

Radio Tracer Studies of Metal-Metal Ion Exchange

If a metal specimen is placed in an aqueous solution containing its own cation and an inert anion such as ClO_4^- , exchange between the solid metal and the metal ion in solution takes place (Fig. 1). The exchange can be followed by introducing a radioactive isotope of the metal under consideration into either the solution or the solid and then using a suitable detector to measure change in activity.

It is probable that the first exchange experiments were performed by von Hevesy (1), who immersed metallic lead in lead nitrate solution containing ^{212}Pb as the tracer. He found that within a very short time lead acquired radioactivity equivalent to complete exchange of more than 100 monolayers. This rapid exchange was explained on the basis of a high rate of self-diffusion within the metal. It is very possible, however, that corrosion of the lead occurred, causing a deposit of Pb^{++} ions to form on local cathodic spots. This deposition of lead would lead to an increase in activity of the specimen over that due to exchange and would result in high values for the exchange current. In any case, these experiments opened the way for many other investigations.

There are two fundamental ways in which exchange studies have been made to yield fruitful data. The first has been to measure total activity acquired as a function of time. Letting

$$da/dt = a_0 D^{1/2} (\pi t)^{-1/2} \quad (1)$$

equal the activity flux per unit area at the surface of the metal, then integration yields

$$a_t = 2a_0 \pi^{-1/2} (Dt)^{1/2} \quad (2)$$

where a_t is the total activity acquired by the metal at time t , D is the self diffusion coefficient and assumed to be a constant, and a_0 is the surface concentration.

The second way has been to measure distribution of activity as a function of depth (2). To describe concentration of exchanged material as a function of depth, the equation

$$a_x/a_0 = \text{erfc} [x/2(Dt)^{1/2}] \quad (3)$$

applies (3), where erfc is the complement of the error function and a_x is the concentration of exchanged material at depth x . The equations used here arise from the theory of homogeneous diffusion and are the exact analogues of the equations for thermal conductivity in a semi-infinite solid (4). The boundary conditions may, to a first approximation, be taken to be those of a semi-infinite solid (in contact with a heat source) because it can be assumed that exchange is taking place equally at each of two faces of a disc or at one face of a disc only. In addition, sufficient material exists in solution so that

during the course of an experiment a_0 is approximately constant, and the thickness of the disc is large relative to the distance traversed by the radioactive material.

In the case of activity versus time experiments, a_t is measured with a suitable counter at time t , and either a_0 or D is assumed known. In experiments where activity is measured as a function of depth a_x , x and t are determined directly and again either a_0 or D is assumed known. It is of interest to note parenthetically that if a_0 is taken as the bulk metal concentration, D can be shown to have a value close to the self-diffusion coefficient of the metal (3).

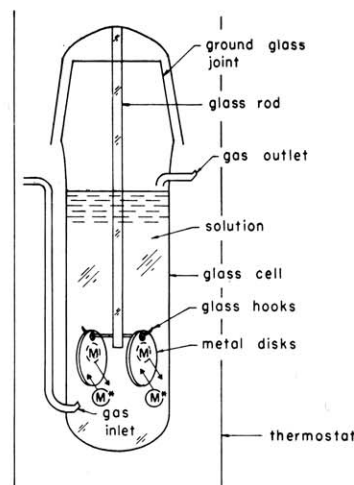


Figure 1. Cell for metal-metal ion exchange studies. M^* is tagged species of M .

Possible Mechanisms for Exchange

Four exchange mechanisms may be considered. Any one of them might apply but they are not all equally likely. It is also quite reasonable to believe that different metals might exchange via different mechanisms.

Mechanism I. Rapid exchange followed by depletion of tracer in the vicinity of the metal specimen. This mechanism, if applicable, would allow for diffusion (in solution) control.

Mechanism II. Exchange taking place through an adsorbed layer. If this were the process and if the activity of adsorbed salt could be measured, it would be found to be deficient in tracer. The rate controlling step would be incorporation of tracer into the adsorbed layer and would imply the necessary corollary that exchange between adsorbed layer and metal is rapid.

Mechanism III. This mechanism would be the converse of II, i.e., exchange between adsorbed layer and metal is slow.

Mechanism IV. Any of the previously described processes could be fast and diffusion within the metal might be rate determining.

