace on the screen is controlled by the x-amplifier and sweep frequency settings. For much of the work reported here a slow sweep (about 3.5 seconds per inch) was obtained by using an external, 8 mfd. low leakage condenser connected between the sawtooth test signal input and ground.

The deflection of the CRO trace, produced by a potential from the bias circuit (B_3 , R_4 and S_5) was used to calibrate the y-axis.

3. Procedure

The necessity for working with pure solutions and clean glassware cannot be over emphasized. The precautionary measures used by other workers (32,33,39) were adopted here.

Sulfuric acid (N/5) was used as the electrolyte. The concentrated acid was re-distilled in a pyrex still at 3 to 4 mm. pressure. The solution was made by volume, using twice distilled and de-oxygenated water. It was stored in a 5-litre pyrex flask connected to the overvoltage cell by pyrex and tygon tubing and fitted with a vacuum line and a hydrogen inlet to allow it to be thoroughly de-oxygenated before use. The solution

was introduced into the cell through stopcock S_2 (Fig. 3).

The hydrogen gas used for clearing the solution and apparatus of air was obtained by passing electrolytic tank hydrogen over silica chips in a silica tube maintained at about 900°C . The gas was passed through a potassium hydroxide bubbler before it was used.

After the overvoltage cell had been thoroughly flushed with hydrogen, the $N/5$ sulfuric acid was introduced. Hydrogen was allowed to bubble through the electrolyte for a further period of about one hour. The electrode was then introduced while a rapid flow of hydrogen through the cell was maintained. A current (about 10^{-5} amp.) was then switched on for at least 30 minutes. This pre-electrolysis was found necessary to obtain a linear buildup of overvoltage for the area measurement. Presumably it served to reduce trace impurities in the solution, or metal oxide film on the cathode surface (40).

For the area measurement, the current was switched off, following the pre-electrolysis, and the overvoltage on the cathode allowed to decay through about 400 mv., as measured against the calomel reference electrode with the potentiometer. A low current (about 10^{-5} amp.) was switched on through the mercury relay switch, M, as described previously, and the cathode-calomel potential was applied to the CRO y-axis input through switch S_9 with switches S_6 and S_8 open (Fig. 4). With a slow sweep, the linear buildup trace was observed on the CRO screen. The slope of the linear trace was easily determined visually with a straight edge. Subsequently the current was measured, the y-axis amplification

determined, and the x-axis calibrated by measuring the rate of traverse of the CRO spot across the screen with a stopwatch. With this information, the slope, x/y , of the linear buildup was calculated in terms of time and volts, and this slope, multiplied by the constant current used, gave the capacitance directly. If, as has been claimed (41,42), the capacity per cm^2 of true surface is 20 mfd., the area may then be readily calculated by dividing the observed capacitance by this value for unit area.

When higher values of the current were used it became necessary to use a more rapid sweep speed. Instead of using the single sweep circuit, the CRO was set at "recurrent sweep" and the x-amplification adjusted so that the spot made a traverse of exactly 2 inches across the screen. Timing about 50 consecutive sweeps with a stopwatch gave an accurate determination of the sweep speed. Instead of the mercury switch, M, the switch S_2 was used to turn on the current.

It seems appropriate to remark here on the precision of the area measurements. For a single electrode it was observed that repeated determinations, after adequate pre-electrolysis, were usually within 5% of one another. It was found, however, that the magnitude of the current had a marked influence on the value obtained. For example, a ten-fold variation in the current produced a variation of as much as 30% in the value of the measured area. Likewise, the measured area was affected, though less severely, by the extent to which the overvoltage was allowed

to decay after the pre-electrolysis. A standard procedure for all electrodes was, therefore, set up arbitrarily as follows:

1. Pre-electrolysis was continued for at least 30 minutes for each electrode, using a current of 10^{-4} amp. ($\pm 10\%$).
2. The overvoltage was always allowed to decay to -0.1 ± 0.01 volt (referred to calomel), before obtaining the linear buildup trace on the CRO.
3. The same value of the current used in the pre-electrolysis was used to obtain the linear buildup trace.

Preliminary Results

The procedure for the earlier experiments was as follows: After fixing the silver disc to the electrode holder it was surfaced on glass with a water slurry of optical emery (#225, National Optical Co.). This freshly prepared electrode was then placed into oxygen-free water for one hour before placing it into the overvoltage cell for the area measurement.

Following the area measurement the electrode was washed with water and placed into the exchange cell containing 0.0047N. silver nitrate solution which contained radioactive Ag ion. Periodically it was removed, washed with water, dried in an atmosphere of nitrogen and counted to follow the course of the exchange reaction with time.

The results of such an experiment for one electrode are given

in Table I. These data are plotted in Fig. 5. After 307 hours total time, the exchange extended to approximately 330 apparent atomic layers (based on the superficial area (page 32)). On the other hand, the Bowden-Rideal measurement gave 52 times planar for the true surface of the electrode.

If the count, x , on the electrode after 307 hours is taken as the equilibrium value, x_{∞} , the plot of $-\log (x_{\infty} - x)/x_{\infty}$ versus time is reasonably linear but the line does not pass through the origin (Fig. 6). Several other electrodes, exchanged in this manner, exhibited the same behavior. The general shape of the log plots is similar to those found by Haissinsky and Cottin (17) for the exchange of mercury ions with mercury. It indicates clearly a rapid initial exchange followed by a prolonged slow process.

The great apparent depth of exchange suggests that the slower process involves local cell action or recrystallization of minute silver particles remaining on the surface after the emery surfacing. It is interesting that visible growth of needle-like crystals from an abraded surface was observed in 2N silver nitrate solution.

A second series of experiments was designed to follow the rapid initial exchange and, if possible, to separate this from the slower process. The procedure was the same as previously except that the initial intervals of exchange were of the order of minutes. An exchange-time curve for this

TABLE I

Exchange as a Function of Time

Emery surfaced silver foil

Superficial area of electrode = 2.5 cm^2 Active AgNO_3 conc. = $0.0047N$ Temperature = 25°C .

Exchange time hours	x counts/min.	x g.atoms $\times 10^6$	$-\log \frac{x_\infty - x^*}{x_\infty}$
0	0	0	0
4.5	2950	0.63	0.15
14.6	4200	0.93	0.25
37	5950	1.31	0.43
58.9	6850	1.51	0.56
85	7500	1.65	0.69
131.5	8200	1.80	0.87
170	8700	1.92	1.10
218	9000	1.99	1.37
271.2	9200	2.03	1.66
307.2	9400	2.07	
* Taking $x_\infty = x$ at 307 hours = $2.07 \times 10^{-6} \text{ g.atom}$			
Bowden-Rideal area = 52 X planar = $0.32 \times 10^{-6} \text{ g.atom}$			

Figure 5

Exchange as a Function of Time

Figure 6

Logarithmic Plot of Exchange as a
Function of Time

rapid initial process is shown in Fig. 7.

In an attempt to separate the several rate processes without a knowledge of x_{∞} , the data were plotted on a much larger scale, a smooth curve drawn through the experimental points, and tangents, dx/dt , determined with a straight edge at various points along this curve. These tangent values were then plotted against the value of x where the tangent was taken. The results of such a treatment for the curve in Fig. 7 are given in Table II and the graph of dx/dt versus x is shown in Fig. 8. The extent of exchange, x , is here given as g.atoms $\times 10^{-6}$, and the time, t , is given in minutes. The intercept of the linear section of the curve on the abscissa gives an exchange, for the initial rapid region, equivalent to 21 apparent atomic layers. This is to be compared with an area of 35 times planar, measured by the Bowden-Rideal method.

The above treatment, though not very satisfactory, indicated that an initial rapid exchange was essentially complete in a matter of several minutes (under the given conditions). It became apparent that the experimental procedure would not be adequate if the initial rapid exchange was to be studied. It was also evident that the slower process, assumed to be due to local cell action, possibly resulting from oxide patches or to recrystallization processes, must be reduced to a minimum so as not to obscure truly reversible kinetic exchange with the surface atoms. The latter reaction seemed the more worthy of study at this point.

Attention was therefore directed to

- (a) reducing the local cell action by preliminary immersion of

Figure 7

Rapid Initial Exchange

TABLE II

Variation of Exchange Rate, $\frac{dx}{dt}$, with x

Emery surfaced silver foil

Superficial area of electrode = 2.5 cm^2

Exchange solution = $0.0047N$

Temperature = 25°C .

Data from Fig. 7

Time min.	x g.atom $\times 10^8$	$\frac{dx}{dt}$ g.atom/min. $\times 10^8$	Time min.	x g.atom $\times 10^8$	$\frac{dx}{dt}$ g.atom/min. $\times 10^8$
1	5	3	10	14	0.45
2	7	2	15	16	0.28
3	9	1.4	25	17	0.24
4	10	1.2	30	22	0.42
5	11	0.8	40	26	0.27
6	12	0.67			
8	13	0.52			

Figure 8

Exchange Rate, dx/dt , as a Function of the
Activity, x , on the Electrode

- the electrodes in inactive silver nitrate solution, and
- (b) reproducing surfaces with respect to exchange during a given time.

Influence of Surface Preparation

It was well recognized by earlier investigators that the method of preparation of the metal surface had a profound influence on the subsequent exchange reaction. In the present experiment was studied the effect of equilibrating abraded and etched electrode surfaces in inactive silver nitrate solution, preliminary to exchange with the active solution. This was done in an effort to eliminate, or at least reduce to a minimum, the so-called local cell action, and thereby to obtain more reproducible results in the exchange reactions.

The abraded surfaces were prepared in the manner outlined previously. The etched electrodes were first surfaced with emery and then etched for one minute in 7N nitric acid. After surfacing, the electrodes were thoroughly rinsed with water and then placed into the "equilibrating cell" (similar to the exchange cell) containing the inactive silver nitrate solution. Following equilibration, the electrodes were transferred to the active exchange solution for one hour. Both the inactive and active solutions were $3 \times 10^{-4}N$ in silver nitrate concentration.

After one hour exchange, the electrodes were removed, thoroughly rinsed with water and placed into the overvoltage cell for an area measurement. They were then dried and counted to determine the increase in activity

during the one hour exchange. The results of these experiments are given in Table III. For comparison are also recorded the "times planar" Bowden-Rideal area measurement and its equivalent in g.atoms, assuming 6.2×10^{-9} g.atom per planar electrode surface.

The results may be summarized as follows:

1. Abraded surfaces show a definite decrease in the extent of exchange after equilibration for several days. There is apparently no significant change in the area measurement.
2. Etched surfaces exhibit a much lower activity uptake than abraded surfaces and this is apparently unaltered by preliminary immersion in the inactive solution.
3. The Bowden-Rideal area measurement shows a general qualitative correspondence with the extent of exchange within a group of similarly prepared surfaces, in that the larger area is accompanied by a larger gain in activity. Such correspondence, however, does not hold, even approximately, between the two types of surface.
4. The activity for "well equilibrated" abraded surfaces agrees fairly well with the area measurement.

In view of the latter observation it seemed worth while to follow again the exchange on an abraded surface, equilibrated for several days, using the method outlined previously, then to observe the loss of activity in the same manner during exchange with inactive silver nitrate solution. Accordingly, an electrode was counted between intervals of exchange with

TABLE III

Influence of Surface Preparation

Superficial area of electrodes = 2.5 cm^2

Exchange time = 1 hour

Active exchange solution = $3 \times 10^{-4} \text{ N}$

Temperature = 25°C .

