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EXCHANGE REACTIONS BETWEEN ZINC AND ITS IONS

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by

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SYNOPSIS

The exchange reaction between zinc metal and zinc ions in solution was studied by means of radioactive zinc-65. Polycrystalline zinc and bi-crystals of zinc were used under conditions where the radioactive material was incorporated either in the solid or the liquid phase. Strain-free clean surfaces were obtained and autoradiographs taken.

The results of the experiments using bi-crystals were interpreted on the basis that a local cell action sets up an electrochemical potential between liquid and solid at the beginning of the reaction. Exchange was found to take place in both directions, but the reaction did not follow a simple logarithmic law.

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RÉACTIONS D'ÉCHANGE ENTRE LE ZINC ET SES IONS

par

J.E. Sandor*

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RÉSUMÉ

On a étudié, à l'aide du zinc radioactif 65, la réaction d'échange entre le zinc métal et ses ions en solution. On s'est servi du zinc polycristallin et bicristallin;dans un cas la substance radioactive etait incorporée à la phase solide, dans l'autre cas à la phase liquide. On a obtenu des surfaces bien décapées et polies, sans deformation, et l'on en a pris des autoradiogrammes.

Les résultats indiquent un effet de pile locale qui engendre une tension électrochimique entre le liquide et le solide au début de la réaction. On s'est rendu compte que l'échange se faisait dans les deux directions, mais cette réaction n'obéit pas à une loi logarithmique simple.

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INTRODUCTION

The extensive use of radioisotopes has made possible the study of many exchange reactions. In 1915, Hevesy (1) showed that in the system $Pb^{++}/Pb(NO_3)_2$ a deep exchange takes place in a very short period of time. Various mechanisms have been suggested for such exchange reactions, but no conclusive explanation has yet been put forward.

The heterogeneous exchange reaction between zinc and its ions has been studied by Rollin (2) in zinc dust, by Gaudin and Vincent (3), Haenney and Mivelaz (4), Matsura (5), and King and Evans (6), in both zinc dust and zinc foil; and Bushmanov and Vozdvizhenky (7) in zinc single crystals. There is generally a discrepancy in the results obtained by the different authors in this field, due to the fact that some factors such as surface preparation, oxidation, corrosion, are not always fully considered.

In this investigation, zinc metal was dipped in different solutions of zinc salt to show, by tagging alternatively the metal and the solution, that the exchange reaction $Zn^{\circ}_{met} \rightleftarrows Zn^{++}_{sol}$ takes place in both directions. The influence of oxide or hydroxide on the exchange was also investigated. Finally, the exchange reaction between zinc bi-crystals and carrier-free solutions of Zn^{65} was studied.

The following factors were considered of importance in this study: 1) preparing undistorted zinc surfaces; 2) working in an oxygen-free atmosphere; 3) minimizing of corrosion and adsorption. It is known that zinc is a soft metal, easily worked, and that the depth of distorted metal after mechanical polishing may commonly extend to at least 20 times the penetration of the deepest scratch (8). For silver, Tingley, Henderson, and Coffin (9) have shown definitely that the exchange reaction is notably different with different surface preparation techniques; the same was found by Simnad and Ruder (10) in several other metals.

Zinc is a chemically reactive metal, easily oxidized, and considerable corrosion can take place in solution in the presence of oxygen as a result of electrochemical action.

EXPERIMENTAL DETAILS

Materials

Zinc Metal: Zinc metal, 99.999% purity, was cast in an argon atmosphere in rods of 1.56 cm diameter. Discs 0.62 cm thick and 1.56 cm in diameter were cut by means of a lathe, annealed 12 hours at 350°C, and mounted in Lucite in such a way that only one face was used in the experiments.

Active Metal: From the same 99.999% Zn rods as before, a number of discs of 1.56 cm diameter were cold-rolled to 78 mm thickness, cut in strips of 2.5 cm length, annealed for 24 hours at 350°C, and sent to Chalk River, Ont. for irradiation. The specific activity after irradiation was 5.1 mc/g. These samples were checked for purity with a 100-channel pulse height analyzer, to see if there was any unwanted activity not resulting from Zn^{65}.

Solutions: Solutions of active and inactive $Zn(NO_3)_2$ were used. The molarities were 10^{-1} and 10^{-2} and the pH varied between 5.2 and 6.2. The active solutions had a specific activity of 0.4 mc/g. The solutions were thoroughly de-aerated.

Carrier-free Zinc: Carrier-free zinc was used in some experiments. Obtained from Nuclear Science and Engineering Corporation (Pittsburgh), it had an activity of 0.8 mc and a specific concentration of 1.1 mc/ml.

Using a standard technique, zinc bi-crystals were grown from seeds provided by Dr. Weinberg. The samples used were 1.87 cm by 1.87 cm and 0.62 cm thick. They were mounted in Lucite in the same way as was the polycrystalline zinc.

Activity Measurements: The activity measurements were done with a 3 in. well-type NaI(Tl) scintillation counter, mounted on a 6656 RCA photomultiplier. The geometry obtained was reproducible within 2%, ie within the statistics of the counting.

For measuring the metal activity, the samples were mounted in 1 in. diameter Lucite mounts which fitted exactly the well of the counter.

In the case of active metal, sample aliquots from the active test solutions were taken and counted in small 5-ml bottles that fitted exactly in a small ring made of Bakelite and placed inside the well.

EXPERIMENTAL PROCEDURE

Preparation of Samples

The polycrystalline samples were mechanically polished with emery papers No. 0/, 00/ and 000/, and on microcloth laps using Al_2O_3 suspensions. They were finally etched with a cold solution of equal parts of HNO_3, C_2H_5OH, and H_2O_2. When the underlying structure of the zinc became visible under a microscope and no twins appeared (12), it was considered that an undistorted surface was obtained.

The bi-crystals were annealed, strongly etched to remove the worked and recrystallized material, and, finally, electropolished by using an orthophosphoric acid-ethanol solution (1:1). A potentiometric circuit was used in the electropolishing, with a voltage of 1.6 V and a current density of 1.5 ma/cm^2. The temperature of the electropolishing solution was 20°C, and the polishing time was 30 minutes.

To avoid oxidation of the samples after etching and rinsing, the samples were immediately immersed in the exchange solution.

Exchange between Inactive Metal and Active Solution

(a) Polycrystalline Metal: After polishing, the metal samples were introduced into a dry box, in which the etching and exchange were carried out in an inert atmosphere of argon. The apparatus was set up so that the exchange process of six samples could be observed simultaneously in the same solution. This solution was kept in a thermostat at 25° ± 0.5°C. The periods of immersion were varied between 1 hour and 1 week.