Experiments

Zinc (5, 6)

Exchange studies were made with polycrystalline coupons of zinc which were immersed in $\text{Zn}(\text{ClO}_4)_2$ solutions. ^{65}Zn was used as the tracer. In the presence of air, corrosion took place to such an extent that much activity pickup was due to precipitation rather than exchange. When dichromate ion was added as a corrosion inhibitor, activity no longer increased with time. This was particularly curious since the metal does not become passive. Whether an impervious oxide film is formed or all adsorption "sites" are occupied by some chromium compound is not known. If air was eliminated from solution, exchange took place and seemed to be controlled by the rate of self-diffusion within the metal.

From the slope of the curve of a_t versus $t^{1/2}$, values for D were obtained. These values ranged from 7×10^{-8} cm^2/sec to 1.3×10^{-10} cm^2/sec if a_0 was set equal to the solution concentration of dissolved salt. Since equation (2) assumes homogeneous diffusion, care must be taken in interpreting results of experiments carried out with polycrystalline material because the diffusion rate depends upon grain size.

Fisher (7) gives a relationship between volume diffusion and grain boundary diffusion as:

$$D_b = 2D_v^{1/2}(\log e)^2/\delta (d \log a_x/dx)^2(\pi t)^{1/2} \quad (4)$$

where D_v is the volume diffusion coefficient, δ is the width of a "dislocation pipe," and e is the natural logarithm base. Assuming this equation to be correct, values for D_b can be calculated using the results of dry diffusion experiments on single crystals of zinc (8, 9). At room temperature D_b is 6.3×10^{-12} cm^2/sec , a value far less than those obtained from exchange experiments. Since at room temperature most of the diffusion in a polycrystalline metal is along grain boundaries, one would expect D_b from equation (4) and D from equation (2) to be about the same. If a_0 is now assumed to be the bulk density of zinc (0.11 gram atoms/ cm^3), D_b and D become almost identical. The results of experiments on polycrystalline zinc lead to the conclusion that initial exchange takes place through an adsorbed layer and that continued pickup of activity with time is due to diffusion in the metal.

Studies of single crystals undergoing exchange should yield more useful data since equation (2) would apply more exactly than it does to polycrystalline metal. Such experiments (6) gave interesting results. D turned out to be on the order of 10^{-18} cm^2/sec when a_0 was assumed to be the bulk density of zinc. This is intermediate between extrapolated values of D for diffusion perpendicular to the symmetry axis of zinc (9.1×10^{-19} cm^2/sec) and parallel to the symmetry axis (1.3×10^{-17} cm^2/sec). It also seemed that complete exchange of a monolayer took place quite rapidly (less than 30 sec). From these results it could be concluded that adsorption and exchange were quite rapid and that continued increase in activity resulted from diffusion within the metal (mechanism IV). Unfortunately, corrosion took place to some extent in all experiments with zinc. This meant that studies of a_x as a function of x (eqn. 3) could not readily be done because for such

experiments immersion times are necessarily long and extensive corrosion would take place.

Cadmium (3, 10)

Cadmium is a very satisfactory metal to work with because of its exceedingly high self-diffusion coefficient, its corrosion resistance, and its ease of electropolishing. ^{115}Cd is used as the tracer. Work with single crystals will be discussed because of difficulty in interpretation of data on polycrystalline specimens. A rod of single crystal cadmium was cut into discs 1.5 mm thick. These discs were immersed in tagged $\text{Cd}(\text{ClO}_4)_2$ solutions for various periods of time. Equation (2) was assumed to apply and with a_0 set equal to the cadmium bulk density, self-diffusion coefficients in substantial agreement with those in the literature were obtained. Figure 2 shows a typical plot of a_t versus $t^{1/2}$ for cadmium in a solution of its own ions and is also indicative of the type of behavior encountered with zinc and silver.

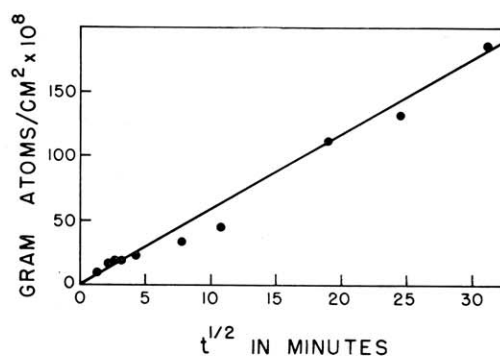


Figure 2. Activity as a function of time.

