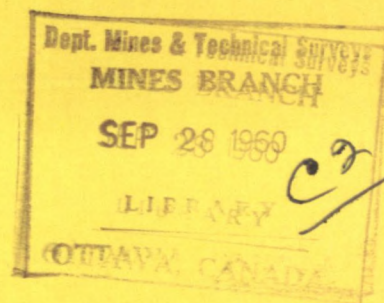




CANADA

**SURFACE EXCHANGE REACTIONS  
OF SILVER AND ITS IONS**



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SURFACE EXCHANGE REACTIONS OF SILVER AND ITS IONS

by

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SYNOPSIS

The exchange reactions between silver and its ions in solution have been investigated by the use of radioactive tracers. Silver of highest purity was cleaned carefully and immersed into a radioactive silver nitrate solution. The course of the early adsorption process and subsequent diffusion of the ions into the interior of the metal was followed in detail, and the diffusion coefficient at room temperature was calculated. The penetration depth was determined by controlled electro-polishing of the metal, and the reverse movement of active ions from the metal into inactive solutions was also observed.

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Direction des mines

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RÉACTIONS D'ÉCHANGE EN SURFACE DE L'ARGENT  
ET DE SES IONS

par

J. E. Sandor\*

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RÉSUMÉ

On a étudié les réactions d'échange entre l'argent et ses ions en solution à l'aide de radioindicateurs. Après avoir décapé avec soin une éprouvette d'argent de la plus grande pureté, on l'a plongée dans une solution de nitrate d'argent radioactif. On a suivi en détail le processus d'adsorption puis la diffusion subséquente des ions au sein du métal, et l'on a calculé le coefficient de diffusion à la température de la pièce. La profondeur de la pénétration a été déterminée par polissage électrolytique contrôlé du métal, et l'on a aussi observé le passage inverse des ions activés du métal dans les solutions inertes.

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## INTRODUCTION

The exchange reaction between metallic silver and its ions in solution has been investigated by several authors. This metal is of particular interest because it is available in high purity, is chemically inert, and has a convenient radioactive isotope, with a half-life of 270 days.

Rollin (1) found that metallic silver, shaken with a silver nitrate solution containing radioactive silver, acquired an activity corresponding to more than 100 apparent atomic layers of silver. Baerg and Winkler (2) found that "abraded" and etched foil exchanged to different depths. They measured the "true" area by the Bowden-Rideal method (3) and tried to correlate surface area and exchange, but concluded that "the metal surfaces were poorly reproducible in respect to both exchange and area". Gerischer and Vielstich (4) observed that after a rapid initial exchange, which depended on the surface treatment, a second, slower increase in observed activity took place, and they attributed this increase to solid state diffusion.

Tingley, Henderson and Coffin (5) concluded from their work that generally there are two mechanisms acting in silver exchange reactions, one "kinetic" and the other a "true exchange"; which one of these was acting depended on the state of the surface.

King and McKinney recently (6) also found evidence that solid state diffusion occurs in silver, accompanying the exchange reaction.

None of the previous work resulted in a consistent explanation of all the observed phenomena. A theoretical study of the heterogeneous reaction was done by Zimens (7). He devised equations relating the progress of the solid-liquid exchange with time, assuming that one of the following processes is the rate-determining one:

- 1) Diffusion across the interface, 2) chemical reaction at the phase boundary, 3) diffusion of the exchanging atoms into the interior of the solid.

The rate laws for these processes are formally similar and are usually of an exponential nature.

It was the purpose of the present experiments to elucidate the exchange between silver and its ions, following Zimens' model.

The main questions to be solved were:

- 1) The reason for a fast exchange to a depth of more than 100 atom layers, 2) the cause of the slow increase in observed activity after the initial exchange, 3) a decision as to which of the three processes in Zimens' model were the rate-controlling ones.

Three major practical factors were considered essential to the success of the experiments: 1) use of high purity materials, 2) avoidance of oxidation and corrosion, and 3) careful preparation of the surfaces.

At the same time an electropolishing technique had to be developed to measure the penetration of the radioactive tracer inside the solid.

It should be stressed that small variations in technique can affect markedly the results of all such exchange experiments.

#### EXPERIMENTAL DETAILS

The radioisotope utilized for all the experiments was silver-110, obtained from Atomic Energy of Canada Ltd. It has a half-life of 270 days, and a complex beta and gamma-ray spectrum with a maximum beta energy of 2.8 MeV and a maximum gamma-ray energy of 1.516 MeV.

All the activity measurements were done with a well-type NaI(Tl) scintillation counter. A statistical analysis of the counting assembly was done using a known source of Ag-110; the test indicated a satisfactory operation of the unit.

A  $10^{-2}$  M silver nitrate solution was prepared with a specific activity of 6.5  $\mu\text{c}/\text{cc}$  and a pH of 6.6. Metal foils were prepared from Johnson-Matthey 99.999% silver. Rods of 1.9 cm diameter and 2.5 cm length were alternately cold-rolled to 50%

reduction and annealed 15 minutes at 500°C, to a final thickness of 0.0025 cm.

From these foils, samples of 1.5 cm<sup>2</sup> area were cut in such a way as to leave a short tip on one of the sides (Fig. 1) to use as a holder during the handling of the samples (silver plated tweezers were used during all the experiments).