(b) Bi-crystals and Carrier-free Zinc: The samples were annealed, strongly etched to remove the worked and recrystallized material, and polished and etched as already described.

Carrier-free de-aerated zinc solutions of pH 6 were used. Argon was bubbled continuously and the samples were immersed for short periods of time--ranging from a few seconds to a few minutes. The samples were then rinsed with water, washed with alcohol and dried, and an autoradiograph was taken with No-Screen X-ray film. Different exposure times--depending on the activity of the samples--were tried, ranging from 8 to 64 hours.

For the purpose of studying the influence of oxidation on the exchange, one sample was pretreated for 24 hours in 10^{-2}M $Zn(NO_3)_2$ solution; a $Zn(OH)_2$ film was formed. Then half of the sample was etched and the other half was left with the hydroxide. Again, care was taken, during the rinsing of the samples, to avoid activities resulting from contamination only and not from exchange itself.

Exchange between Active Metal and Inactive Solution

The irradiated samples were immersed for short periods in an apparatus like that sketched in Figure 1, which has argon bubbling continuously through the solutions. The volume of solution was 100 ml, and new portions were used for each immersion period. Aliquots were taken out and counted for 30 minutes in a well-type scintillation counter.

To ensure radiochemical purity, solution samples were checked for possible contamination with the gamma-ray spectrometer. Samples had to be rinsed carefully in order to remove all traces of the etching solution prior to the exchange experiment.

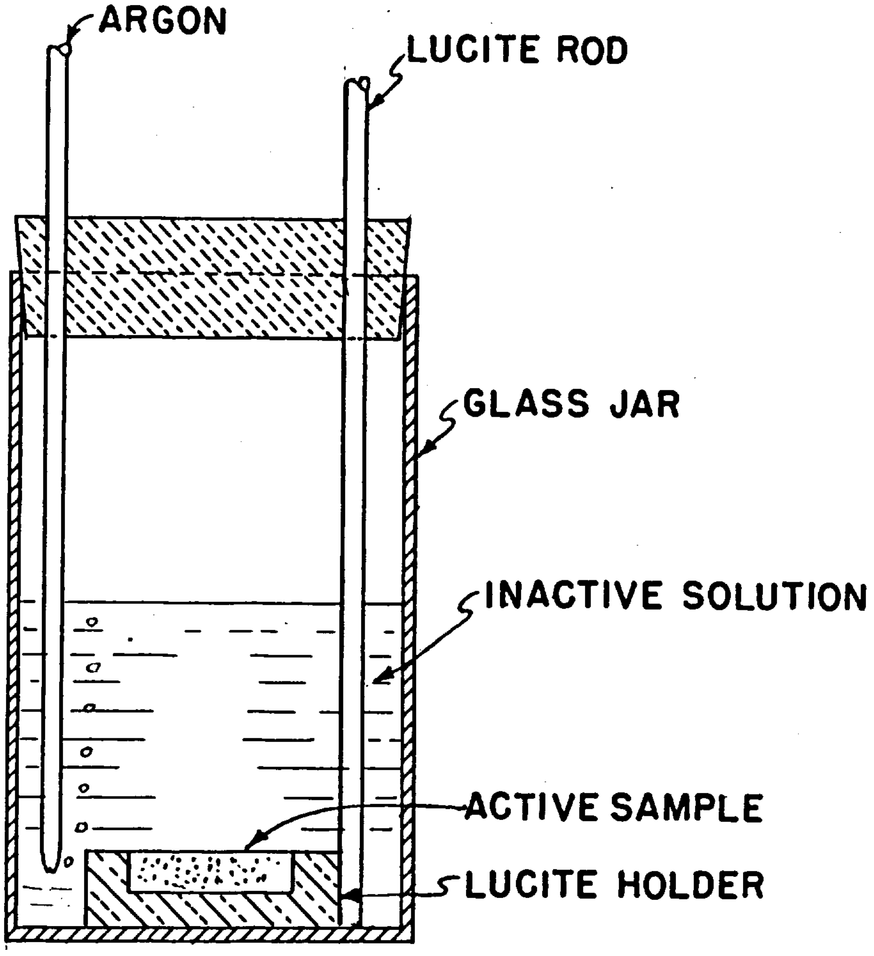

FIG. 1- APPARATUS FOR EXCHANGE REACTION ACTIVE METAL AND INACTIVE SOLUTION.

RESULTS

Some preliminary experiments were done with 0.1 M solutions of $ZnCl_2$ and $ZnSO_4$ at pH 6, but corrosion was observed. The concentration of the solutions was chosen to be between 10^{-1} and 10^{-2} M, because Matsura (5) has found that considerable adsorption takes place at concentrations below 10^{-3} M. At a pH higher than 6.5 there is hydrolysis of the zinc, and below pH 5 some corrosion takes place. Therefore, most of the tests were done at pH 6.

1. Active Solution-Inactive Metal

It has been shown by MacKay (13), and others, that any homogeneous exchange reaction can be described by the following type of equation:

$$- \log (1 - F) = kt \qquad .....1)$$

where F is the fraction exchanged, k is a constant, and t is the exchange time. For a heterogeneous reaction, this type of equation holds as long as the reacting mixture remains chemically unchanged, and only if the isotopic distribution is uniform in each phase during the course of the reaction.

The results of the experiments done so far indicate that the activity increase (or exchanged fraction) varies exponentially with time (Figures 2 and 3) but not in accordance with Equation 1.