Since D is quite high, 10^{-15} cm^2/sec at room temperature, sufficient diffusion takes place during the course of experiments (about one week) that activity as a function of depth can be explored with the hope of obtaining meaningful data. For cadmium, an electropolishing technique was adopted whereby thin layers could be removed from the discs leaving a uniform surface that was bright and shiny. From the weight of the metal removed, the number of monolayers could be calculated and hence the distance of penetration into the disc. By measuring the activity after each electropolishing, the activity at each successive "level" could be obtained. Figure 3 shows a plot of a_x versus x .

Silver (2, 6, 11)

The most extensive metal-metal ion exchange studies have been made with silver, possibly because corrosion is not a problem. I. I. Tingly (11) measured the rate of exchange between the (111), (100), (110), and (311) surfaces of single crystal silver using ^{110}Ag as the tracer. It was concluded that the initial step in the process is most likely adsorption which takes place very rapidly (about one or two sec), followed by exchange which reaches an equilibrium rate after about 15 minutes. The rate controlling process then seems to be self-diffusion.

Two outstanding points of this study were the "reverse exchange" experiments and the correlation of diffusion rate with the number of silver atoms in a given crystal plane. Using equation (4) with a value of 1.44

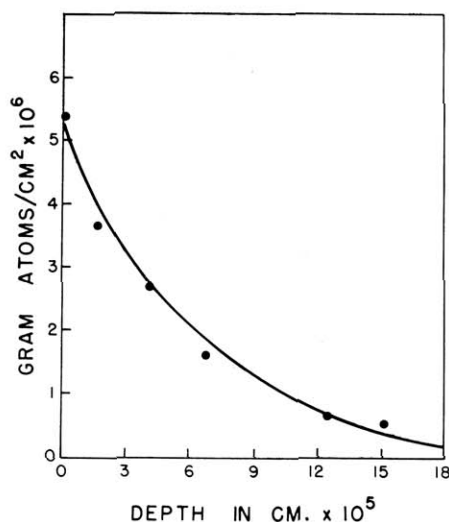


Figure 3. Residual activity as a function of depth.

$\times 10^{-8}$ cm for δ and a value of 4.5×10^{-33} cm²/sec for D_v , the following results were obtained:

$$D_b = 2.1 \times 10^{-21} \text{ cm}^2/\text{sec} \text{ for (111) plane}$$

$$D_b = 1.5 \times 10^{-21} \text{ cm}^2/\text{sec} \text{ for (100) plane}$$

$$D_b = 6.1 \times 10^{-22} \text{ cm}^2/\text{sec} \text{ for (110) and (311) planes}$$

This decrease in D_b is roughly proportional to the decrease in concentration of atoms in these four planes. Note that D_b is here used because penetration of silver atoms into silver seems to follow grain boundary diffusion at room temperature. This probably indicates that silver diffuses along dislocations rather than from lattice site to lattice site.

Due to the "reverse" exchange studies, i.e., studies where the metal specimen was made active and the solution inactive, it can be said with great certainty that the whole process is an exchange. The metal became deactivated in an exactly analogous manner to the way in which it became active. If exchange did not occur, the initial portion of the curve of desorption versus time would not be the reverse of the adsorption of activity versus time curve.

In the exchange study where a_x was measured as a function of x , the etching technique was a quick dip of the specimen in a CrO_3 and H_2SO_4 solution. King, *et al.* (10), found that electropolishing did not work well as a technique for removing layers of silver.

Iron (12)

Iron seems to be an anomaly in the world of self-diffusion and exchange experiments. Polycrystalline iron, immersed in active $\text{Fe}(\text{ClO}_4)_2$ and $\text{Fe}(\text{ClO}_4)_3$, showed negligible penetration of tagged iron. All pickup of activity could be attributed to corrosion products and it is even doubtful that surface exchange occurs at all. Why this should be is not at present known.

Discussion

It seems apparent that in the metals Zn, Cd, and Ag the exchange process is reasonably described by some form of mechanism IV. However, there are still many interesting questions unanswered. What is the detailed mechanism for the charge transfer process (electrons must also exchange at sometime). What is the effect of inhibitors on the surface? What is the structure of the liquid in the immediate vicinity of the disc? What is the effect of crystal imperfections on the rate of exchange and the diffusion mechanism? These are a few of the problems which should intrigue chemists who might wish to give some thought to this area of chemistry. It is also entirely possible that an understanding of metal-metal ion exchange could some day shed light on the overall problem of metal dissolution as well as afford an excellent way to measure self-diffusion coefficients at low temperatures.

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