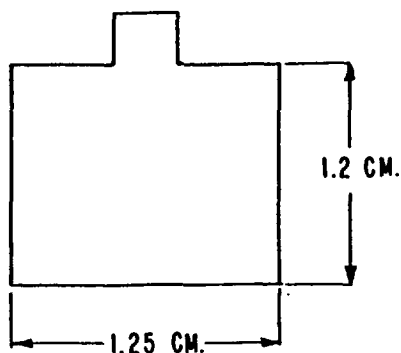


Figure 1. - Shape of Silver Foil Samples.

These foils were cleaned in boiling ethanol for 1 hour, electropolished in a cyanide bath for 10 minutes, annealed for 20 minutes at 400°C, and finally electropolished again for 10 minutes. Samples prepared in this way showed no surface deformation when X-ray diffraction pictures were taken. These samples also stayed bright and untarnished when stored for considerable periods.

It was found that high annealing temperatures or long annealing periods produced some thermal etching, and that the pits were noticeably broadened during electropolishing.



## EXPERIMENTS ON EXCHANGE AS A FUNCTION OF TIME

To find out if there was a continuous increase in activity after long periods of immersion\*, 12 samples were left in a 100 cc Petri dish containing 50 ml of radioactive solution. The Petri dish was kept, for the duration of the experiments, in a well-shielded lead castle.

To simplify the handling of the specimens, they were attached by their tips to a ring of Lucite with a drop of paraffin. In this way some samples were immersed for as long as 37 days. This arrangement was adopted to avoid concentration changes in the solution by evaporation, and at the same time to make it possible to subject at least 12 samples simultaneously to exchange processes.

The solution was not stirred; it was assumed that even without agitation the diffusion through the diffusion layer in the liquid was much faster than the solid state diffusion in the metal and so this factor would not influence the final results.

(The ratio  $\frac{D_l}{D_s} = 10^{12}$ .)

The samples were taken out at regular intervals, rinsed carefully with cold water and alcohol, dried, and counted in the scintillation counter. The first counting was done after

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\* Note: By "long" is understood more than 1 day.

9 days of immersion. No counting was done at the beginning of the exchange, because previous experiments had established a very rapid increase in activity during the first few minutes of the exchange. In the work described here the emphasis was on the longer term exchange, particularly to show whether there is a continuous increase in activity in the samples, and whether this slow increase is due to solid state diffusion.

A small correction had to be made to take into account the decay of the radioisotope.

## EXPERIMENTAL RESULTS

### Activity Increase as a Function of Time

The results of the long-term immersion tests are plotted in Fig. 2 in terms of apparent layers of exchanged atoms as a function of time of immersion. The relation between adsorbed activity and equivalent atom layers had been established in an auxiliary electropolishing experiment. The first count was obtained after 9 days of immersion, and subsequent ones at intervals of three or four days.

The points correspond to different samples, but it seemed better to plot the average curve of the different samples than to draw a curve for each sample. There is some scatter in the points, but this was not the case when each sample was counted individually.

From this curve it can be seen that the activity increases approximately as a function of the square root of time, as expected if a diffusion process is the rate-determining process.

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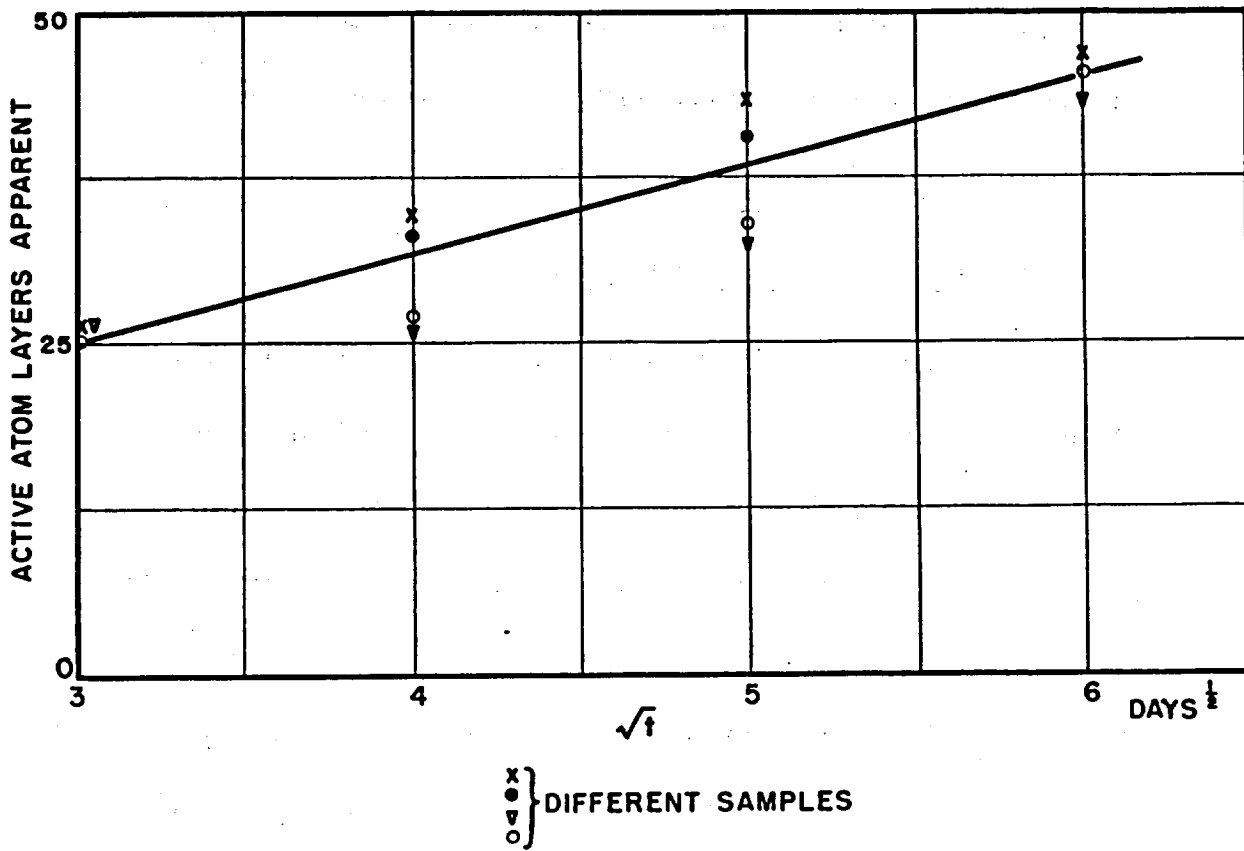