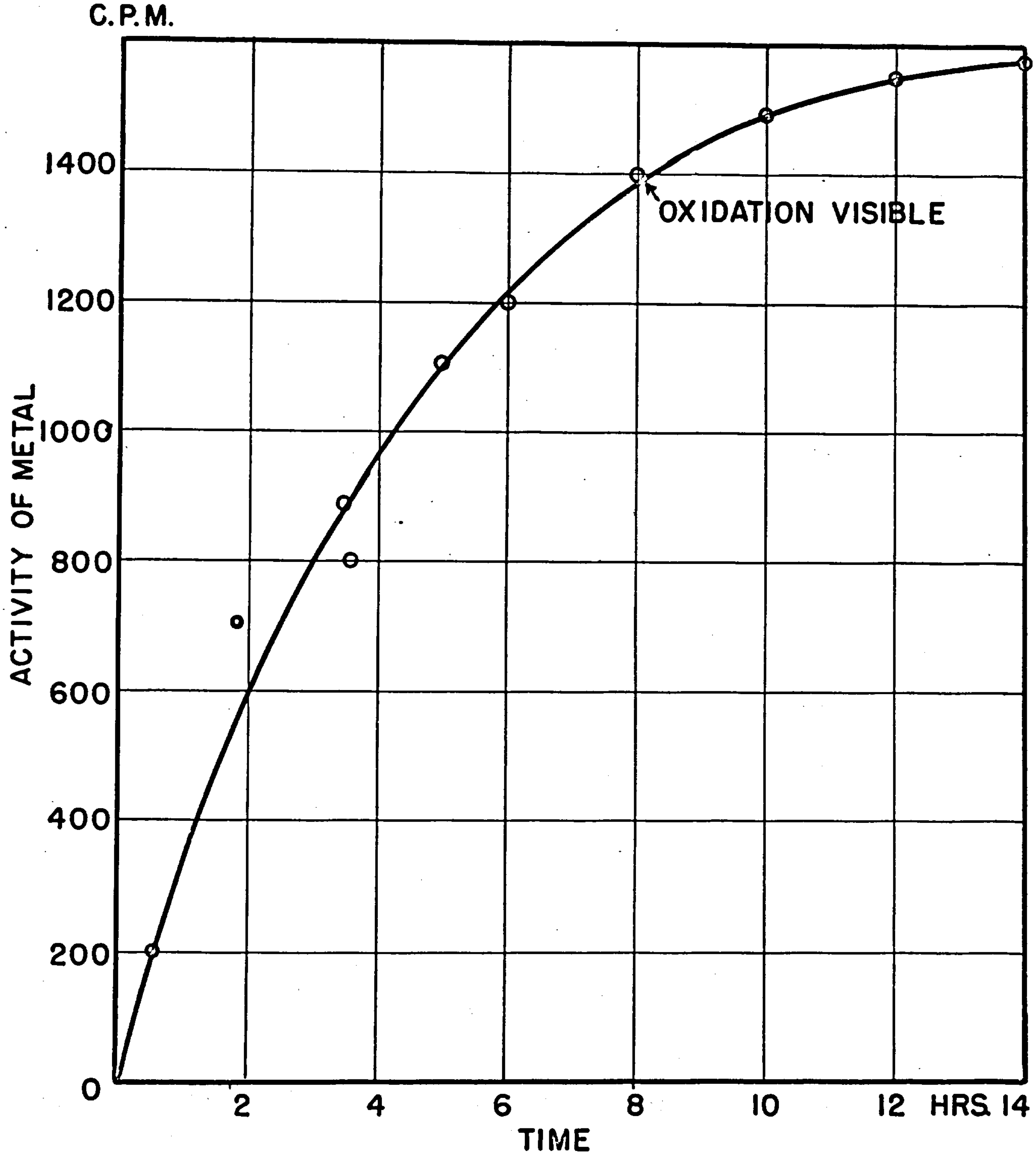

FIG. 2- EXCHANGE BETWEEN INACTIVE METAL AND ACTIVE 10^{-1} M $Zn(NO_3)_2$ SOLUTION.

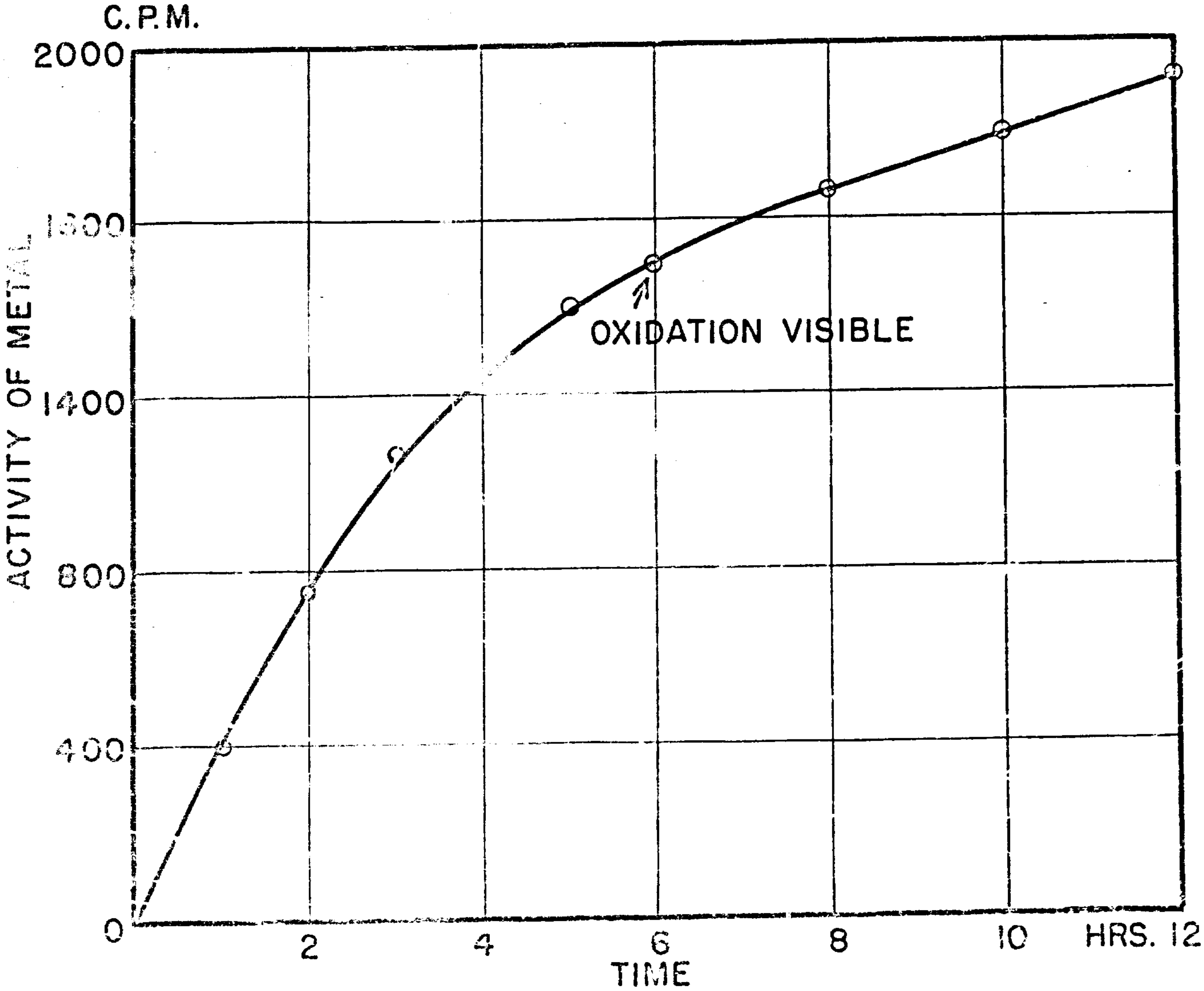

FIG. 3-EXCHANGE BETWEEN INACTIVE METAL AND ACTIVE 10^{-2} M $Zn(NO_3)_2$ SOLUTION.