Electrode	Equili- bration time	x g.atom X 10 ⁸	Bowden-Rideal Area Measurement	
			g.atom X 10 ⁸	times planar
Abraded Surfaces				
1	0	15.2	9.0	14.5
2	0	22.8	9.4	15.2
3	10 hrs.	8.2	8.7	14
4	35 "	12.7	10.9	17.6
5	75 "	13.1	11.2	18
6	80 "	11.9	11.8	19
7	12 days	7.8	13.3	21.5
8	15 "	8.9	9.1	14.7
9	15 "	8.4	8.4	13.5
10	17 "	8.5	9.2	14.8
11	17 "	9.6	9.9	16

Table III (cont'd.)

Electrode	Equili- bration	x	Bowden-Rideal Area Measurement	
	time	g. atom X 10 ⁸	g. atom X 10 ⁸	times planar
Etched Surfaces				
1	0.3 hrs.	1.25	4.0	6.4
2	3.5 "	2.08	6.2	10.0
3	6.5 "	1.87	5.9	9.5
4	14.0 "	1.24	5.0	8.0
5	13.0 "	1.60	4.0	6.5
6	18.5 "	1.24	3.7	6.0
7	19 "	2.34	4.8	7.8
8	22 "	1.59	4.5	7.3
9	25 "	1.18	4.6	7.4
10	25 "	1.35	4.5	7.2
11	25 "	1.32	3.8	6.1
12	27 "	1.45	4.6	7.5
13	36 "	1.66	4.6	7.5
14	38 "	2.18	4.3	6.9
15	40 "	1.66	4.9	7.9
16	45 "	1.29	6.7	10.8
17	48 "	1.56	6.0	9.7
18	51 "	1.37	4.7	7.6
19	53 "	1.56	6.8	11.0

active solution and after 100 minutes the reaction was reversed. The results for such an experiment are given in Table IV and represented graphically in Fig. 9..

Although the activity is again in agreement with the area measurement after 100 minutes exchange with the active solution ("forward reaction"), the subsequent "reverse" reaction indicated that much of this activity had entered non-exchangeable positions on the surface. This apparent "burial" of activity was again interpreted to indicate local cell action.

The general lack of agreement between the extent of exchange and the Bowden-Rideal area measurement, particularly with etched electrodes, suggests exchange largely with "active centres", in harmony with Paneth's experiments with natural crystals (27). On the other hand, Bowden and Rideal more cautiously consider the "capacitance area" to be that accessible to hydrogen deposition. It does not follow that the extent of exchange should correspond to such an accessible area or to the true surface area.

Several other experiments, made in conjunction with those given in Table III, were considered worthy of further investigation. After counting the activity, one of the abraded and equilibrated electrodes was again placed into the overvoltage cell and rendered cathodic for about ten minutes. It was then removed, quickly rinsed with water and transferred to the active exchange solution for another 30 minutes. After this period it had picked up an additional activity almost as great as

TABLE IV

Exchange as a Function of Time

Superficial area of electrode = 2.5 cm^2 Silver nitrate concentration = $3 \times 10^{-4} \text{N}$ Temperature = 25°C .

Preliminary equilibration - 48 hours

Forward Reaction		Reverse Reaction	
Exchange time min.	x counts/min.	Exchange time min.	x counts/min.
0	0	0	5400
1	750	1	4380
4	1770	2	4000
10	2580	4	3360
15	2980	5	3140
20	3400	8	2850
25	3680	13	2720
31	3940	20	2480
40	4330	30	2240
60	4700	50	2150
100	5400	70	1980
		100	1860
Bowden-Rideal Area		{before equilibration = $26.6 \times \text{planar} = 1.6 \times 10^{-7} \text{ g.atom}$ {after exchange = $19.7 \times \text{planar} = 1.2 \times 10^{-7} \text{ g.atom}$	
g.atoms exchanged in 100 minutes		(Forward reaction - 1.2×10^{-7} (Reverse reaction- 0.79×10^{-7}	

Figure 9

Exchange as a Function of Time

(Forward and reverse reactions)

that during the first one-hour period. Similarly, an etched electrode was observed to exchange, during 15 hours, to an extent equivalent to 2.38×10^{-8} g.atom. An additional exchange period of only 5 minutes, after cathodic treatment in the overvoltage cell, resulted in an activity increase of 0.6×10^{-8} g.atom.

These observations suggested that part of the activity counted on the electrode was present in the form of an adsorbed ionic double layer which was not adequately removed, even by the rather thorough water wash that followed the exchange. Such ionic silver, if present, would be expected to be deposited on the electrode when it was rendered cathodic, in the pre-electrolysis preparatory to the Bowden-Rideal area measurement. It, therefore seemed advisable to make a further study of such cathodic treatment on subsequent activity uptake in active silver nitrate solution.

The Effect of Preliminary Cathodic Treatment

It may be recalled that the pre-electrolysis had been found necessary before a Bowden-Rideal area measurement could be made, i.e. before a linear buildup of potential could be obtained. Studies have been made (39) of the manner in which the cathode potential varies with the time (at constant current) during this electrolysis. The amount of electricity consumed during the time required for the hydrogen overvoltage to reach its maximum value was associated with deposition of a "close packed" monatomic layer of hydrogen on the cathode. For a large number of copper and silver

electrodes, good overall agreement was found between the area which would be occupied by this deposited hydrogen, and the area subsequently measured by the Bowden-Rideal method.

Without making any assumptions about the nature of the electrode processes during the period of pre-electrolysis, it seemed advisable to study these potential-time curves (overvoltage curves) as a possible measure of adsorbed silver ions. For example, Evans and Miley (43,44) developed a technique, later perfected by Campbell and Thomas (45,46), which makes use of such curves in potassium chloride electrolyte for the measurement of oxide film thickness on metal electrodes.

In preliminary studies the overvoltage curves were determined by measuring the cathode-calomel potential changes with a potentiometer. A typical curve obtained in this way is shown in Fig. 10. Campbell and Thomas have used the inflection point in such a curve as a measure of the electricity consumed in the reduction of the film. In experiments given here, the steep portion of the curve was extrapolated to the value of maximum overvoltage, $E_{\max}$, as indicated in the figure. Multiplication of the value of the time in seconds at the point of intersection, by the constant current used, I , was taken as the amount of electricity, Q , consumed in the initial electrolyzing process. The extrapolation was more easily made by observing the overvoltage curve on the CRO screen, using a slow sweep, and this method was used in all but the preliminary work.

Experiments were then made to determine a possible relation between Q , obtained from the overvoltage curve and additional gain in

Figure 10

"Overvoltage Curve"

activity by an electrode after it had been rendered cathodic. An etched and washed electrode was subjected to pre-electrolysis in the overvoltage cell to reduce any oxide which might remain on the surface after etching. The electrode was then removed and quickly rinsed, immediately after switching off the current, and transferred to the active exchange solution for one minute. Following this, the electrode was rinsed, an overvoltage curve carefully taken and the amount of electricity, Q , required to attain the maximum overvoltage determined in the manner described above. After the gain in activity had been determined the electrode was again rendered cathodic in the overvoltage cell and placed into the active solution for about one minute. The whole process was repeated five times on this electrode. The results of this experiment are given in Table V.

It is clear from these data that, following the first immersion in the active solution, the gain in activity, expressed as micro-coulombs, is in good agreement with the values of Q determined. The large activity uptake during the first immersion period is presumably due mainly to exchange with surface atoms.

A second experiment was made in the same manner except that in some cases the overvoltage was allowed to decay partly in the overvoltage cell before the electrode was removed and placed into the active solution. The times of immersion in the active solution were also increased. The experimental conditions were altered in this way to determine whether the immersion time affected the value of Q or the activity increment and also whether the potential state of the electrode before immersion produced

TABLE V

Effect of Cathodic Treatment

Superficial area of electrode - 2.5 cm^2 Active solution - $3 \times 10^{-4} \text{ N}$

Exchange Time min.		Total Activity coulombs $\times 10^6$	Q coulombs $\times 10^6$	Activity gain coulombs $\times 10^6$
1	1	1960	580	1960
2	1.5	2580	530	620
3	1	3080	530	500
4	1	3540	535	460
5	1	4140	560	600
6	1	4830	590	690

Mean activity gain for 2, 3, 4, 5 and 6 = $570 \mu\text{-coulomb}$ Mean value of Q for 2, 3, 4, 5 and 6 = $550 \mu\text{-coulomb}$

TABLE VI

Effect of Potential State of Electrode

Superficial area of electrode - 2.5 cm^2 Active solution - $3 \times 10^{-4} \text{N}$

	Exchange Time min.	Potential state of Electrode just before removal from the overvoltage cell	Total Activity coulombs $\times 10^6$	Q coulombs $\times 10^6$	Activity gain coulombs $\times 10^6$
1	10	overvoltage	2030	670	2030
2	5	overvoltage	2720	620	690
3	5	overvoltage	3250	585	530
4	5	decay to 0.0 volt*	3760	635	510
5	5	decay to +0.1 volt*	4150	620	390
6	5	overvoltage	4720	620	570

* Potentials referred to calomel electrode

any alteration in the gain of activity. As can be seen from the data given in Table VI, neither of these factors had any significant influence.

It was still not conclusive from these experiments that the gain in activity resulting from repeated immersion in active solution was due to adsorbed ions which remained on the surface and that Q was the amount of electricity required to discharge such ions. The electrode might, for example, have been covered by a layer of hydrogen atoms after the electrolysis, and these might subsequently have reduced silver ions when the electrode came into contact with the active exchange solution. However, if this were the explanation, the quantity, Q , should be independent of the concentration of silver ion.

Experiments were therefore made to determine the effects on Q of changes in concentration of silver ion. To avoid the possibility of any side effects in the overvoltage cell (containing sulfuric acid) due to the nitrate ion, silver sulfate was used in these experiments. The silver was inactive since interest here lay only in the effect on the overvoltage curves. The experimental procedure was similar to that used above, i.e. the electrodes were first rendered cathodic in the overvoltage cell, then rinsed and transferred to the silver sulfate solution with a minimum exposure to air. The solutions were maintained oxygen-free by continually bubbling nitrogen through them. After immersion, the electrode was quickly rinsed and a determination of Q made immediately after placing it into the overvoltage cell. Concentrations of 10^{-2} , 10^{-4} , 10^{-6} and 10^{-8}

equivalents per litre in silver sulfate were used. The results for three different electrodes are given in Table VII. In Fig. 11 the data are represented graphically as $-\log[\text{Ag}^+]$ versus Q .

From the slope of the line in Fig. 11 a capacity, C , may be calculated as

$$C = \Delta Q \sqrt{\frac{2.3RT}{nF}} \Delta \log [\text{Ag}^+]$$

The capacity per apparent cm^2 is obtained by dividing the total capacity by the area of the electrode (2.5 cm^2). The values obtained in this way are given in Table VII, together with those obtained by the Bowden-Rideal method. It may be noted that Veselovskii (47) has obtained a value of 620 mfd. per cm^2 for an etched silver surface by potentiometric measurement of adsorption of silver ions from a solution of silver nitrate.

These experiments, however, seemed to leave little doubt that the overvoltage curves give a fairly good measure of the adsorbed activity. It was therefore decided to continue the exchange experiments on individual electrodes, with a view to establishing surface atom exchange as a function of time, using determinations of Q to measure adsorbed activity.

Exchange on Etched Electrodes

From the previous experiments (Table III) it had become apparent that etched surfaces were less subject than ground surfaces to local cell action. For this reason etched electrodes were used in the experiments described below.