Figure 2. - Exchange as a Function of Time of Immersion.

In Fig. 3 is plotted the resultant mean curve of three selected samples where the activity pickup was higher than for the others. This may have been caused by some disturbance of the adsorption equilibrium, or by a deformation of the surfaces during the handling which interfered with the reaction exchange-solid state diffusion. This curve does not fit the equation  $A_t = f(\sqrt{t})$ .

#### Measurement of Penetration Depths

To find out if there was a measurable penetration of the radioactive isotope, and to calculate a self-diffusion coefficient for silver, the "exchanged" specimens were electropolished under reproducible conditions. It was ascertained that the same period of electropolishing removed the same weight of silver each time. In addition to this, before electropolishing the samples were immersed in the electrolyte for short periods of time - ranging from one second to one minute - without applying electrical current, to see which portion of the activity was "re-exchangeable". The remaining activity in the samples was then counted.

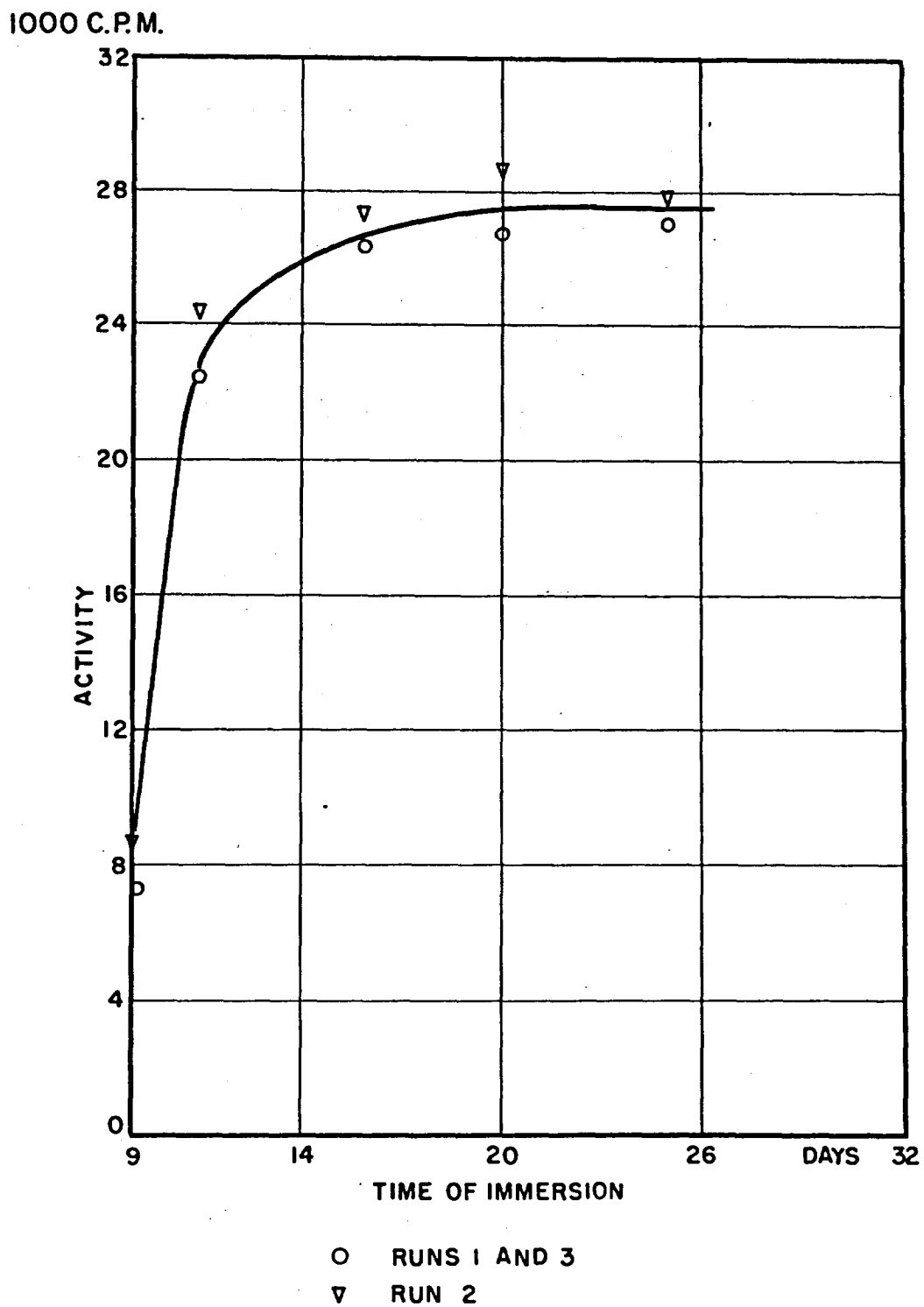


Figure 3. - Exchange as a Function of Time of Immersion.  
High pickup of Activity.