In Figures 4 and 5 the logarithm of the exchanged fraction is plotted as a fraction of time and it is seen that the slope is not constant. At the same time it was observed that some visible film, presumably $Zn(OH)_2$, was formed during the second stage of the reaction marked in Figures 2 and 3. The onset of this film formation can not be accurately determined. It was found that exchange equilibrium was approached after 48 hours. Experiments with one week of immersion showed considerable scatter of results.

2. Active Metal-Inactive Solution

When the exchange was done at pH 4.8 in distilled water, a continuous dissolution was observed--due possibly to corrosion. No continuous increase in activity took place at pH 5.2 and 6.2; the aliquots taken had an activity slightly higher than the background. The same happened when a sample was pretreated for 24 hours in 10^{-2} M $Zn(NO_3)_2$ solution. When the exchange was done for 1 to 6 seconds, wide scattering was obtained giving unreliable results.

During the last set of experiments, when the exchange time was 1 to 6 minutes, the curve shown in Figure 6 was obtained. The samples were etched before each immersion. The curve presented in Figure 7 was obtained when the samples were etched only at the beginning. No difference was observed between tests at pH 5.2 and tests at pH 6.2. From the experiments reported in

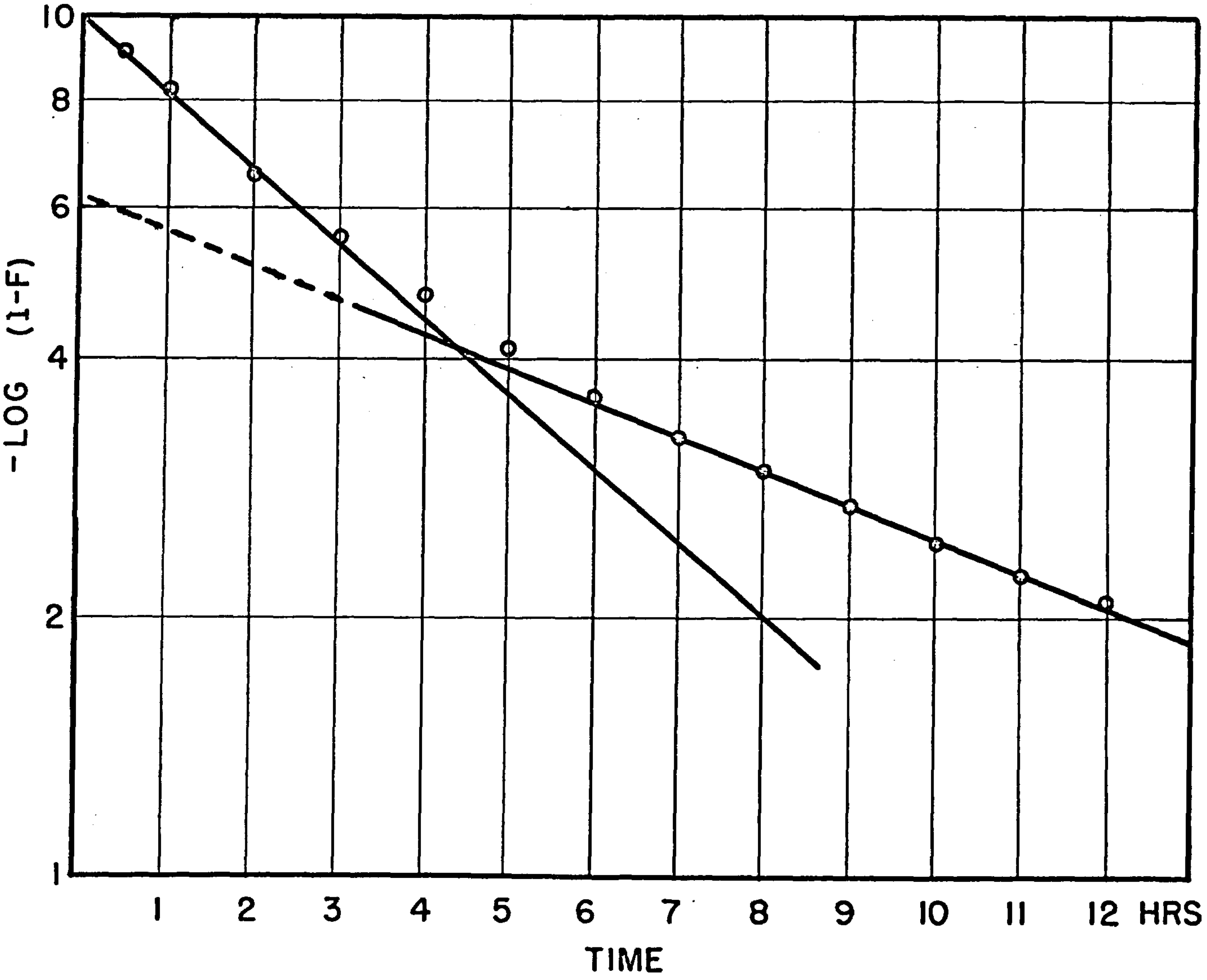

FIG. 4 - FRACTION EXCHANGE AS FUNCTION OF TIME. 10^{-1} M $Zn(NO_3)_2$ SOLUTION.