TABLE VII

The Effect on Q of Silver Sulfate Concentration

Superficial area of electrodes - 2.5 cm^2 Room temperature = 25°C .

Ag_2SO_4 conc. N	Immersion time	Q coulombs X 10^6	Capacitance
Electrode 1			
10^{-8}	1 hr.	315	By Adsorption = 610 mfd./cm. ²
10^{-8}	4.5 hr.	268	
10^{-6}	0.5 hr.	472	
10^{-6}	0.5 hr.	472	
10^{-6}	6 min.	470	By Bowden-Rideal method = 150 mfd./cm. ²
10^{-4}	15 min.	623	
10^{-2}	15 min.	850	
Electrode 2			
10^{-6}	15 min.	374	By Adsorption = 250 mfd./cm. ²
10^{-6}	22 hr.	354	
10^{-4}	1 hr.	452	By Bowden-Rideal method = 145 mfd./cm. ²
10^{-4}	4 hr.	438	
10^{-2}	10 min.	517	
Electrode 3			
10^{-6}	45 min.	586	By Adsorption = 745 mfd./cm. ²
10^{-4}	15 min.	805	
10^{-4}	22 hr.	820	
10^{-2}	10 min.	1040	By Bowden-Rideal method = 165 mfd./cm. ²
10^{-2}	3 hr.	1010	

Figure 11

The Effect of Concentration of Ag^+ on Q

To reduce the possibility of oxide film formation on the surfaces, each electrode was used only once in an exchange reaction. Different electrodes were allowed to exchange for different periods of time. The electrodes of one series were equilibrated for 15 hours in an inactive solution of silver nitrate before exchange with the active solution. In another series, the electrodes were exchanged directly without preliminary equilibration.

The preparation of the electrodes was as follows: the silver disc was fixed to the electrode holder and the surface abraded with emery and etched for one minute in 7N nitric acid. It was then thoroughly rinsed with twice distilled water, placed into the overvoltage cell and a cathodic current (10^{-4} amp.) passed for 30 minutes to decompose any oxide or discharge any silver ions which might remain on the surface after it was etched. The potential change with time in this preliminary electrolysis indicated that approximately 1000 micro-coulombs was required for the decomposition. It was apparent from this that even prolonged washing did not remove all the silver ions or oxide. After the electrolysis the electrode was quickly rinsed and transferred to the inactive silver nitrate solution for 15 hours (for the first series) and then to the active exchange solution. For the second series, the electrodes were transferred directly to the active solution after the electrolysis.

After the exchange period, the electrode was rinsed with water, placed into the overvoltage cell and an overvoltage-time curve taken as quickly as possible. Following this, a Bowden-Rideal capacitance measure-

ment was made and an area calculated. The electrode was then removed, dried and the gain in activity determined.

The results of these two series of experiments are tabulated in Tables VIII and IX. The "total activity" is the total as counted on the electrode. Q has its usual significance and the "exchange activity", which is the total activity less the value of Q , gives a value for the activity which is assumed to be due to exchange with surface atoms. For comparison, these quantities are all given in terms of micro-coulombs. The Bowden-Rideal "times planar" area is also given.

In spite of the poor reproducibility of the surfaces it is evident that several hours were required for the equilibrated electrodes to gain the same total activity as that acquired by the non-equilibrated electrodes in a rapid (1 to 10 minutes) initial exchange.

Perhaps of greater interest is the variation of "exchange activity" in the two series of experiments. This quantity is seen to increase much more slowly for the equilibrated surfaces and evidently accounts for the slower overall rate of exchange for these electrodes. This observation suggests that an ionic double layer, already present on these surfaces before contact with the active solution, limits a rapid exchange process to this layer and presents an energy barrier to exchange with the surface atoms. This is in harmony with the views expressed by Hevesy and Blitz (5) and with Zimens' process of rate control by diffusion through an adhering solution layer (1). However, to explain the apparently

TABLE VIII

Exchange with Etched, Equilibrated Electrodes

Equilibrating solution - $3 \times 10^{-4}N$

Exchange solution - $3 \times 10^{-4}N$

Superficial area of electrodes - 2.5 cm^2

Temperature = 25°C .

Electrode No.	times planar area	Exchange time hours	Total activity	Q coulombs $\times 10^6$	Exchange activity
1	6.0	0.016	930	830	100
2	7.3	0.83	1220	1230	
3	6.3	0.25	1320	922	398
4	9.1	0.50	2000	1130	870
5	5.9	0.75	1570	800	770
6	8.0	1.16	2180	1100	1080
7	8.2	1.50	1710	1180	530
8	9.0*	2.08	2340	1240	1100
9	6.7	3.50	1820	990	830
10	6.5	5.0	1830	1010	820
11	8.2	8.0	2000	1500	500
12	7.3	12.50	2040	975	1065
13	7.2	24.00	2370	1170	1200
14	7.7	49.50	3030	1270	1760
15	8.8	77.0	3220	1390	1830

TABLE IX

Exchange with Etched, Non-equilibrated Electrodes

Exchange solution - $3 \times 10^{-4}N$ Superficial area of electrodes - 2.5 cm^2 Temperature = 25°C .

Electrode No.	times planar area	Exchange time hours	Total activity	Q	Exchange activity
				coulombs $\times 10^6$	
1	7.8	0.16	2110	697	1413
2	7.6	0.16	1880	756	1124
3	7.9	0.16	2130	614	1516
4	8.0	0.16	2190	766	1420
5	7.8	0.16	1980	792	1390
6	8.0	0.50	2530	980	1550
7	7.7	0.50	1820	676	1150
8	8.7	1.00	1740	803	940
9	8.2	2.50	2400	965	1435
10	6.8	5.00	2000	780	1510
11	7.4	7.5	2470	920	1550
12	7.2	24.00	3200	955	2250

very rapid initial gain of "exchange activity" for non-equilibrated surfaces, it must at the same time be assumed that, in the initial absence of a double layer on these surfaces, exchange with surface atoms is very rapid and indeed nearly complete during the time consumed in the formation of such a layer.

It may be noted that an overall discrepancy appears to exist between the Q values for the two series of experiments; the equilibrated surfaces, in general, exhibit larger Q values. The possibility of oxide film formation during transfer from one solution to another cannot be discredited. It is even within the realm of possibility that the nitrogen used for clearing the solutions contained traces of oxygen sufficient to form an oxide film. However, no evidence of this was detected in the experiments on adsorption of silver sulfate (Table VII) where nitrogen, purified in the same manner, was used.

Comparison of the Bowden-Rideal area measurements with the gain in activity (Tables VIII and IX) again indicates a general qualitative correspondence. Corrections based on these measurements, however, were not considered sufficiently reliable to warrant their inclusion here.

In view of the poor reproducibility of the electrode surfaces and the ever present risk of oxide formation during the transfer between solutions, it was felt that further progress in the direction of a kinetic study would be impossible under the experimental conditions. Attention was therefore directed to development of a procedure which would permit observation of the increase of activity on a single electrode continuously,

without exposure of the surface to the air at any time during the course of the exchange reaction.

Continuous Exchange

As indicated previously, it was hoped that this study might ultimately give some indication of the influence of crystal orientation on the kinetic behavior of the exchange reaction. It was therefore especially desirable to study the complete reaction with a single specimen of the metal, if possible without exposing the surface to air at any time during the course of the reaction.

The kinetics of reversible exchange seemed of particular interest here, rather than study of the irreversible accumulation of activity on the metal due to local cell action. The previous work had indicated that silver surfaces etched in nitric acid exchanged to a relatively low extent only. This was associated with limited local reaction on such a surface. This method of preparation of the silver foils was therefore selected for experiments involving continuous exchange.

The advantages of following the exchange reaction by determining the accumulation of radioactivity on the metal surface have been indicated previously. This procedure is particularly favorable when the exchange is limited to low values, as with etched specimens. To meet the requirement of undisturbed exchange by a procedure which would at the same time permit continuous determination of the accumulated activity on the metal surface,

the possibility of measuring the radiation through a thin film of the exchange solution was examined. This method gave promise of application here in view of the penetrating characteristic of the high energy gamma radiation emitted by the silver isotope used (35).

Preliminary investigations indicated that a film of water 1 mm. in thickness diminished the count obtained from a given specimen by about 60%. With appropriate adjustment of the ratio of active to inactive isotopes in the exchange solution, to obtain a relatively high count from an etched surface, this absorption of radiation was not considered excessive. Accordingly, a technique was devised in which the exchange solution flowed as a thin film over the silver surface.

Briefly, the apparatus consisted of a very shallow, circular exchange cell, bounded on one side by the silver foil on which exchange occurred, and on the other by a thin plastic "window". The space between was filled with the exchange solution which passed through the cell, from a circulating system, via capillary conduits attached to the cell in diametrically opposite positions. An end-window Geiger tube was placed in front of the plastic window of the cell to detect the radioactivity acquired by the silver. A detailed description of the various components and procedures follows.

1. The Exchange Cell Proper

A cross-sectional diagram of the cell is shown in Fig. 12 (lower section). It was made from a solid lucite rod 2 inches in diameter and 2 inches long. One end was machined flat with a 20/1000-inch depression,

Figure 12

The Exchange Apparatus

3/4 inch in diameter, in the centre. Capillary holes were drilled obliquely from the circumference into the lucite block to meet the depression as shown. They were enlarged at the outer end with a bottoming drill to accommodate glass capillary tubes (G,H), through which the exchange solution was circulated. These tubes were sealed in with a chloroform solution of lucite and a dam of "glytol" cement on the outside for strength.

The silver electrode, a disc of 2.5-cm^2 area and of the same stock as previously used, was roughened on one side and fixed firmly in the depression by slightly wetting the lucite with a drop of chloroform. When necessary, electrical contact with the electrode was made through a silver spring which in turn made contact with the brass rod running through the middle of the block.

A teflon sheet, 1.5/1000 inch in thickness, placed over the front face of the block, covered the depression and served as the "window" of the cell. It was held in place by a flat brass ring, tightened with six brass screws. The cell, together with its immediately associated stopcocks and flow tubes, was rigidly mounted as a unit in a lucite framework.

2. The Circulating System

In relation to the cell, this system is also shown in Fig. 12 (upper section). The entire system was of pyrex glass. Either ball and socket, or standard taper joints were used to join the component parts.

To preclude the possibility of contaminating films on the exchanging silver surface, no grease was used in either the joints or the stopcocks. The exchange solution was placed in the 200-ml. vessel, B, and pumped to the upper reservoir, C, by means of a "gas lift" (based on a design by Mason and Rochow (48)). Nitrogen, purified over hot copper, was used as the pumping gas. From C, the solution flowed by gravity through the tubes leading to the lower inlet of the exchange cell which was horizontally mounted. After passing through the cell, it was returned to B and again pumped up to C. The direction of flow is indicated by the arrows in the diagram. The solution in the flasks was continuously bubbled with purified nitrogen to sweep out dissolved oxygen and maintain an inert atmosphere.

In much of the experimental work it was desirable to "reverse" the reaction after a certain period of "forward" exchange with active solution. For this purpose, a parallel circulating system, similar to that already described, was connected at E and F (Fig. 12). This system contained inactive silver nitrate solution and, by simple manipulation of stopcocks S_1 and S_2 , the exchange reaction could be reversed at any time.