TABLE 1

Exchanged Samples Immersed in the Electropolishing  
Solution without Applying Current

Sample No.	History	Time of immersion in electrolyte, sec.	Initial activity, c.p.m.	Remaining activity, c.p.m.	Loss of activity
1	Exchanged 34 days	1	14,000	8900	36%
	Stored 60 days	60		7000	50%
2	Exchanged 34 days	1	12,000	7700	36%
	Stored 30 days	60		6100	49%
4	Exchanged 37 days	1	25,000	18,000	28%
	Stored 60 days	60		14,300	43%
6	Exchanged 31 days	1	13,600	7700	43%
	Stored 60 days	60		6800	50%
8	Exchanged 25 days	1	25,000	19,200	23%
	Immediately after	60		14,600	42%
9	Exchanged 25 days	1	24,600	18,000	27%
	Immediately after	60		10,600	57%

In Table 1 are summarized the results of the immersion of the samples in the electrolyte without applying current. It is evident that more than 40 per cent of the activity is "exchangeable", and that between 20 and 45 per cent of the activity is lost after the first second of immersion; in addition to this, the samples that picked up higher activity (Fig. 3) have a higher fraction of "exchangeable" atoms.

The results of the experiments done by progressively electropolishing the exchanged samples show that there is a measurable penetration of the radioactive tracer.

In Fig. 4a are plotted the penetration curves of some of the samples listed in Table 1. The logarithm of the activity in c.p.m. is plotted as a function of the time of electropolishing. It was established by previous experiments that, under the operating conditions used, in the exchanged samples one minute of electropolishing was equivalent to removing an amount of silver equivalent to a thickness of one micron.

It was observed that there was a large decrease of activity after removing the first 0.13 to 0.25 micron, and then a much smaller decrease in activity when a subsequent comparable thickness was removed.

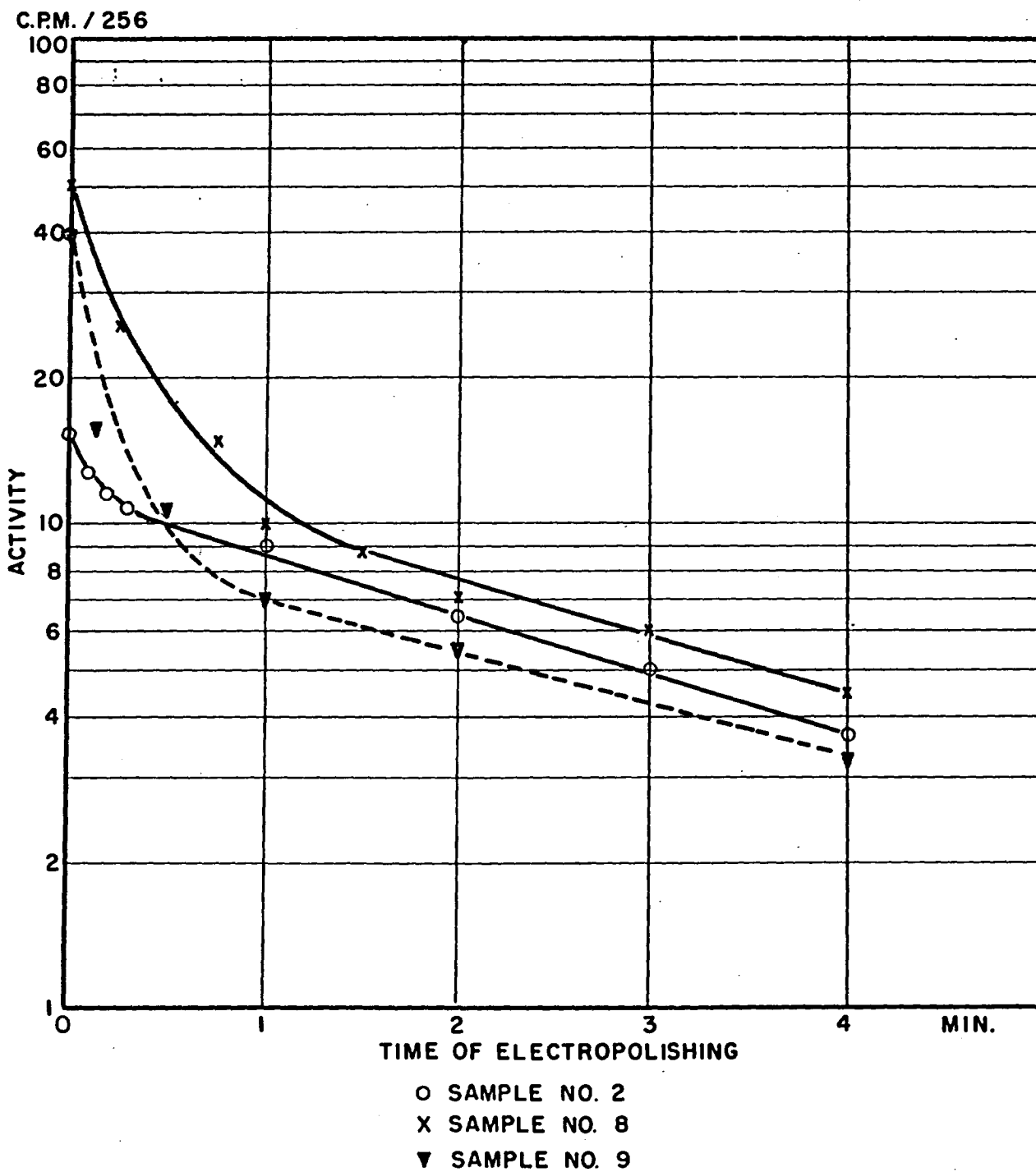


Figure 4a. - Penetration Curves for Fresh Samples.