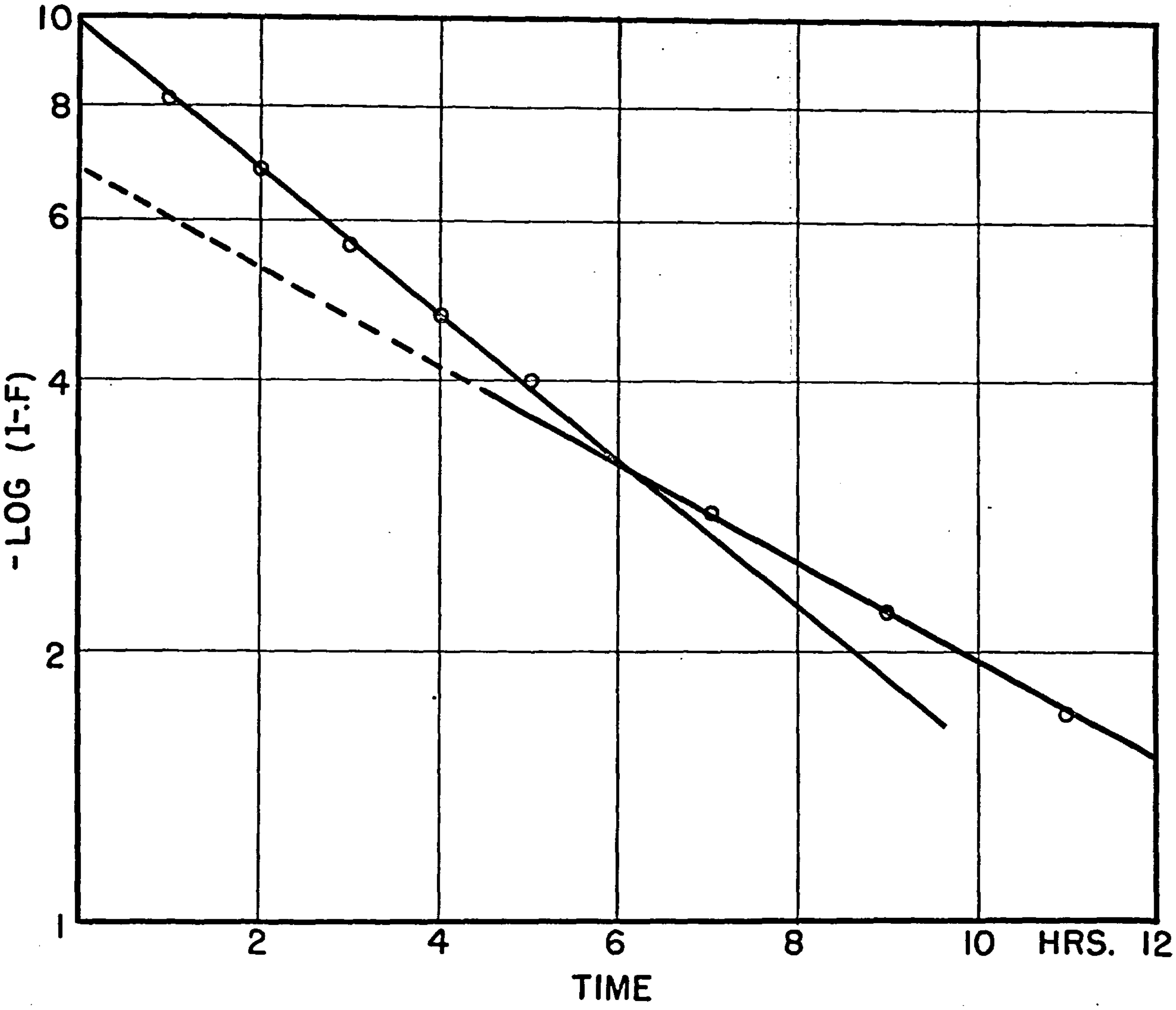

FIG. 5 - FRACTION EXCHANGE AS FUNCTION OF TIME 10^{-2} M $Zn(NO_3)_2$ SOLUTION.

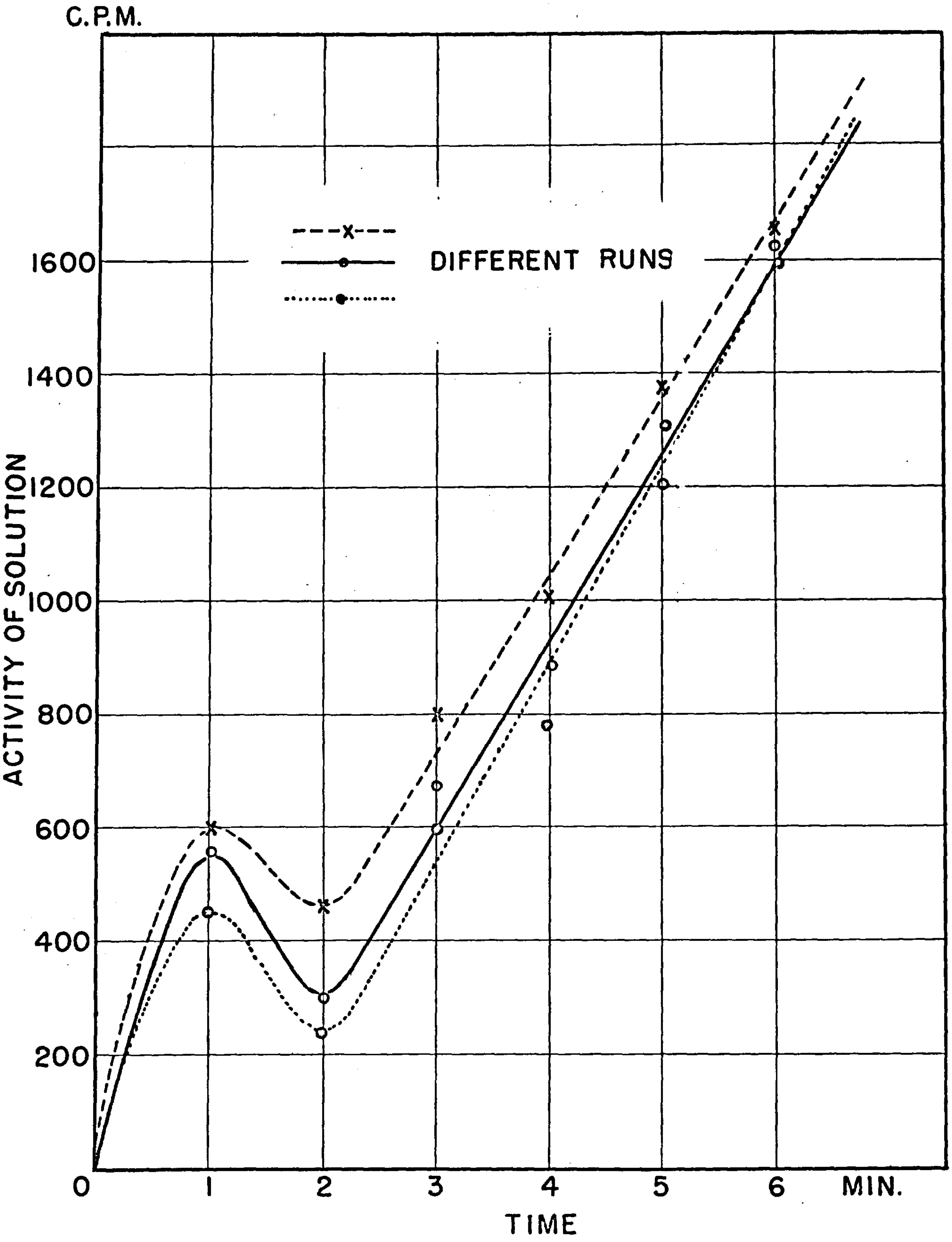

FIG. 6 - EXCHANGE BETWEEN ACTIVE METAL AND INACTIVE $Zn(NO_3)_2$ SOLUTION.