Previous work with etched electrodes had indicated that an oxide film appeared to remain on the surface after the etching. Provision was made to introduce sulfuric acid electrolyte into the cell so that the silver could be rendered cathodic, in situ, to reduce such a film. Electrical contact was made as described earlier. A compartment, A, containing a platinum anode, was attached to the system with a ball and socket joint

as indicated in Fig. 12. N/5 sulfuric acid, of the same purity as previously used for the area measurements, was admitted to the cell and to the anode compartment through the inlet, I, and stopcock S₃. The same electrical circuit as used earlier in overvoltage and area measurements was used to supply the electrolyzing current.

3. The Counting Equipment

A somewhat unique situation was presented by the fact that the active sample to be counted was rigidly fixed in position. For occasional reference to a counting standard it became necessary to provide for easy and accurate location of the Geiger tube relative to either the cell or the standard. A compact castle for the tube was therefore constructed and mounted on bearings which permitted easy lateral and rotational motion.

The ends of two concentric brass tubes, 8 inches long, were welded onto a brass plate with a centre hole the same size as that of the inner tube. This centre tube was just large enough so that the end-window Geiger tube fitted snugly into it, while the outer tube was $5\frac{1}{2}$ inches in diameter. The annular space between the two tubes was filled with lead. The front end of this "castle", constituted of the plate, was recessed to permit the Geiger tube flange base to be seated, on a rubber ring shock absorber, flush with the outer surface of the plate. The Geiger tube was held firmly in position by a flat brass ring screwed to the plate and extending over the recess and base flange of the tube.

Suitable insulated connectors were fitted at the back end of the castle for the high tension source and the ground lead.

This cylindrical castle was then mounted horizontally on an inverted "T" slide to permit lateral motion. The slide, in turn, rested on a heavy steel bearing plate and was centred on this plate by a stub shaft which ran a short distance into the bottom of the slide base. This provided for easy rotational motion. The whole assembly was fitted squarely in front of the window of the exchange cell described above. With suitable stops on the slide and on the bearing plate, the castle could be accurately and easily positioned with respect to either the cell or the counting standard which was fixed radially from the rotational axis of the castle, at 90° from the cell position.

The scale of 64 counter used was manufactured by Instrument Development Laboratories. It was a self-contained unit which included the high tension source for the Geiger tube and a pre-amplifier. The output of the scalar operated a register through a relay actuated by an interval timer.

The entire exchange apparatus, except the counter, was mounted in an insulated enclosure from which light was excluded except during experimental manipulations. The air in the enclosure was thermostated and circulation maintained by a fan. During manipulations, of course, the apparatus was exposed, and the surrounding air temperature altered somewhat, but the large difference in heat capacities of the apparatus

and the surrounding air prevented any significant temperature alterations of the exchange system. Moreover, the time of exposure during an experiment was usually only a few minutes and the air temperature in the enclosure was restored within a few minutes. It was concluded that temperature fluctuations of the apparatus ordinarily did not exceed 0.5°C .

4. Experimental Procedure

The silver disc was fitted into the cell in the manner described earlier, with the teflon window removed. After the lucite was set and dry the metal surface was scraped and etched by running 7N nitric acid over it. This was followed by a thorough water wash. A teflon sheet was drawn taut over the cell recess and lucite face, and the brass ring placed over it. The screws holding this ring were then forced through the taut sheet and the excess plastic cut away after the ring was well tightened. The teflon served as an efficient gasket between the brass ring and lucite face.

When the cell unit was connected into the other components of the apparatus, sulfuric acid electrolyte was run through the cell into the anode compartment. The silver electrode was then rendered cathodic for a few minutes using a current of about 10^{-4} amp. The acid was then thoroughly flushed out by flowing inactive silver nitrate solution through the cell and out of the anode compartment drain, S₅. The inactive solution was circulated for an additional two or three hours to equilibrate the surface before the exchange with the active solution was commenced.

In addition, this procedure permitted removal of any gas bubbles trapped in the cell, prior to the exchange. These could be easily seen through the transparent teflon window and could be expelled by slight pressure on the window. The use of the inactive solution was adopted in all but the first experiment.

In all instances, the concentration of the exchange solutions, both active and inactive, was $10^{-5}N$ in silver nitrate. The volume of solution used in each circulating system was 200 ml. The active solution contained radioactivity equivalent to about 0.04 millicurie. This gave a count, for the given counter geometry of the cell, of about 1000 counts per minute for each superficial atomic layer exchanged. The relatively low concentration selected rendered the initial rate of exchange measurable and precluded an excessively high count from the film of exchange solution in the cell, while still producing a relatively high count from the exchanged activity on the electrode. The rate of flow of the solution through the cell was about 2 ml. per minute, or about 2×10^{-8} g.atom of ionic silver per minute. This was considered sufficiently rapid that the rate of exchange would not be limited by transport of material to the cell. Since the exchange seldom exceeded an apparent depth of 4 atomic layers of the metal (2.4×10^{-8} g.atom) the ratio of active to inactive isotopes in the solution (containing a total of 2×10^{-6} g.atom of silver) remained essentially constant throughout an experiment. The extent of exchange was, therefore, directly proportional to the count (with a maximum error of only about 1%). Moreover, the count from the solution in the cell remained essentially unaltered.

Several hours before the experiment was to begin, the exchange solutions were placed into the circulating system to permit them to be thoroughly flushed with nitrogen before use.

To observe the variation of activity on the silver surface, the counter was operated continuously during the experiment. It was started by a switch on the interval timer, simultaneously with opening stopcock S_2 to admit the exchange solution to the cell. As the exchange progressed, the cumulative count recorded on the register was noted at one-minute intervals. This cumulative count was subsequently plotted against the time and a smooth curve drawn through the experimental points. A typical curve is illustrated in Fig. 13.

To ascertain the amount of activity present at any instant, in counts per minute, tangents were determined at various points on the cumulative count curve. To insure that the precision of this procedure was adequate, six different individuals were asked to make independent tangent determinations at one point on a typical curve. The values thus obtained showed a maximum deviation of 2.5% from the mean.

The activities determined in the above manner included, of course, the count obtained from the solution in the cell as well as the usual background count. To correct for these, a similar treatment was given the data obtained for a blank experiment, with the silver electrode replaced by a very thin glass slide of the same size as the silver disc. The counts per minute obtained in this way were subtracted from the values

Figure 13

Cumulative Count Curve

(Experiment 1)

obtained earlier. It is perhaps somewhat doubtful whether this procedure was entirely justifiable, in view of possible adsorption of activity by the glass slide (49). If significant adsorption occurred, the applied corrections would be too high. However, rough estimates of the count to be expected from the solution in the cell indicated that the values obtained were not too high and that an adsorption effect was probably negligible. Moreover, the total background count for the blank experiment reached a value which increased only very slowly after one minute.

It must be emphasized that each experimental point on the cumulative count curves was subject to errors due to statistical fluctuations in the rate of radioactive disintegration. Because of the dynamic nature of the exchange reaction and the method of determining the activity, this factor could not be adequately taken into account. However, the procedure of drawing a smooth curve through the points tended to reduce the error from this source and it was concluded that it probably never exceeded $\pm 5\%$.

The operating voltage of a Geiger tube tends to shift to higher values as the tube is used. This manifests itself as a decrease in sensitivity of the tube for a given voltage. The effect, however, is insignificant, provided the tube has not detected more than about 10^6 disintegrations. Since continuous counting, without reference to a standard, was necessary for periods of an hour or more, care was taken to insure that the tubes used were in good condition in this respect.

Experiment 1

For the first experiment, the circulating system for the inactive solution had not been installed and therefore a somewhat different procedure from that given above was adopted. After the silver electrode had been rendered cathodic, in the presence of the sulfuric acid electrolyte, the cell was thoroughly flushed with twice distilled and oxygen-free water. It was admitted through the inlet, F, where the inactive solution system was later connected.

Before the exchange experiment was commenced, a few ml. of the active solution was by-passed through stopcock, S₃, and outlet, I, to expel the solution in the conduits together with any trapped air. The exchange was then begun with the counter operated in the manner already described, to obtain the cumulative count curve. The first section of this curve is shown in Fig. 13.

The results of the activity determinations by the tangent method for this experiment are given in Table X. Included also are the results for the subsequent blank experiment and the resultant corrected values for the exchange on the electrode. These quantities are given in counts per minute. To illustrate the relative magnitudes of the count obtained from the solution in the cell and the background, and that from the electrode, the data are plotted in Fig. 14. Here the time scale is logarithmic to compress the data into one graph. The experiment was continued for several days and it is apparent that the silver

TABLE X

Continuous Exchange

(Experiment 1)

Superficial area of electrode = 2.5 cm^2 Active AgNO_3 conc. = 10^{-5}N Temperature = 25°C .

Time min.	x counts/min.	Blank counts/min.	x (corrected) counts/min.
0	320	320	0
1	1050	990	60
2	1310	1030	270
3	1600	1030	570
4	1830	1030	800
5	1980	1060	920
6	2110	1060	1050
7	2300	1060	1240
8	2430	1060	1370
9	2500	1060	1440
10	2620	1090	1530
11	2690	1090	1600
14	2940	1090	1850
17	3070	1090	1980
20	3200	1090	2110
25	3330	1120	2210
30	3420	1120	2300
35	3460	1150	2310
40	3580	1150	2430
50	3650	1150	2500
60	3740	1180	2560
70	3780	1180	2600
80	3900	1180	2720

Table X (cont'd.)

Time min.	x counts/min.	Blank counts/min.	x (corrected) counts/min.
90	3900	1180	2720
100	3970	1180	2790
135	4260	1200	3060
150	4260	1200	3060
185	4300	1220	3080
230	4400	1250	3150
255	4500	1250	3250
320	4600	1280	3320
440	4900	1340	3560
515	5100	1340	3760
615	5250	1380	3870
755	5440	1440	4000
960	5700	1480	4220
1225	5960	1550	4410
1395	6070	1600	4470
1695	6340	1660	4680
2025	6720	1730	4990
2715	7050	1850	5200
3135	7300	1920	5380
3505	7500	1970	5530
4590	7690	2100	5590
5625	8120	2300	5820
7505	8650	2500	6150

Exchange at 7505 min. $\equiv 4 \times 10^{-8}$ g.atom $\equiv 6.5$ apparent atomic
layers

Figure 14

Continuous Exchange

(Experiment 1)

continues to acquire activity almost indefinitely. The "blank count" is also seen to increase slowly over prolonged periods. This is presumably due to absorption of activity by the lucite of the cell, although it was largely removable by thorough rinsing with dilute nitric acid and water.

At the end of the experiment the silver disc was carefully removed and fixed to one of the electrode holders which were used in the earlier work (page 26). The activity on the electrode was then determined in the manner indicated on page 27 and, by comparison with a calibrated standard, the extent or depth of exchange was calculated (page 30).

It is apparent that a comparatively rapid exchange occurs initially and that this is followed by a slower process. It is tempting to explain the results on the basis of a rapid reversible exchange of atoms and ions, followed by a slow recrystallization on the surface, in which activity is incorporated into a new crystal structure. If the slower reaction is irreversible in the above sense, its influence should not be effective in a reverse exchange with inactive solution. That is, the removal of activity should be due only to reversible exchange. (This line of reasoning would not be applicable if, for example, the metallic silver were active throughout.) Subsequent experiments were, therefore, designed to study the reverse reaction as well.

Experiment 2

In accordance with the procedure given previously, and following

a two-hour period of equilibration of the electrode, the exchange reaction was extended over a period of three hours in the "forward direction", i.e. with active solution. The reaction was then reversed, using the inactive silver nitrate solution in the parallel circulation system. The variation of the activity on the electrode in the latter reaction was again determined by the method of tangents, from a cumulative count curve. This curve was similar to that for the forward reaction (as illustrated for experiment 1 in Fig. 13) except that it was convex to the "count axis" rather than the time axis. The activities were corrected for the total background, obtained as a blank experiment. Since the method for applying the corrections has already been indicated, only the final results will be given here.