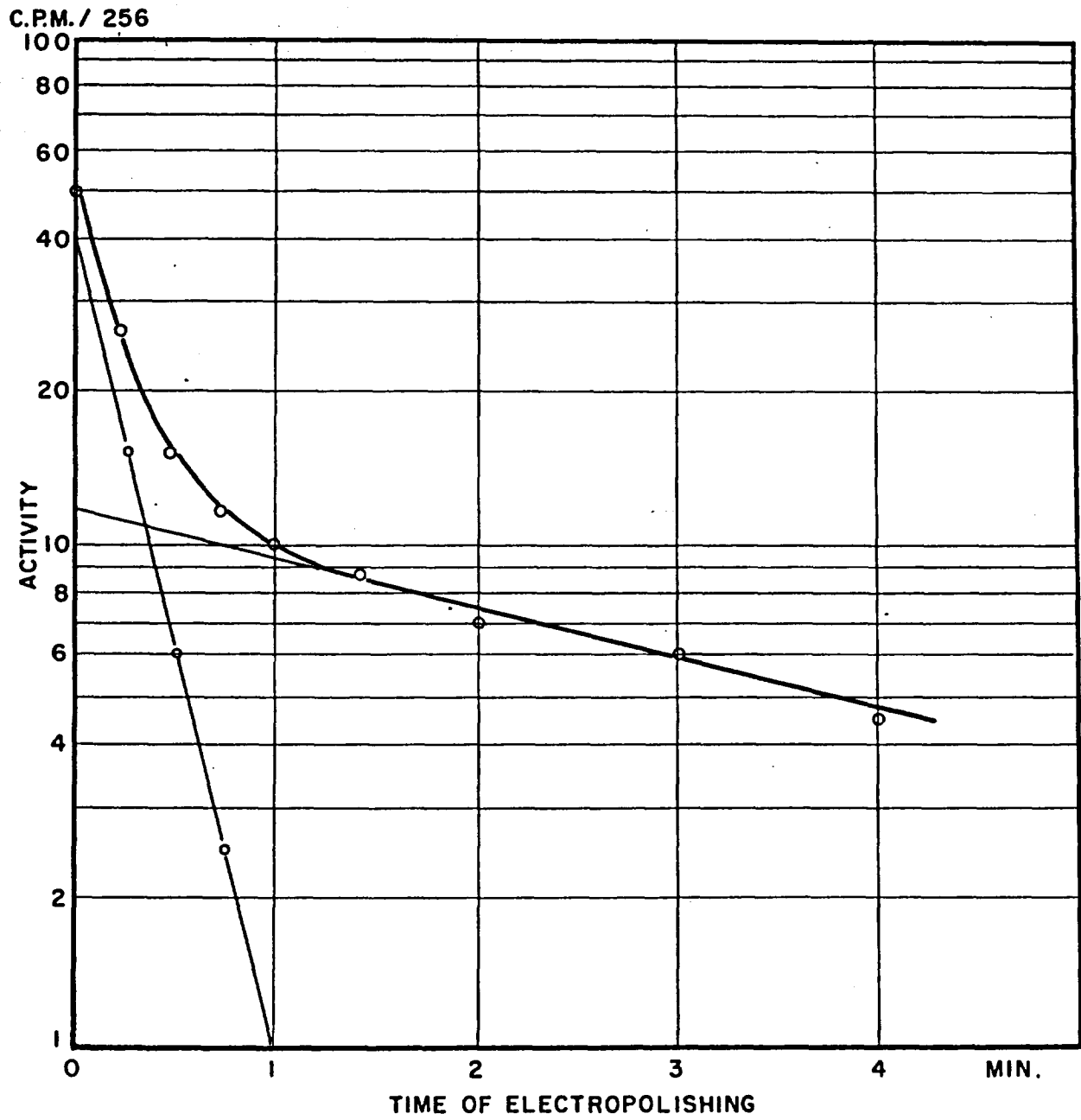


Figure 4b. - Penetration Curves. Analysis of Typical Curve.