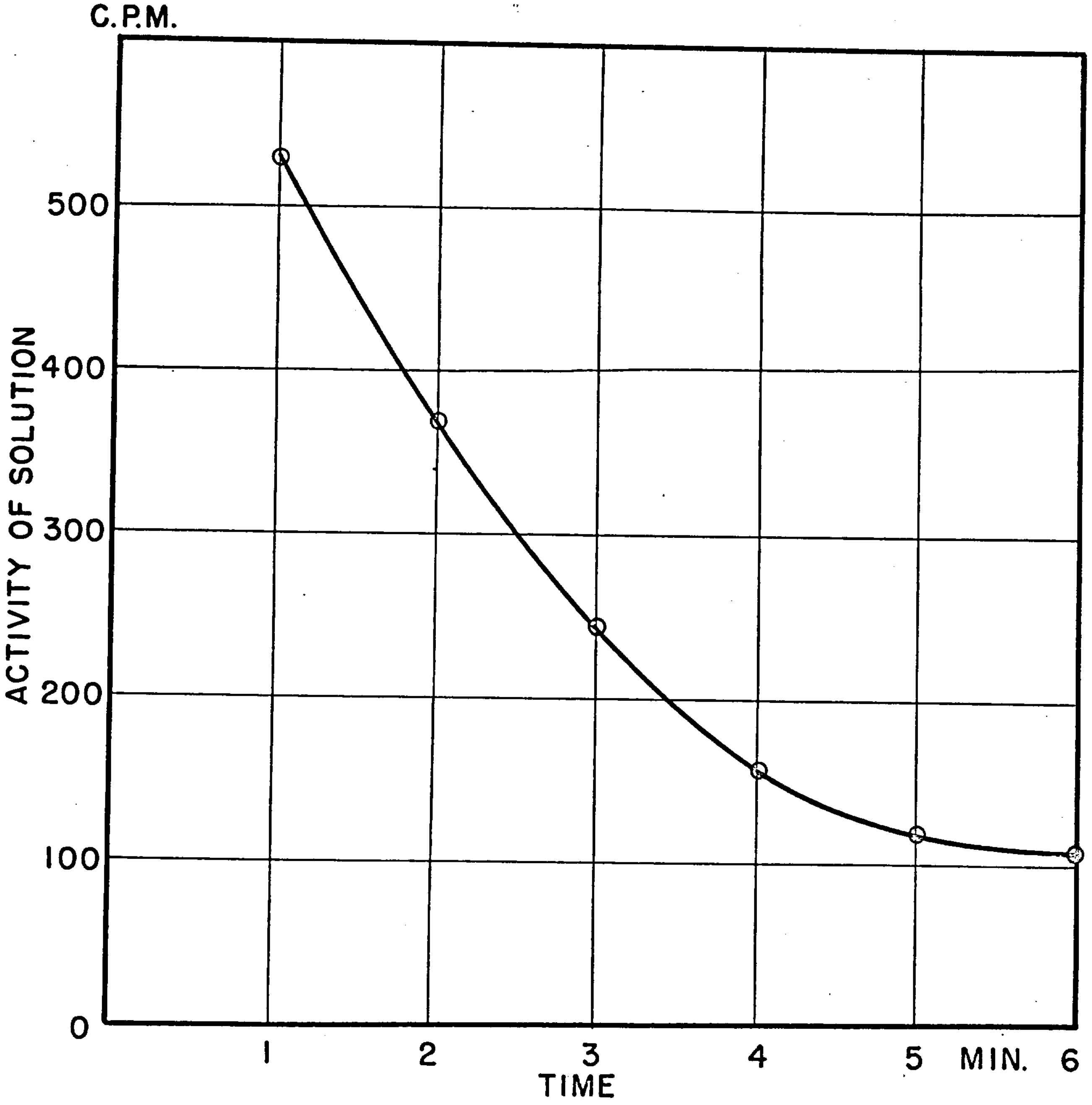

FIG. 7 - EXCHANGE BETWEEN ACTIVE METAL AND INACTIVE $Zn(NO_3)_2$ SOLUTION.

Figure 6 it was calculated that a rapid exchange takes place: in 6 minutes, twenty apparent layers of atoms took part in the exchange.

3. Bi-crystal Experiments

The autoradiographs of three bi-crystal samples shown in Figure 8 showed a preferential exchange in one of their crystal faces. At the same time it was observed that the difference in activity acquired by each crystal soon disappeared and that after 30 seconds an even distribution of activity was obtained. (Figure 8a corresponds to 10 sec immersion, 8b to 20 sec, and 8c to 30 sec.)

Preferential exchange was shown also by a bi-crystal that was markedly twinned, and it was seen that exchange takes place much more slowly in the twinning plane (Figure 9).

A sample pretreated for 24 hours and half-etched showed much higher activity in the oxide layer than in the etched layer, but in this latter area a clear difference could be seen in comparing the exchange between each grain (Figure 10).

The autoradiograph of Figure 11 shows that there is a difference in activity between worked and unworked areas, as has been shown in silver and other metals (9).