It was a simple matter to repeat forward and reverse reaction cycles indefinitely on the same silver surface. In this experiment the surface was subjected to four such exchange cycles - two at a temperature of 31°C ., one at 19.5°C . and another at 40°C . In each cycle the exchange with the active solution was restricted to three hours. No definite time limit was, however, set for the subsequent reaction with the inactive solution but in every case it was continued for at least three hours to insure that all exchangeable activity participated in the reaction.

Between the cycles, the exchange solutions were renewed to avoid excessive alteration of the ratio of active to inactive isotopic ions. In each instance the solutions were thoroughly flushed with nitrogen before use. When the solution flow was switched from one

circulating system to the other a small volume (about 0.5 ml.) from the exchange cell and tubing was transferred to the next solution. This produced some alteration in the relative amounts of isotopes in the solutions but this effect was quite insignificant for one cycle, since the total volume in each system was comparatively large (200 ml.).

The results for this experiment are given in Table XI to XIV inclusive. The various exchange cycles for the electrode are designated "Experiment 2-a, 2-b, etc.", and each table includes the results for both the forward and reverse reactions for the particular cycle. The activity, x , acquired by the metal in each particular reaction is given in counts per minute. The extent or depth of exchange ($x_{180} - x_0$) during the three hours for the forward reaction and that for the reverse process ($x_0 - x_\infty$) are also given in terms of apparent atomic layers (page 32) and designated by Δx .

It was evident from these data that the reverse reaction reached an equilibrium relatively rapidly, since the activity on the electrode decreased to a constant value well before the end of three hours. Similarly, the forward reaction proceeded only very slowly after several hours. This was interpreted to indicate that a reversible exchange, which was of particular interest here, was rapid and essentially complete in the three hours allotted for the forward reaction, under the given conditions. It may be noted that in all these experiments the activity acquired by the metal was never entirely removable by exchange with the inactive solution. From 10 to 20% had entered "deep seated" or non-

exchangeable positions on the surface.

The applicability of the first order rate law to the experimental data is illustrated in Figures 15 to 18. The results were plotted according to the equation,

$$-2.3 \log Q = kt \text{ - - - - - (9)}$$

where $Q = \frac{x_{180} - x}{x_{180}}$ for the forward reaction

and $Q = \frac{x - x_{\infty}}{x_0 - x_{\infty}}$ for the reverse reaction

Here x_{180} is the value of the activity, x , acquired by the metal during the three hours exchange in the forward direction, and x_0 and x_{∞} are the initial and final activities respectively for the reverse reaction.

Perhaps the most significant feature to which attention should be directed is the definitely segmented appearance of the graphs. A simple explanation for this behavior is that the rate of exchange is constant for a relatively large proportion (about 60% for the initial reaction) of the exchangeable atoms on the surface. It is well known from theoretical considerations (28) that the energy required to remove an atom from different crystal faces may vary markedly depending on the crystal face involved. In particular, these energies have been calculated for silver crystals and marked differences in the chemical reactivities of the various faces of single crystals have been observed (50,51). Consideration of the silver surfaces studied here (rolled foils) suggests that a large number of tiny crystallites with random orientations would be exposed at the surface (52). It may then be expected that the exchangeable

TABLE XI

Experiment 2-a

Temperature = 31°C.

AgNO₃ conc. = 10⁻⁵N

Forward Reaction			Reverse Reaction		
Time min.	x counts/min.	-log Q	Time min.	x counts/min.	-log Q
0	0	0.0	0	1840	0.0
1	77	0.018	1	1770	0.040
2	260	0.066	2	1520	0.099
3	570	0.161	3	1420	0.133
4	650	0.182	4	1270	0.194
5	860	0.251	5	1160	0.242
6	950	0.322	6	1040	0.304
7	980	0.331	7	935	0.370
8	1100	0.398	8	880	0.404
9	1190	0.456	9	820	0.446
10	1250	0.500	10	760	0.499
12	1370	0.602	12	700	0.560
15	1470	0.708	15	580	0.692
17	1520	0.777	17	530	0.767
20	1590	0.876	20	500	0.824
25	1690	1.125	25	435	0.960
30	1740		30	400	1.02
45	1790		45	370	1.16
55	1840		55	290	1.74
70	1860		80	270	
90	1860		95	260	
180	1840		155	260	
			180	260	

 $\Delta x = 1.95$ atomic layers $\Delta x = 1.66$ atomic layers

Figure 15

Applicability of First Order Rate Law

(Experiment 2-a)

TABLE XII

Experiment 2-b

Temperature = 31°C.

AgNO₃ conc. = 10⁻⁵N

Forward Reaction			Reverse Reaction		
Time min.	x counts/min.	-log Q	Time min.	x counts/min.	-log Q
0	0	0	0	1980	0
1	300	0.072	1	1750	0.067
2	460	0.116	2	1560	0.132
3	650	0.174	3	1400	0.222
4	770	0.215	4	1280	0.257
5	900	0.264	5	1180	0.324
6	1020	0.312	6	1100	0.347
7	1110	0.355	7	1010	0.402
8	1180	0.395	8	940	0.452
9	1250	0.431	9	870	0.509
10	1300	0.462	10	800	0.568
12	1390	0.523	12	720	0.662
15	1480	0.594	15	630	0.788
17	1460	0.579	20	570	0.910
20	1500	0.667	30	520	1.04
25	1630	0.742	40	450	1.32
30	1700	0.839	50	410	1.62
35	1740	0.910	70	380	2.40
40	1770	0.970	100	370	
50	1820	1.076	180	370	
60	1850	1.15			
80	1880	1.29			
100	1900	1.38			
120	1920	1.49			
140	1940	1.59			
160	1960	1.89			
180	1980				
$\Delta x \approx 2.1$ atomic layers			$\Delta x \approx 1.7$ atomic layers		

Figure 16

Applicability of First Order Rate Law
(Experiment 2-b)

TABLE XIII

Experiment 2-c

Temperature = 19.5°C.

AgNO₃ conc. = 10⁻⁵N

Forward Reaction			Reverse Reaction		
Time min.	x counts/min.	-log Q	Time min.	x counts/min.	-log Q
0	0	0	0	1680	0
1	170	0.046	1	1280	0.134
2	310	0.089	2	1110	0.204
3	450	0.138	3	970	0.276
4	570	0.181	4	870	0.336
5	670	0.220	5	790	0.388
6	750	0.257	6	730	0.436
7	830	0.298	7	670	0.490
8	900	0.332	8	610	0.538
9	970	0.377	9	580	0.577
10	1030	0.415	10	540	0.622
11	1090	0.455	11	520	0.646
12	1130	0.490	12	490	0.688
14	1200	0.550	14	450	0.736
16	1250	0.592	16	430	0.767
18	1280	0.627	20	400	0.839
20	1300	0.654	25	360	0.921
25	1410	0.796	30	310	1.07
30	1400	0.785	40	250	1.33
40	1460	0.886	50	210	1.67
60	1460	0.886	70	180	
80	1470	0.940	100	180	
120	1550	1.10	180	180	
150	1610	1.38			
180	1680				
$\Delta x \equiv 1.78$ atomic layers			$\Delta x \equiv 1.58$ atomic layers		

Figure 17

Applicability of First Order Rate Law

(Experiment 2-c)

TABLE XIV

Experiment 2-d

Temperature = 40°C.

 AgNO_3 conc. = 10^{-5}N

Forward Reaction			Reverse Reaction		
Time min.	x counts/min.	-log Q	Time min.	x counts/min.	-log Q
0	0	0	0	1650	0
1	160	0.045	1	1610	0.013
2	270	0.079	2	1390	0.096
3	400	0.120	3	1250	0.151
4	520	0.167	4	1150	0.203
5	640	0.206	5	1070	0.241
6	740	0.260	6	1010	0.282
7	830	0.326	7	930	0.326
8	910	0.350	8	880	0.363
9	980	0.391	9	830	0.402
10	1030	0.426	10	780	0.446
12	1110	0.482	11	750	0.475
15	1180	0.548	12	710	0.512
18	1230	0.595	14	640	0.594
20	1250	0.620	16	590	0.664
25	1370	0.767	18	560	0.704
30	1430	0.880	20	560	0.704
35	1480	0.980	25	470	0.880
40	1510	1.07	30	410	1.028
50	1570	1.30	35	400	1.07
60	1590	1.41	40	380	1.21
70	1610	1.57	50	350	1.42
90	1630	1.82	70	330	1.62
120	1650		100	310	1.85
150	1650		130	290	
180	1650		150	290	
			180	290	
$\Delta x = 1.74$ atomic layers			$\Delta x = 1.44$ atomic layers		

Figure 18

Applicability of First Order Rate Law

(Experiment 2-d)

atoms on those crystal facets with similar indices exchange at the same rate and the different types of crystal faces exposed result in the several exchange rates observed.

Superimposed on the exchange with surface atoms on crystal faces is the incorporation into the lattice of non-exchangeable activity during the forward reaction. Since different crystal faces exhibit dissimilar chemical reactivities, electrochemical potentials must exist among the several faces. Such potentials have been observed on single crystals of zinc, for example (53). These potential differences are expected to result in local cell action in which the faces of greatest binding energy behave as local cathodes. This is evidently manifested in the deep seated exchange observed in the forward reaction. In the reverse exchange, when the ions in solution are essentially all inactive, deposition on cathodic regions will have negligible effect on the observed change in activity, while solution from anodic regions (faces of lower binding energy) can only result in a decrease of surface activity of somewhat greater rate than that corresponding to reversible exchange. It is significant, therefore, that several rates are observed for the reverse reaction as well as for the forward exchange.

It is interesting that the graphs show considerable variation in shape between cycles. However, this is perhaps not surprising in view of surface structural change which must occur as a result of slow recrystallization, as indicated by the deep seated exchange observed. Any influence of the temperature on the rate of reaction was doubtless

obscured by this effect.

An exception to straight-line sections in the plotted data is seen in Fig. 17 for experiment 2-c. However, since the silver specimen was the same as for the other experiments, this must be attributed to some extraneous factor, such as the formation of a gas bubble in the cell during exchange.

Experiment 3

A third experiment was made on another silver specimen, using a series of cycles similar to that described for experiment 2. The reactions appeared to be somewhat erratic - more so than could be adequately accounted for by statistical fluctuations in the rate of counting. For this reason it was felt that the tangent method for determining the activities would not be suitable. Instead, for the most part, the counts per minute during a given time interval were taken directly from the cumulative count data. The time intervals during which the count was taken are indicated in Tables XV to XVIII. Suitable corrections for background count were made as described previously. The results for each cycle, which are represented graphically in Figures 19 to 22, exhibit a behavior similar to that observed for experiment 2, i.e. several rates of exchange are manifested. The segmented character of the graphs, however, is not so pronounced as observed previously.

From earlier work it was realized that some of the activity observed on the metal was probably present as an adsorbed ionic double

TABLE XV

Experiment 3-a

Temperature = 25°C.