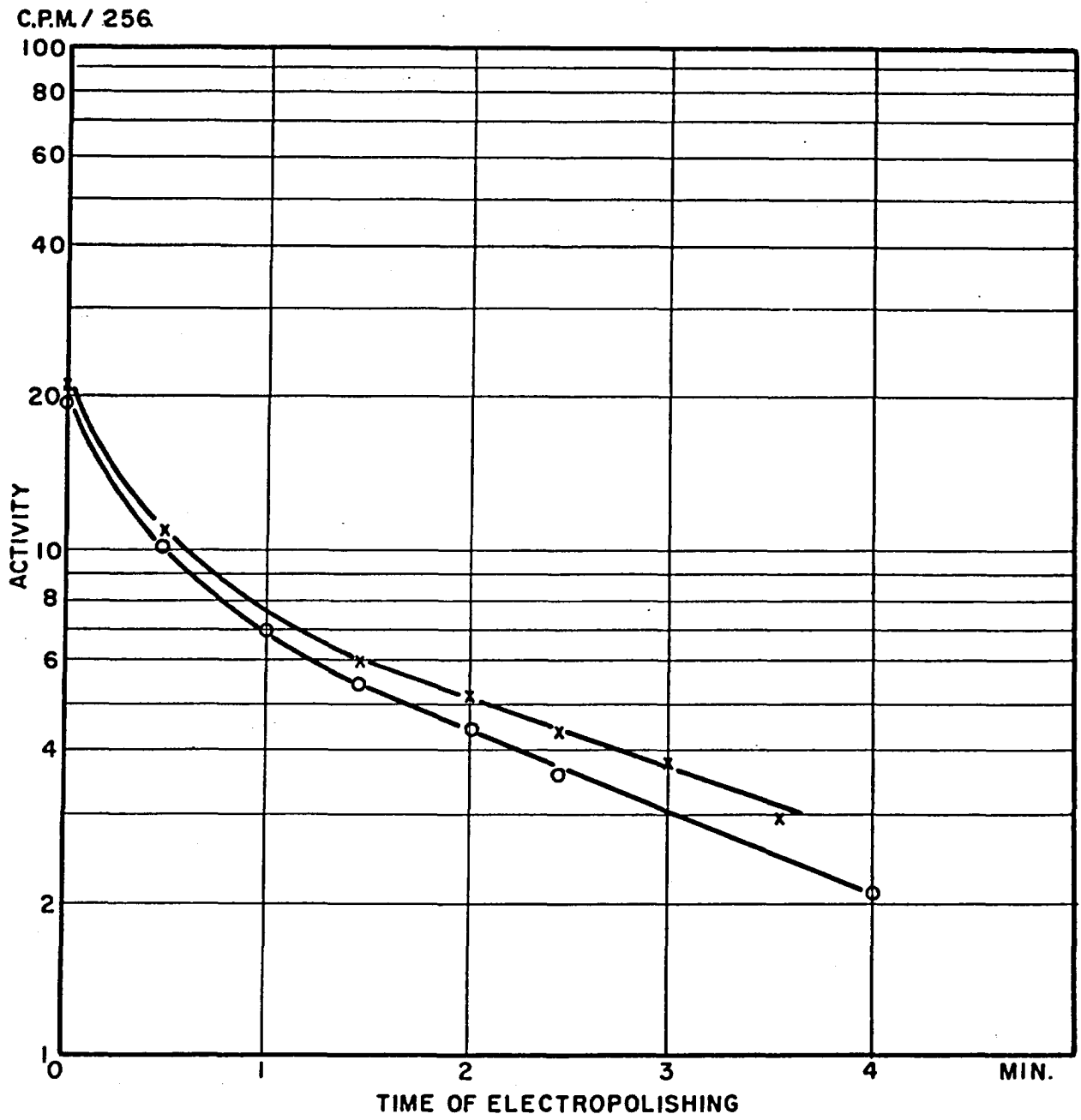


Figure 5. - Penetration Curves for Aged Samples.

It can be seen in Fig. 4b that the penetration curves are clearly the combination of two independent exponential functions, representing two processes proceeding at different rates.

It is observed that long storage of the foils after the exchange process affected the slope of the second part of the curves, and it made some difference in their initial slope. This effect is shown in Fig. 5. Longer storage times tended to flatten this first part.

#### CALCULATION OF DIFFUSION COEFFICIENT

From the data of the penetration curves the self-diffusion coefficient of silver at room temperature was calculated.

Fisher (8) made an analysis of the relation between grain boundary diffusion coefficient  $D_b$  and volume or lattice diffusion  $D_v$ . He arrived at an expression

$$D_b = 2 D_v^{\frac{1}{2}} (\log e)^2 / \delta \left( \frac{d \log a_x}{dx} \right)^2 (\pi t)^{\frac{1}{2}}$$

where  $e$  is the logarithm base, and  $\delta$  the grain boundary thickness.

The same author assumed for  $\delta$  a value of  $5 \times 10^{-8}$  cm, that has since been criticized (9) because it is very hard to establish a uniform thickness for the grain boundaries of metals, but it can be used as an approximation.  $D_v$  can be calculated from the formula of Hoffman and Turnbull (10):

$$D_v = 0.395 \exp(-49,500/RT) \text{ cm} \cdot \text{sec}^{-\frac{1}{2}}$$

The value at 25°C is  $D_v = 9.8 \times 10^{-38} \text{ cm}^2/\text{sec}$ . Inserting this value in the equation for  $D_b$ ,

$$D_b = 6 \times 10^{-11} / \left( \frac{d \log a_x}{dx} \right)^2 t^{\frac{1}{2}} \text{ cm}^2/\text{sec}$$
$$= 2.2 \times 10^{-19} \text{ cm}^2/\text{sec}$$

where  $a_x$  = activity,

$x$  = penetration, and

$t$  = time of exchange.

The slope of the straight part of the curves of Fig. 4a and a value of  $t = 34$  days were used for the calculation.

#### DISCUSSION AND CONCLUSIONS

The results of the present work, added to the experimental results of other authors, can give a complete picture of the whole exchange process. In the absence of corrosion, oxidation or local cell action, in the case of silver, a rapid exchange takes place between the surface atoms of the metal and the ions in the liquid on immersing the electropolished foils in the exchange solution. At the same time, some local cell action due to the presence of different crystal faces may take place, but in a polycrystalline material the electromotive force resulting from this difference must be negligible.