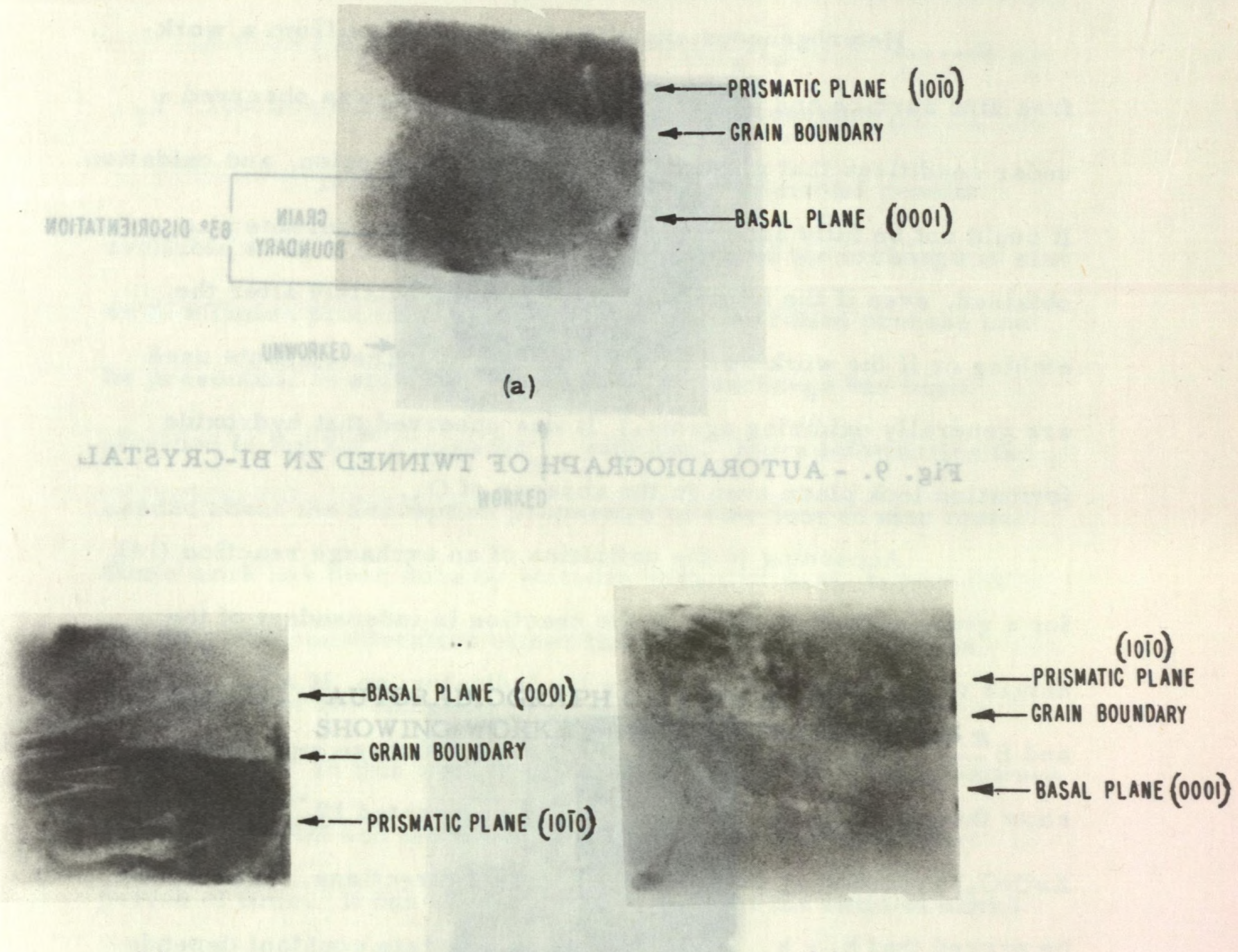

Fig. 8. - AUTORADIOGRAPHS OF ZN BI-CRYSTALS

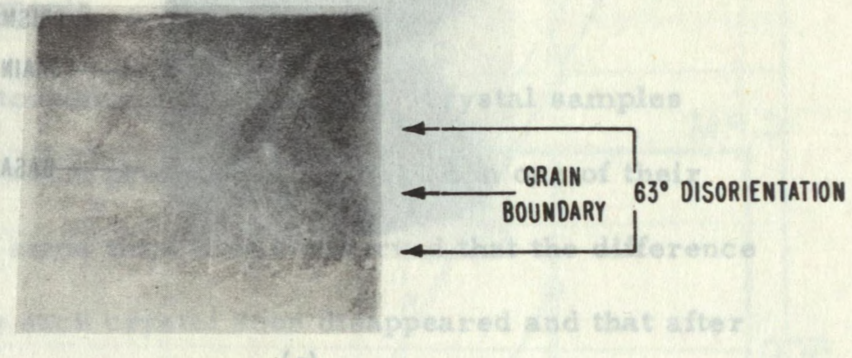

Fig. 9. - AUTORADIOGRAPH OF TWINNED ZN BI-CRYSTAL

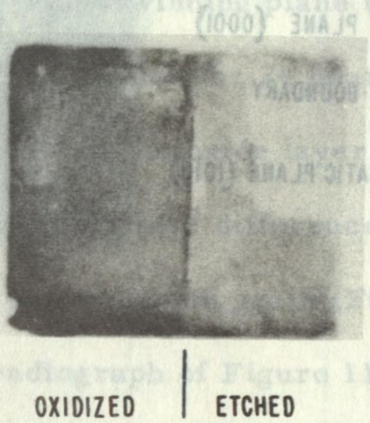

Fig. 10. - AUTORADIOGRAPH OF A PREFERENTIALLY OXIDIZED ZN BI-CRYSTAL

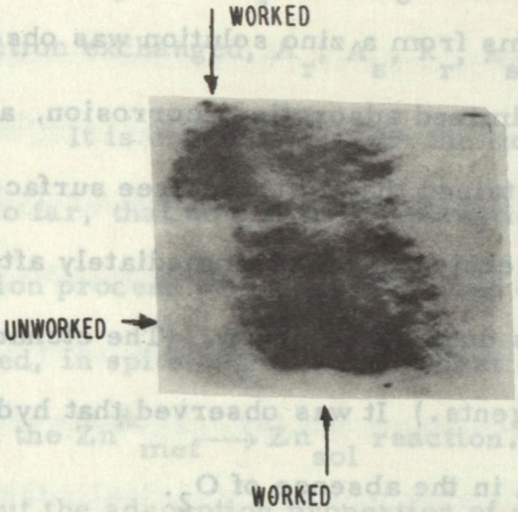

Fig. 11. - AUTORADIOGRAPH OF A ZN BI-CRYSTAL SHOWING WORKED AND UNWORKED AREAS

DISCUSSION AND CONCLUSIONS

Heterogeneous exchange between atoms from a work-free zinc surface and atoms from a zinc solution was observed under conditions that minimized adsorption, corrosion, and oxidation. It could not be fully ascertained that an oxide-free surface was obtained, even if the immersion followed immediately after the etching or if the work was done under argon. (The etchants used are generally oxidizing agents.) It was observed that hydroxide formation took place even in the absence of O_2.