AgNO₃ conc. = 10⁻⁵N

Forward Reaction			Reverse Reaction		
Time min.	x counts/min.	-log Q	Time min.	x counts/min.	-log Q
0	0	0	0	5840	0
1	330	0.027	2.5-3	4660	0.127
2	740	0.058	3-4	4550	0.143
3	1070	0.088	4-5	4300	0.178
4	1340	0.113	5-6	4040	0.225
5	1590	0.139	6-7	3840	0.246
6	1820	0.162	7-8	3680	0.274
7	2000	0.182	8-9	3620	0.284
8	2220	0.208	9-10	3500	0.308
10	2450	0.237	10-11	3300	0.345
11	2700	0.268	11-12	3180	0.372
14	3020	0.317	12-13	3000	0.382
15	3200	0.346	14-15	2940	0.430
16	3360	0.374	15-16	2800	0.464
17	3420	0.384	16-17	2680	0.497
18	3600	0.414	17-18	2680	0.497
20	3750	0.446	18-19	2680	0.497
22	3860	0.472	19-20	2400	0.590
24	3960	0.523	20-21	2540	0.547
26	4200	0.555	21-22	2440	0.578
30	4500	0.638	24-25	2340	0.614
35	4600	0.678	26-27	2200	0.678
40	4780	0.745	29-30	2100	0.724
50	5180	0.951	30-32	2000	0.782
55	5250	0.991	32-34	1940	0.810
59	5300	1.032	35-38	1850	0.866
75	5400	1.15	38-40	1750	0.939
80	5450	1.18	40-42	1820	0.886
100	5550	1.32	42-45	1700	0.987
115	5740	1.77	45-47	1700	0.987
125	5700	1.66	47-50	1630	1.05
151	5800	2.16	55-60	1580	1.11
175	5840		95-105	1410	1.38
			1080	1220	
$\Delta x \approx 6.17$ atomic layers			$\Delta x \approx 5.05$ atomic layers		

Figure 19

Applicability of First Order Rate Law
(Experiment 3-a)

TABLE XVI

Experiment 3-b

Temperature = 25°C.

AgNO₃ conc. = 10⁻⁵N

Forward Reaction			Reverse Reaction*		
Time min.	x counts/min.	-log Q	Time min.	x counts/min.	-log Q
0	1220	0	0	5260	0
0-1	1250	0.002	1	4760	0.058
2-3	1900	0.071	2.5	4420	0.105
3-4	2000	0.094	4	4220	0.133
4-5	2220	0.123	5	4100	0.153
5-6	2250	0.128	6	3960	0.177
6-7	2460	0.160	7	3800	0.201
7-8	2520	0.168	8	3650	0.231
8-9	2770	0.212	9	3610	0.237
9-10	2900	0.232	10	3550	0.250
10-11	2950	0.243	11	3300	0.301
11-12	3080	0.266	12	3100	0.348
12-13	3260	0.306	13	3000	0.372
13-14	3330	0.319	14	2980	0.380
14-15	3450	0.349	15	2940	0.389
15-16	3580	0.380	17	2860	0.414
16-17	3640	0.395	20	2700	0.465
18-19	3900	0.468	21.5	2510	0.526
20-21	3900	0.509	23	2400	0.569
21-22	4040	0.519	28	2240	0.640
23-24	4070	0.530	30.5	2160	0.670
25-26	4200	0.577	35	1960	0.799
26-27	4060	0.526	44.5	1860	0.883
27-28	4200	0.577	47.5	1750	0.979
28-29	4320	0.633	55	1700	1.04
29-30	4280	0.614	80	1550	1.28
30-31	4400	0.676	90	1530	1.33
32-33	4450	0.692	100	1480	1.47
35-37	4440	0.690	120	1460	1.54
37-38	4500	0.722	150	1430	1.68
38-40	4610	0.724	175	1440	1.62
180	5260		1080	1350	
$\Delta x = 4.43$ atomic layers			$\Delta x = 4.15$ atomic layers		

* Following one hour water circulation

Figure 20

Applicability of First Order Rate Law

(Experiment 3-b)

TABLE XVI I

Experiment 3-c

Temperature = 25°C.

AgNO₂ conc. = 10⁻⁵N

Forward Reaction			Reverse Reaction*		
Time min.	x counts/min.	-log Q	Time min.	x counts/min.	-log Q
0	1350	0	0	5700	0
0-1	1350	0	0-1	5500	0.03
1-2	1740	0.040	1-2	5380	0.049
2-3	2030	0.073	2-3	5060	0.104
3-4	2380	0.114	3-4	4930	0.128
4-5	2560	0.138	4-5	4800	0.154
5-6	2880	0.176	5-6	4680	0.181
6-7	3000	0.201	6-7	4600	0.196
7-8	3120	0.214	7-8	4600	0.196
8-9	3180	0.230	8-9	4480	0.225
9-10	3420	0.273	9-10	4350	0.258
10-11	3410	0.272	10-11	4280	0.274
11-12	3740	0.333	11-12	4160	0.310
12-13	3670	0.320	12-13	4350	0.258
13-14	3860	0.361	13-14	4100	0.330
14-15	3980	0.390	16-17	3970	0.370
15-16	4180	0.437	17-18	3910	0.394
18-19	4220	0.462	19-20	3970	0.372
19-20	4300	0.469	20-21	3910	0.394
21-22	4550	0.550	22-23	3780	0.442
23-24	4730	0.620	23-24	3740	0.455
29-31	4900	0.699	29-31	3520	0.558
34-36	5100	0.802	34-35	3520	0.558
39-41	5230	0.886	40-42	3560	0.592
44-46	5380	1.023	40-46	3400	0.631
49-51	5470	1.137	55-60	3300	0.690
58-60	5460	1.125	79-81	3140	0.827
79-81	5580	1.31	85-95	3150	0.816
95-100	5670	1.57	150-160	2970	1.03
120-130	5740	1.85	178-184	2900	1.17
150-160	5780	1.89	300	2850	1.28
170-176	5800		1200	2690	
$\Delta x \approx 4.73$ atomic layers			$\Delta x \approx 3.2$ atomic layers		

* Following cathodic treatment of electrode

Figure 21

Applicability of First Order Rate Law

(Experiment 3-c)

TABLE XVIII

Experiment 3-d

Temperature = 25°C.

 AgNO_3 conc. = 10^{-5}N

Forward Reaction			Reverse Reaction		
Time min.	x counts/min.	-log Q	Time min.	x counts/min.	-log Q
0	2690	0	0	6350	0
1.5-2	3470	0.096	0-1	6150	0.026
2-3	3640	0.130	1-2	5640	0.095
3-4	3700	0.140	2-3	5340	0.146
4-5	3880	0.172	3-4	5200	0.165
5-6	4140	0.218	4-5	5200	0.165
6-7	4200	0.230	5-6	4960	0.211
7-8	4250	0.242	6-7	4840	0.235
8-9	4440	0.281	7-8	4780	0.247
9-10	4400	0.273	8-9	4530	0.302
10-11	4460	0.286	9-10	4530	0.302
11-12	4650	0.329	10-11	4680	0.272
12-13	4770	0.364	11-12	4350	0.350
13-14	5000	0.429	12-13	4360	0.346
14-15	4920	0.408	13-14	4160	0.402
15-16	4920	0.408	14-15	4170	0.400
16-17	4980	0.426	15-16	4110	0.420
18-19	5170	0.488	16-17	4180	0.398
19-20	5100	0.466	17-18	4060	0.438
21-22	5160	0.486	18-19	3990	0.461
22-23	5300	0.535	19-20	4000	0.458
25-26	5220	0.507	24-26	3840	0.514
26-27	5340	0.556	29-31	3780	0.541
27-28	5400	0.585	34-36	3600	0.625
28-29	5720	0.762	39-41	3500	0.674
29-30	5600	0.682	44-45	3450	0.708
39-41	5650	0.717	55-60	3350	0.770
49-51	5800	0.824	75-85	3230	0.860
54-56	5860	0.872	95-105	3220	0.872
75-85	6010	1.032	300	3020	1.10
120-130	6220	1.42	1380	2870	1.43
175-185	6350		2880	2750	2.40
			3600	2730	
$\Delta x \approx 3.9$ atomic layers			$\Delta x \approx 3.8$ atomic layers		

Figure 22

Applicability of First Order Rate Law

(Experiment 3-d)

layer. It therefore seemed of interest to determine the extent to which such adsorbed material might influence the observed behavior. It was felt that the adsorbed activity should be removable by a prolonged water wash. This was done in experiment 3-b, following the forward reaction. Twice distilled and oxygen-free water was used for this purpose. It entered the system at I, and was drained through stopcock S₅ (Fig. 12). The washing was continued for one hour but, rather surprisingly, no significant loss of activity was observed. If adsorbed activity was present, it was not removed by this procedure. This would be in accord with the observations made earlier, that it was very difficult to remove such activity by a simple water wash.

In experiment 3-c the reaction was again allowed to proceed in the forward direction for three hours. Sulfuric acid electrolyte (N/5) was then run into the cell and the electrode rendered cathodic for a few minutes (at a current of about 10^{-4} amp.) to deposit any adsorbed silver ions. In the subsequent exchange with inactive solution, 31% of the activity acquired in the forward reaction remained on the metal even after 20 hours. In contrast only 7% was not removable in the previous exchange cycle. This would seem to indicate that about 20% of the observed exchange is concerned with an adsorbed layer of ions.

Equally interesting is the kinetic behavior of the exchange following the cathodic treatment. A plot with a definite curvature is obtained from the data for the reverse reaction (Fig. 21), which indicates clearly a surface structure of a completely heterogeneous

character. This suggests that the deposition of ions occurred in random, "out-of-lattice" positions. Although a curved plot is obtained for a still further exchange cycle (Fig. 22), recrystallization of the deposited activity appeared to take place. This seems apparent from the very slow removal of activity when the exchange with inactive solution was continued for several days (Table XVIII).

It is of interest also to compare the overall results of experiments 2 and 3. These are summarized in Table XIX for convenience. In this table the forward and reverse reactions are designated by F and R respectively. Approximate values of the initial rates of exchange were obtained from the slopes of the linear sections of the graphs. These slopes, multiplied by 2.3, are given in the Table for comparison. Included also are the values of total extent of exchange (Δx) for each reaction of the various cycles, in terms of the apparent atomic layers involved. "Deep seated" exchange is given in per-cent of the activity acquired in the forward reaction, which was not removed in the reverse exchange.

A pronounced difference in the apparent depth of exchange is observed between the two silver specimens studied, even though they were both obtained from the same stock and both prepared by etching with nitric acid. It may be remarked that the specimen used in experiment 3 had a dull, more heterogeneous appearance than did the other silver electrode, after etching. This suggests a greater true surface area for the former sample and this is apparently borne out by the more

TABLE XIX
Summary of Results for Experiments 2 and 3

Exchange Cycle	Reaction	Temp. °C.	Initial Rate min ⁻¹	$\Delta x(\text{max.})$ atomic layers	Deep seated Exchange
2-a	F	31	0.11	1.95	15%
	R	31	0.11	1.66	
2-b	F	31	0.11	2.1	19%
	R	31	0.13	1.7	
2-c	F	19.5	0.10	1.78	11%
	R	19.5	?	1.58	
2-d	F	40	0.11	1.74	17%
	R	40	0.10	1.44	
3-a	F	25	0.09	6.17	18%
	R	25	0.06	5.05	
3-b	F	25	0.055	4.43	7%
	R	25	0.055	4.15	
3-c	F	25	0.071	4.73	cathodic treatment 31%
	R	25	?	3.2	
3-d	F	25	?	3.9	2%
	R	25	?	3.8	

extensive exchange observed.

The initial rates of exchange, although they can only be regarded as approximate, also differ by a factor of as much as 2 for the two experiments. It is difficult to explain this except on the basis of entirely different crystal orientations exposed at the surfaces of the two specimens. It is very unlikely that the rate was at any time governed by the rate of flow of exchange solution through the cell. This should have resulted in a curved plot of the data, convex to the time axis, but this has not been observed.