To measure the extent of reversibility of this exchange reaction, the reverse experiment was carried out. It was found that close to 50% of the activity of the samples was lost

after a few seconds of immersion in an inactive silver nitrate solution. This would indicate that the adsorbed (chemisorbed and ionic double-layer) atoms re-exchange readily with the solution; the results are plotted in Fig. 6.

The results of the long-term experiments on the increase of activity with time gave a clear indication that a diffusion process was involved. The penetration curves confirmed this supposition. It was found that fast exchange at the surface is followed by diffusion of the atoms inside the solid.

It follows that two different mechanisms are acting, a fast diffusion process down to a depth of 300 atomic layers, followed by a much slower one at greater depth.

The diffusion coefficient found in the present study for this second process is  $D = 1.37 \times 10^{-20} \text{ cm}^2/\text{sec}$ , which differs little from  $D = 6.14 \times 10^{-22} \text{ cm}^2/\text{sec}$  calculated from Hoffman and Turnbull's results (10).

The difference of two orders of magnitude can be explained either as a result of extrapolation, because the work of Hoffman and Turnbull was done at high temperatures, or because there is a difference in the activation energy, indicating that another mechanism is acting at low temperatures.

Other authors found a difference of 4 or 5 orders of magnitude; this can be attributed to less pure samples, or to less

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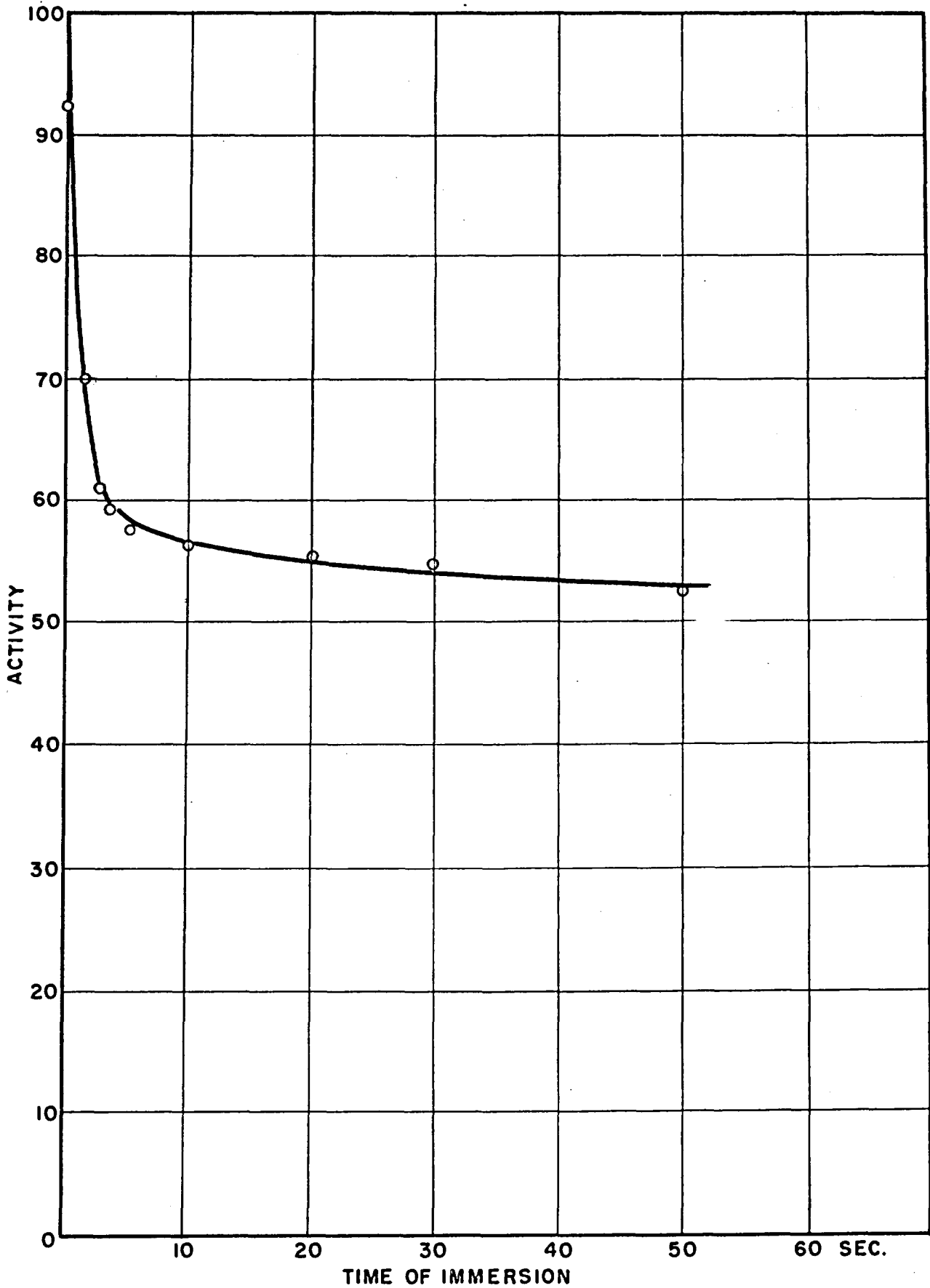


Figure 6. - Reverse Exchange. Active Metal Immersed in Inactive Solution.

well polished surfaces.

It is an accepted theory that self-diffusion in face-centred cubic metals takes place by a lattice vacancy mechanism.