According to the definition of an exchange reaction (14), for a given system the rate of the reaction is independent of the nature of the compound tagged by the indicator; so, if $A^{*} \xrightarrow{k_1} B$ and $B^{*} \xrightarrow{k_2} A$; then $k_1 = k_2$. The results of these experiments show that an exchange takes place with de-aerated 10^{-1} or 10^{-2} M $Zn(NO_3)_2$ solution at pH 5.2 or 6.2 in both directions. It could not be proved that $k_1 = k_2$, because the specific rate constant depends on various factors and the conditions of the experiments were different in each case.

It has also been seen that the results of the $Zn^{*}_{sol} \longrightarrow Zn_{met}$ reactions do not fit the equation $-\log(1-F) = kt$, because the reaction is controlled by either a recrystallization or a self-diffusion process. It would fit an exponential function of two terms, as Matsura (5) found, of the general form:

$$F = 1 - \left[A_r \exp(-k_r t) + A_s \exp(-k_s t)\right] \qquad .....2)$$

F = fraction exchanged, A_r, A_s, k_r, k_s = constants.

It is concluded, from the experimental results available so far, that no positive explanation of the exchange of zinc as a diffusion process or a recrystallized controlled process can be presented, in spite of the fact that fast exchange has been obtained in the $Zn^{*}_{met} \longrightarrow Zn_{sol}$ reaction. More information is needed about the adsorption properties of zinc ions in zinc metal. Some work has been done by Matsura with zinc dust, but he did not take into consideration either the surface oxidation or the preparation of the samples.

In this work a deep exchange has been found between the active metal and the inactive solution in a relatively short period of time. It can be assumed, then, that the ratio of atoms adsorbed to atoms exchanged must be a very small one. King and Schochet (15) found, in silver experiments, that 50 times as much silver exchanged as silver salt was adsorbed, one monolayer forming at the adsorption equilibrium. The explanation of the preferential exchange that takes place with zinc bi-crystals is open to argument. The exchange reaction is not a simple one. In addition to exchange with surface atoms, there always takes place an exchange resulting from local cell action, as postulated by Hevesy (1). It is the author's suggestion that the rapid exchange noticed at the beginning of the experiments is due mainly to this type of mechanism, ie, one crystal face behaves as an anodic area and the other as a cathodic.

It has been known for some time that the different crystallographic faces of a metal have different electrochemical and physical properties, and hence different electrode potentials, dissolution and oxidation rates, and adsorption. Preferential adsorption could also take place, but the solutions were very dilute, adsorption is a relatively slow process, and finally the immersion periods were very short.

The experiment performed with a half-oxidized and half-etched sample showed that the oxide layer picked up much more activity than did the etched one. This would indicate that the preferential exchange could be caused by preferential oxidation (possibly by the same electrochemical corrosion mechanism as mentioned before). The fact that the activities were soon evened out in the samples indicated that a very small "exchange current" flowed between the two "electrodes".

In support of this idea, the recent work of Bushmanov and Vozdvizhenky (7) shows that different crystal faces of zinc single crystals that are connected together act as a galvanocouple. They also found that the different faces exchange at different rates.

It has to be pointed out that in the carrier-free solutions the concentration of the tracer is so low that the products formed may not be the same as those formed at ordinary concentrations, because of rate effects, equilibrium shifts, etc. In some respects this is an advantage, because with so low a concentration no spurious precipitations can happen, since the solubility product cannot be exceeded.

No final explanation was found for the sharp peaks at the first part of the curves of Figure 6. There is some evidence mentioned in the literature that zinc has an intermediate stage of oxidation: Zn^+. So, it is proposed as a conjectural explanation of the curves of Figure 6 that the reaction $Zn \longrightarrow Zn^+$ occurs, followed by fast dismutation $Zn^+ \longrightarrow Zn^\circ + Zn^{++}$, the system not being in equilibrium. The possibility is ruled out that only an accidental factor is involved, such as some activity resulting from impurities in the irradiated samples, because no such impurity was found on checking the exchange solution with a gamma-ray spectrometer.

While there is strong evidence that an exchange reaction is involved as a first step in the activity pick-up, this reaction is likely accompanied by other processes, eg corrosion and oxidation.

There are considerable variations in the exchange processes described in the literature, mainly because of difficulties in obtaining reproducible, clean metallic surfaces that correspond in composition and structure to the bulk of the metal.

It is believed that the surfaces used in this work were of a cleanness comparable with or better than those used in published experiments, but the variations in surface conditions make direct comparisons of results difficult. Even in the case where an oxide-free surface is obtained it is always covered by a thin layer of gases and vapours. Holm and Meissner (16) in their work on platinum had to heat platinum wires for hours at 1100°C in a perpetually evacuated glass vessel, the walls of which were cooled with liquid hydrogen, to obtain a thoroughly degassed surface.

Another problem that has to be solved is to obtain an exact knowledge of the "true" area of the sample, as compared with the geometric area, because in exchange experiments the results are generally expressed in "number of exchanged atom layers".

Several methods are available to determine the surface roughness of metals and some general information is available about the average height of the "hills" and "valleys" in a metallic surface (17); this magnitude is of the following order:

In steel, lapped or polished - 2 to 25 x 10^{-6} cm
die-cast - 40 to 400 x 10^{-6} cm
ground - 50 to 250 x 10^{-6} cm
turned, shaped - 300 to 600 x 10^{-6} cm

There are no similar figures for zinc, but since it is a very soft metal and flows very easily during the polishing operations, one can expect its figures to be different by a factor of 10 at least.

The results can be summarized as follows:

1. The zinc exchange reaction takes place with work-free zinc surfaces in de-aerated 10^{-1} and 10^{-2} M $Zn(NO_3)_2$ solutions at pH 5.2 to 6.2, and it takes place in both directions.

2. The reaction $Zn^{++}_{sol} \longrightarrow Zn^{\circ}_{met}$ cannot be described by the simple equation log (1-F) = -kt, in which F is the exchanged fraction, k is a constant, and t the time of exchange.

3. Fast exchange has been found in the reaction $Zn^{\circ}_{met} \longrightarrow Zn^{++}_{sol}$, indicating that adsorption was low compared with exchange under the conditions of the experiments.

4. ZnO and $Zn(OH)_2$ are formed in the metallic samples, preventing the exchange from continuing. $Zn(OH)_2$ is formed even in the absence of air.

5. Preferential exchange has been found to take place in zinc bi-crystals.

6. It is suggested that the deep exchange mechanism involved in the short periods is a local cell action, one crystal behaving as an anode and the other as a cathode.

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