If the reaction obeyed a first order rate law, the rate constant should be,

$$k = R \frac{a + b}{ab}$$

as indicated in the introduction (page 4). If the amount of exchangeable material in solution (b) is much greater than that on the metal (a), the expression reduces approximately to $k = R/a$, whence the rate, R, at which atoms and ions (both active and inactive) exchange is given by $R = ka$. Using the initial rates in Table XIX for $\underline{k}$ and Δx for $\underline{a}$, a rough estimate of R may be obtained. A value of about 0.2 apparent atomic layers per minute is obtained for experiment 2 and 0.2 to 0.4 for experiment 3.

DISCUSSION

While it is recognized that factors within the solid or solution phase may exercise considerable influence on heterogeneous exchange reactions, the present investigation has been largely concerned with the influence of surface structure on the exchange between silver and its ions in solution. In view of the somewhat varied nature of the experiments which have been made it seems advisable to summarize briefly the results obtained before discussing their significance.

A. Preliminary work indicated that the exchange with emery-surfaced foils extended through hundreds of apparent atomic layers of the metal during periods of several days. Slow accumulation of activity appeared to continue almost indefinitely. Bowden-Rideal area measurements made in conjunction with these experiments showed that such specimens might exhibit a true surface as much as 50 times the planar value. The activity acquired by the abraded surfaces was only partly removable in inactive silver nitrate solution, which indicated deep-seated exchange due to irreversible processes on the surface.

B. An overall qualitative correspondence appeared between the Bowden-Rideal area measurements and the extent of exchange during a given period of time for similarly prepared surfaces. However, comparison

of the exchange with the area measurements showed no agreement among abraded and etched specimens. The latter always exhibited relatively little exchange, much less than might be expected on the basis of the area measurements, assuming all surface atoms to enter into the exchange reaction.

C. The exchange was found to be reduced for abraded surfaces when these were "equilibrated" in an inactive silver nitrate solution for several days preliminary to the exchange reaction. No obvious reduction in exchange was observed with etched specimens.

D. Some of the radioactivity observed on the exchanged surfaces was found to be present in adsorbed ionic form which was difficult to remove by a simple water wash. It was possible to measure the magnitude of such activity by an electrometric method. This adsorbed material appeared to affect the kinetics of exchange with etched foils but the results were not conclusive.

E. Continuous observation of the exchange with etched specimens indicated again an indefinite slow increase of activity on the metal. Exchange in the forward and reverse directions clearly showed several rate processes for a single specimen and the kinetics was found to vary between cycles of forward and reverse exchange with any one surface. Non-exchangeable activity was acquired by the silver in exchange with active solution as shown by the fact that the activity was not entirely removable in the reverse reaction.

Perhaps one of the more remarkable of these results was the indefinite accumulation of activity on the metal over prolonged periods of time. The possibility immediately arises that this is due to diffusion of atoms from the surface into the interior of the metal. It has been tacitly assumed by most workers, and throughout the presentation of results here, that this effect is negligible. This is perhaps obvious from the low values of the coefficient of self-diffusion generally exhibited by solid metals (58). In particular, the coefficient, D , for silver has been found (54) to be given by

$$D = 0.895 e^{-45900/RT} \text{ cm}^2/\text{sec.}$$

in the temperature range, 725 to 950°C. Assuming that the equation is valid to ordinary temperatures, D is approximately $8.6 \times 10^{-30} \text{ cm}^2/\text{day}$. By use of Fick's diffusion equation,

$$\frac{dc}{dt} = -D \frac{dc}{dx}$$

a rough estimate may be made of the rate of transfer, dc/dt , of active silver atoms across an atomic layer one cm^2 in area and about $3 \times 10^{-8} \text{ cm}$. in thickness, separating a cube of active isotopes from one of inactive isotopes. The concentration of atoms in each cube is $5.9 \times 10^{22} \text{ atoms/cm}^3$ and the concentration gradient, dc/dx , of active isotopes across the separating layer about $2.0 \times 10^{30} \text{ atoms/cm}^2$. Substituting this value and that for D above into the equation, the rate of transfer, dc/dt , is equal to about 20 atoms per day through one atomic layer 1 cm^2 in area. This is indeed a very small rate of transfer, and it is there-

fore apparent that the extensive exchange frequently observed must be due to some other irreversible local processes on the surface.

In assessing the significance of the profound difference in exchange with abraded and etched silver specimens (Table III), reference may be made to the results obtained for the exchange with insoluble salts by Paneth (27) and others (23). It will be recalled that fresh precipitates of the salts recrystallized rapidly and this resulted in complete distribution of the isotopes throughout the solid. With aged precipitates the "radioactive area measurements" agreed well with the values obtained by dye adsorption or microscopic methods. Serious discrepancies appeared, however, when well formed natural crystals were studied. The "exchange area" was then vastly inferior to other area measurements. These results bear a striking resemblance to those obtained here with freshly abraded, aged and etched silver foils, when the exchange is compared with the Bowden-Rideal area measurements (Table III).

Paneth (27) and Zimens (7) have explained the exchange behavior of insoluble salts on the basis of the elements of crystal growth theory laid down by Volmer (55) and by Kossel and Stranski (28). Although these theories apply explicitly to crystal growth from the vapor, they can probably be applied in principle to growth from solution and it seems profitable to make use of the concepts to gain an understanding of the exchange processes with metals. To do so it will be necessary to review the principles of the theories, particularly some recent contributions treating with equilibrium crystal forms which are of special interest here.

For a crystal surface in equilibrium with its vapor, there are in the order of 10^{15} atoms per cm^2 of surface, with about 10^9 adsorbed atoms and as many vacant lattice sites in the surface. In addition, there will usually be some steps on every surface, the height of each step being of atomic dimensions (incompleted atomic layers). The energy of removal of the atoms from the various surface positions may be calculated from the interaction energy between atoms. Although the theories are not sufficiently advanced for exact evaluation of these energies for a crystal in solution, the relative values will be about 1.68:0.87:0.006 for an atom in a flat surface, at a corner position in a step "kink" and an adsorbed atom respectively (28). For a crystal to grow, dissolve or exchange with ions in solution or with atoms in the vapor, some kind of steps must exist at some time in the surface. Any of the surface reactions may progress readily if discontinuities are present when the crystal is in equilibrium with its vapor or with its ions in solution. However, if there are no steps or "kinks" at equilibrium, then these must be created and a large hindrance to reaction appears.

Burton and Cabrera (56) have made an investigation of the concentration of steps or "Frenkel terraces" on a surface in equilibrium. Crystal faces are divided into two classes, close-packed and stepped. A close-packed surface is defined as one in which all the surface atoms are at the same distance from a plane parallel to the surface. In all other cases the surface will present a stepped appearance. By way of illustration, in the simple cubic system, (100) and (110) surfaces are

close-packed, all others are stepped. In a stepped surface, the terraces are pieces of close-packed surface. For a $(1n0)$ surface of a simple cubic crystal the terraces will be (100) surfaces. Similarly, Stranski (57) has shown that the corners of a crystal are "rounded off" through the presence of a finite number of faces of higher index and so are not truly rounded. Calculations show (56) that the concentration of lattice vacancies or kinks in a close-packed surface at equilibrium is negligible, while the concentration of kinks in a step in equilibrium is high. It is therefore apparent that any reactions on the surface, including exchange, are most likely to occur at the steps of incompleated atomic layers and that positions between steps play almost no part in any surface reactions.

It should be emphasized that a flat crystal surface in contact with its vapor or with a solution will have on it a number of atoms in out-of-lattice positions. Although their number may be relatively small they are probably highly mobile on the surface. This will be particularly so in solution, as a consequence of impacts from solvent molecules. This concept of mobile atoms has been amply substantiated by many investigations (58), one of the most remarkable of which is Volmer's observation on mercury (59). In condensation of mercury from the vapor phase at low temperatures, mercury needles were observed to grow at a rate one thousand times more rapidly than could be accounted for by gaseous collisions at the point of growth. He also observed crystal growth beyond the solution level on a partially immersed crystal (60). Because of

the mobility of the out-of-lattice atoms, frequent collisions with step positions will occur and they will therefore play a prominent role in any reactions which take place at the step positions. They may, thus, be regarded as another "2-dimensional gas phase" as it were, in equilibrium with the atoms at the edges of incompleated atomic layers. In this way the terraces or flat regions of low index crystal faces act as a "collecting ground" for mobile atoms.

An exchange reaction between ions in solution and the atoms of a metal may now be viewed as occurring most easily with a relatively few out-of-lattice atoms on the flat surfaces of crystal faces. These in turn, because of their mobility, interchange positions rapidly with atoms at the steps, as Zimens (7) has suggested for the exchange with insoluble salts. The interchange of atoms on the terraces with those at step positions will be facilitated by the existence of "kinks" in the steps, while the atoms within a close-packed surface will not exchange at all or only very slowly because of their high binding energy. Thus, exchange with ions may be expected to occur almost exclusively at the edges of incompleated atomic layers, either directly or via the few out-of-lattice atoms on the flat surfaces between steps. The more nearly perfect a crystal is, the less easily will it exchange with ions in solution.

It is now easy to understand the different results obtained for the exchange experiments with abraded and etched silver foils. Mechanical abrasion may be expected to cleave the silver crystallites

on the surface in a variety of directions, exposing a virtually infinite number of crystal faces with completely random orientations (of both low and high indices). Aside from increasing the overall exposed area, this is precisely the condition which should lead to the extensive exchange observed, by way of the steps on faces of high indices and at crystallite edges and corners.

On the other hand, with etched silver foils, the process of solution of the metal in nitric acid would doubtless, according to the theoretical considerations, occur largely at the edges of incomplete atomic layers, as a reverse process of growth. The steps, largely responsible for exchange, will therefore tend to disappear, leaving the crystallites on the surface surrounded by a relative preponderance of planes of low index. This idea might be restated in terms of a tendency toward a minimum surface free energy. The resulting planes of low index exchange only very slowly if at all. This, then, accounts for the comparatively small exchange observed with these specimens (Table III).

The processes involving the accumulation of deep-seated or non-exchangeable activity by the silver foils have already been considered from a thermodynamic viewpoint. Crystal faces of different reactivity were treated as local anodes and cathodes which result in recrystallization phenomena on the surface. This is manifested in the "burial" of activity. According to the theories of growth, this process must involve the "anodic" dissolution of incompleated atomic layers on those faces consisting of terraces of lowest binding energy (Burton-Cabrera model)

and growth of the terraces of highest binding energy (cathodic regions). As the process continues, the steps on the surfaces will tend to disappear, hence the number of exchangeable atoms (at step positions) decrease. This adequately accounts for the reduced exchange observed with aged specimens of abraded silver foils.

According to the Kossel-Stranski theory (28), the difference in reactivity of different crystal faces may be attributed to differential bonding along the few principal directions within the crystal lattice. On the basis of nearest neighbor interatomic energies, Fricke (61) has made calculations of the work of formation of a crystal surface per atom, for various crystal faces of different metals. As an example, for silver the values are $193\frac{1}{4}$ and $168\frac{3}{4}$ erg/cm.² per atom for the (001) and (111) crystal faces respectively.