It has already been shown that in diffusion curves for polycrystals, unusually high activity was noted at small penetration depths (11). The same result is found in the present study, so it is probable that there is a much more disordered and loose structure of atoms close to the surface exposed to the solution.

This would explain the high rate of adsorption at the beginning of the exchange reaction. It also accounts for the fact that in cold-rolled samples there is a faster diffusion than in annealed specimens, and for the observation that pretreating the surfaces in inactive silver before the exchange experiments tends to decrease the exchange rate.

The whole process can be pictured as in Figure 7, i.e., similar to the interdiffusion of two solids.

The smallest diffusion coefficient is in the solid phase and it is the rate-determining factor in the whole exchange process under near-equilibrium conditions at the surface.

The atoms move from a solid lattice structure through a "fast diffusion" layer, through a phase boundary, through the liquid diffusion layer, and finally to the bulk of the liquid.

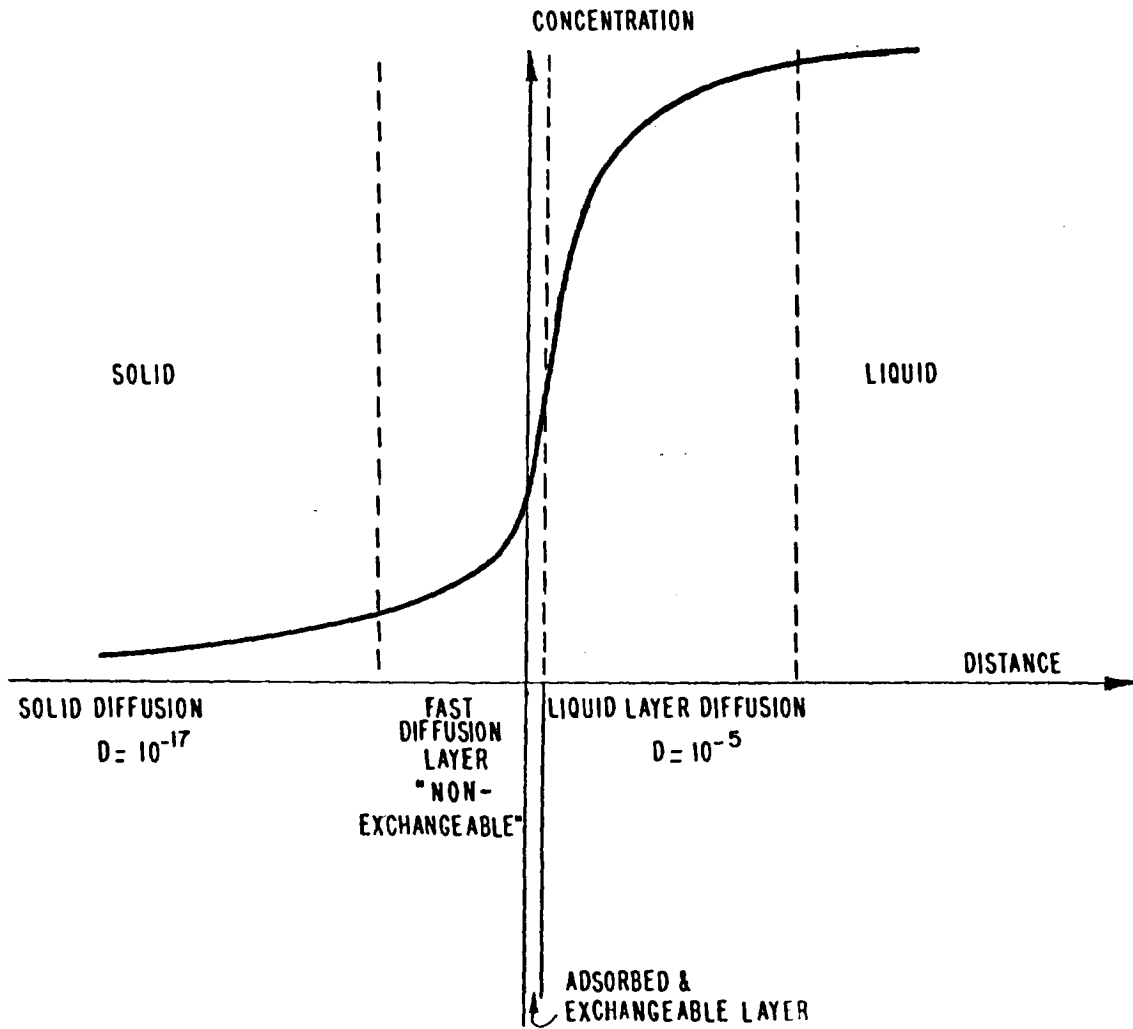


Figure 7. - Diagram of Exchange Layers.



To Summarize:

1) A continuous increase in activity was found by immersing electropolished and annealed silver foils in a silver nitrate solution containing radioactive silver, for periods of 9 to 37 days. The adsorption process was a square root function of time.

2) Close to 50% of the activity was lost by reverse exchange when the exchanged samples were immersed in inactive silver nitrate solution; the remainder was removed from the contact area by diffusion into the interior of the metal.

3) The measurement of the penetration of the radioactive isotope after exchange was carried out using an electropolishing technique and showed an exponential distribution with depth.

It is concluded that a fast diffusion occurs close to the surface, followed by a slower one inside the metal. The calculated diffusion coefficient in the bulk of the solid does not differ much from the one calculated from Hoffman and Turnbull's results.

4) A model of the whole process is proposed, assuming that self-diffusion in the solid is the rate-determining process.

## ACKNOWLEDGMENTS

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