The literature contains a vast amount of experimental evidence to substantiate the concepts of directional binding in crystals. The most striking demonstration is perhaps that of etch patterns on spherical single crystals of metals (50,62). The machined spherical form of the crystal exposes all possible crystal faces at the surface. Chemical etching then reveals a characteristic pattern which depends on the reactivities of the various faces exposed. (Etch pits on polycrystalline specimens may, in fact, be used to determine crystal orientation (63).) The oxidation of a silver single crystal was observed by Gwathmey (50) to occur preferentially on the (111) face as would be expected from Fricke's calculations. Erdy-Gruz (51) observed that preferential deposition

of silver in layers on specific faces of spherical single crystals of silver always occurred, but not necessarily on those faces which would be expected to grow, namely those of highest binding energy ($\{100\}$ faces). The deviations were explained on the basis of preferential adsorption of molecules and ions present in the solutions.

In the field of catalysis, theoretical calculations have shown that the activation energy for adsorption of hydrogen should be a minimum for the (110) plane of nickel (64). In agreement, it has been found experimentally that the rate of catalytic reaction between hydrogen and ethylene on nickel films is greatest when the (110) plane of nickel is parallel to the surface (65). The exchange of carbon monoxide, adsorbed on an iron catalyst, with gaseous CO was observed by Eischens (66) using radioactive carbon as tracer. It was found that when the data were plotted according to the first order rate law, a segmented plot was obtained showing different rates of reaction for various fractions of the CO adsorbed on the catalyst. This was explained on the basis of differential bonding on the surface.

The several rates of exchange observed in the present investigation, using the method of continuous, uninterrupted exchange, have already been explained on the basis of crystal orientation. To bring this in line with the postulate that exchange occurs almost exclusively at step positions on otherwise flat crystal faces, reference may again be made to the calculations of Burton and Cabrera (56). It has already been mentioned that reaction at the steps will be facilitated by the

existence of "Frenkel kinks" in the steps. The probability, n , for having a kink at a given place on a step is given by

$$n = e^{-E/kT}$$

where E is the energy of interaction between neighboring atoms. One "kink" is found for about ten atoms in a step and one hole or atom "Adsorbed on the face of the step" for about one hundred atoms. Since the interaction energy between atoms varies with crystal face, the number of "kinks" in a step, and therefore the rate of exchange at the step, will vary with the crystal face. In addition, the number of atoms in out-of-lattice positions on those faces of low binding energy may be expected to be greater than on those of higher energy, and thus increase the rate of exchange on such a face.

It has been tacitly assumed to this point that the silver specimens used (rolled foils) in the present experiments were entirely crystalline. For rolled metals this is borne out by X-ray diffraction experiments (63). However, more severe cold working or polishing can reduce the crystalline fragments to a state which gives X-ray patterns typical of amorphous material (67). Such amorphous metal would be expected to lead to extensive exchange and exhibit a kinetics different from that for crystalline material. Of special interest here are the investigations made by Coffin and Tingley (9), also on the silver-silver nitrate exchange but with emphasis on the amorphous forms of the metal. They observed that polished silver foils exchanged to apparent

depths of 100 atomic layers in 0.1N active silver nitrate during 24 hours or more, while annealed, etched (crystalline) specimens acquired, in a matter of seconds, a maximum activity corresponding to only 10 atomic layers. On the other hand, etched surfaces of unannealed or cold worked foils showed visually distinct crystalline and "non-crystalline" (amorphous) metal. These specimens exchanged to apparent depths commensurate with that of polished surfaces. Autoradiographs of the exchanged surfaces indicated that the amorphous regions behaved anodically with respect to the crystalline regions. Although the influence of annealing or cold working has not been examined in the present study, the magnitude of exchange on the etched surfaces studied are in reasonable agreement with the results obtained by Coffin for etched, crystalline specimens. This would support the assumption that the silver used was entirely crystalline.

It remains now to consider the influence on the exchange processes of ions adsorbed on the surface. In the exchange reactions with etched foils, some of the activity was found to be present in ionic form, probably as an ionic double layer. It appeared, from the results of exchange with equilibrated, etched specimens (as compared with non-equilibrated surfaces) (Tables VIII and IX) that such adsorbed material decreased the rate of exchange, though the results were not entirely conclusive. The manner in which adsorbed ions might affect the rate of reaction is not clear. Zimens (29) has reasoned that the reaction rate should increase with increasing adsorption, i.e. with increased con-

centration. He suggests that the variation of the rate of exchange with concentration should obey a law of a form similar to an adsorption isotherm, and that the rate should attain a maximum value at complete coverage of the surface with adsorbed material. However, qualitative observations do not bear out this line of reasoning. It will be recalled that Hevesy and Blitz (5) found a decreased rate of exchange with lead sols for which a high degree of adsorption was postulated. Likewise, Kolthoff (26) observed a slower rate of exchange, in the presence of a large excess of lead nitrate, in the exchange with lead sulfate precipitates.

A possible line of speculation is that adsorption of anions or other bath constituents occurs in a more or less static manner, and that this reduces the mobility of the out-of-lattice atoms on the flat crystal faces, hence reduces the rate of exchange. Evidence for such behavior has been indicated, for example, in the deposition of metals in the presence of adsorbed hydrogen ions (68).

At first sight it would appear that silver ions in an adsorbed state would "exchange" rapidly with the ions in solution. While electrodeposition of these adsorbed ions indicated (page 108) that they would account for about 20 to 25% of the observed exchange, the initial rate of exchange was essentially constant to at least 60% exchange (Experiment 2, page 89). It must then be concluded that "exchange" with adsorbed ions cannot be distinguished from reaction with exchangeable surface atoms. This would imply that exchange of adsorbed metal ions

with surface atoms is comparatively rapid and that the overall rate of exchange on a particular crystal face is governed by other factors, perhaps adsorbed anions or solvent molecules. Rate control by anions in the double layer at the interface has been suggested by Audubert to explain the dependence of exchange rate on anions in solution as observed by Haissinsky (14). This would be compatible with the directional reactivities of various crystal faces, in view of the preferential adsorption which has been observed (51,65). The ionic adsorption factor, however, can not be established from the meagre data available.

In some of the exchange experiments made in the present study with etched silver foils, the magnitude of adsorbed ionic activity was measured by an electrometric method. This consisted of placing the silver electrode into a sulfuric acid solution immediately after exchange with an active silver nitrate solution, and measuring the quantity of electricity, Q , required to change the potential of the electrode from the static value to that of maximum hydrogen overvoltage. The measured Q values were associated with the reduction of adsorbed silver ions and good agreement was found with the activity gained in repeated immersion of the silver in active solution (Table V). The validity of this method of measuring adsorbed silver ions was substantiated by the linear relation found between Q and the logarithm of the concentration of silver ions in the solutions from which adsorption had taken place.

It is interesting to note the possible significance of these results in respect of the theories of hydrogen overvoltage. The voltage

usually associated with deposition of hydrogen is the difference between the static (zero current) potential of the cathode in the acid solution, and that where steady evolution of hydrogen takes place, at a given current. The results obtained here suggest that the overvoltage may, in large part, be due to metal ion or concentration polarization. The steady state electrode potential in the acid solution would then be determined, presumably, by the presence of metal ions in the vicinity of the electrode surface. This would be in harmony with some of the views expressed by Gatty and Spooner (69). It may be remarked here that the zero potential in the acid solution was always attained from more negative values for freshly abraded electrodes, while for surfaces which had been placed in silver nitrate solution and probably retained an adsorbed layer of metal ions, the static potential was always attained from more positive values.

A number of studies on the adsorption properties of silver in silver nitrate solutions are reported in the literature. The values obtained by different investigators are somewhat variable but they are all in the order of 5×10^{-9} moles of silver ion per cm^2 on etched specimens in 10^{-3} N silver nitrate solutions (70,71). Compared with this, 1.8 to 3.5×10^{-9} mole/ cm^2 were observed here for etched foils in 10^{-4} N silver sulfate solutions.

The adsorption capacity of etched silver in silver nitrate solution was measured by Veselovskii (47) and found to have a value of 620 mfd./ cm^2 . Compared with this, the polarization capacity, based on the current flow required to change the electrode process from anodic to

cathodic, was 640 mfd./cm.² Veselovskii obtained the adsorption capacity from the linear plot of $\log (Ag^+ \text{ conc.})$ vs. the amount adsorbed, expressed in terms of coulombs. The point of intersection of the straight line with the zero adsorption line gave the point of zero charge on the metal at a silver nitrate concentration of $10^{-12}N$. In the present study the data indicated the point of zero charge to lie in the range 10^{-11} to $10^{-14}N$ in silver sulfate concentration (Fig. 11).

The Bowden-Rideal capacity values for the three electrodes for which adsorption data were obtained, were all about 150 mfd./cm.² On the other hand, the adsorption capacities, determined from the isotherms (Fig. 11) were 2 to 5 times greater (Table VII). It is difficult to account for these large discrepancies and any attempt to interpret their significance would, at present, be purely speculative.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

The contribution of this investigation to the knowledge of exchange reactions between a metal and its ions in solution may be summarized as follows:

1. The exchange between silver ions and silver foils prepared by mechanical abrasion extends through several hundred apparent atomic layers of the metal over a period of several days and continues almost indefinitely. Area measurements of the silver specimens by the Bowden-Rideal method indicate that the true surface area may be as much as 50 times planar. The radioactivity acquired by these surfaces in active silver nitrate solutions is only partly removed in an inactive solution. This is interpreted to indicate local cell action on the surface during exchange.
2. During one hour in $3 \times 10^{-4}N$ active silver nitrate the exchange with abraded surfaces is usually greater than would be expected from the Bowden-Rideal area measurements, assuming surface atom exchange only. Under the same conditions, foils etched with nitric acid exchange to apparent depths of 1.5 to 3 atomic layers of the metal while the area measurements would indicate a true surface of 6 to

10 times planar. This is interpreted, on the basis of the theories of crystal form and growth, to indicate that the crystallites on etched surfaces are relatively free of imperfections, where exchange is most likely to take place.

3. For abraded surfaces, the exchange during one hour is reduced by preliminary immersion in inactive silver nitrate solution for several days. The acquired activity during a given time interval then shows an overall correspondence with the respective Bowden-Rideal area measurements among different silver specimens. No reduction in the extent of exchange, by preliminary equilibration, was observed with etched foils.
4. Some of the radioactivity observed on etched silver specimens is present on the surface in ionic form and is difficult to remove by a simple water wash. The magnitude of this adsorbed ionic silver may be measured by an electrometric method which is described. The adsorption from a silver sulfate solution, measured by this method, varies linearly with the logarithm of the silver ion concentration. For an etched silver electrode the adsorption capacity found in this way is 2 to 5 times greater than the capacity measured by the Bowden-Rideal method.
5. The exchange with etched and equilibrated specimens appears to be slower initially than that with similar surfaces which were rendered cathodic in an acid solution preliminary to exchange. This might be

interpreted to indicate that adsorbed material reduces the initial exchange rate with equilibrated surfaces.

6. An apparatus is described which permits a kinetic study of the exchange reaction by continuous measurement of the radioactivity on the metal through a thin film of the exchange solution. The data obtained with this apparatus show a rapid initial exchange followed by a prolonged slow accumulation of radioactivity on an etched silver surface in $10^{-5}N$ active silver nitrate.

When the exchange with active solution is reversed after three hours, by reaction with inactive solution, the acquired activity is not entirely removable but attains a constant value in less than three hours. A segmented graph is obtained when the kinetic data are plotted according to the first order rate law. This is interpreted to indicate several rates of reaction which are dependent on the differential atomic bonding on the various crystallite faces exposed on the surface of the metal. This would be in agreement with the predictions suggested by the theories of crystal growth.

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