

Exchange of Radioactive Silver with Silver Chloride Suspensions

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These values are believed to be accurate to about 0.001Å. According to Jette³ and co-workers, the lattice constant of 4.043Å corresponds to a gold-iron solid solution containing 3 percent of iron by weight. This seems to disagree with our results hitherto described, as we always found in an annealed specimen a phase with a Curie temperature near room temperature which, presumably, contained more than 8 percent of iron. The explanation is that, during cooling, the annealed specimen in this case was left at 340°C overnight so that the precipitated gold-rich phase should almost be in equilibrium at that temperature. If we check up with Jette's³ solubility limit curve again, we find that the solubility of iron in gold at 340°C is just about 3 percent. The annealed specimen for x-ray investigation was later checked by magnetic measurements. The results are about the same as shown by the curves in Fig. 2. The only difference is that, in this case, we no longer find any Curie point near room temperature.

Thus, both magnetic and x-ray measurements prove the non-uniform nature of the precipitation process in the gold-iron alloys. The absence of the precipitated iron-rich phase in the Debye-Scherrer pattern of the annealed specimen shows that its quantity must be very small. This supports the conclusion obtained by Jette³ and co-workers that the intermetallic compound AuFe₃ in Hansen's¹ phase diagram does not exist and that the solubility of gold in α -iron is very small. The fact that the lines of the precipitated gold-rich phase are fine in contrast with the spotted lines of the original supersaturated phase also substantiates the conclusion arrived at by previous investigators⁵ that in non-uniform precipitation, the original grains in the sample are not preserved.

In conclusion, the authors wish to express their appreciation to Dr. B. M. Loring for taking the x-ray pictures.

⁵ R. Becker and W. Döring, *Ferromagnetismus*, Sections 26 and 27 (Springer, Berlin, 1939).

Exchange of Radioactive Silver with Silver Chloride Suspensions

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From exchange experiments on radioactive silver in solution with silver chloride in suspension, it can be shown that the silver ions in solution are constantly exchanging with the silver ions in the precipitate. This exchange is not limited to the surface of the crystals, but, probably by means of self-diffusion, is propagated into the precipitate. A steady radioactive state obtains when a homogeneous distribution of the radioactive silver throughout the whole system is reached. The time necessary to obtain a given fraction of complete exchange for a given amount of precipitate depends strongly on the area of the crystal surface.

THE exchange of silver ions in solution with silver chloride in suspension was studied, using radioactive silver as an exchange indicator. It was observed that the radioactive silver undergoes quite a rapid exchange with the precipitate, indicating that in all cases after sufficient time, a homogeneous distribution of the radioactive silver throughout the whole system can be obtained. The phenomenon was studied in detail with respect to the concentration of the silver in

solution and the amount of precipitate used, with respect to the previous treatment of the silver chloride leading to different crystal sizes and consequently to different surfaces as determined by the dye adsorption method, and with respect to the effect of temperature. The influence of dyes previously adsorbed on the precipitates was also investigated. A possible interpretation of the observed curves in terms of diffusion and crystal size is given.

APPARATUS AND PROCEDURE

The arrangement of the apparatus is shown in Fig. 1. The shaking beaker was constricted to prevent splashing of the precipitate throughout the whole vessel. As can be seen, it was suspended on a rubber tube and shaken by an eccentric pulley and could be immersed in a small bath into which water was pumped continuously from a large thermostat. The temperature was $25^{\circ} \pm 1^{\circ} \text{C}$.

For the radioactivity measurements a counter system was used. The counter tube was of the liquid jacket pipette type already described.¹ For each experiment a clean Corning fritted glass dipping filter was used. The counter tube was connected to a Neher-Harper self-quenching arrangement in connection with a Reich scale of four scaling circuit and a Cenco counter. A timer accurate to $\frac{1}{10}$ second was used for automatically timing the counting interval. The counting system was tested in regard to reliability. The radioactive silver was produced by proton bombardment of palladium in the University of Rochester cyclotron. The palladium was dissolved in nitric acid, silver added as

carrier, and precipitated as silver chloride. The precipitate was washed and the silver electroplated from ammonia solution. A stock solution of radioactive silver nitrate was prepared by dissolving a weighed amount of this electrolytic silver in nitric acid. After evaporation to dryness the silver nitrate was dissolved in a known amount of water. Non-radioactive silver nitrate was prepared from the purest available silver according to the standard procedure. The sodium chloride solution was prepared from pure sodium chloride.

The silver chloride for the experiments was always prepared in the same way, but was given different subsequent treatments. To measured amounts of 0.10 *M* sodium chloride, 1 ml of 0.1 *M* nitric acid was added and to this solution a 1-percent excess of 0.10 *M* silver nitrate was added with stirring in about 20 seconds. All the manipulations with the precipitate were done in photographically inactive red light. After the treatments to be described below, the coagulated precipitate was centrifuged at low speed for 3 minutes, then the liquid was decanted, the precipitate shaken for 1 minute with 30 ml of 10^{-3} *N* nitric acid, centrifuged, and the shaking repeated with water. The suspension was centrifuged again and the precipitate drained and partly dried in vacuum for a short time. To the damp precipitate (containing about 0.1 g water) 40 ml of the radioactive silver solution of a previously determined radioactive strength and known silver content was added and shaken in the apparatus described. After an arbitrary time, five to twenty minutes, liquid was drawn into the counter (filling time about 30 seconds) and the counts recorded during four minutes. The liquid was then returned to the original solution by applying pressure. The time was measured from the addition of the radioactive solution to the time when the counter tube was half filled with the liquid. The uncertainty in this measurement is about 30 seconds. Somewhat higher activities can be expected with this method of determining the radioactivity, because 6 ml solution removed from the bulk of the solution each time for about 5 minutes while its activity was being measured, took no part in the exchange. This error becomes small after long shaking periods. The error introduced by the

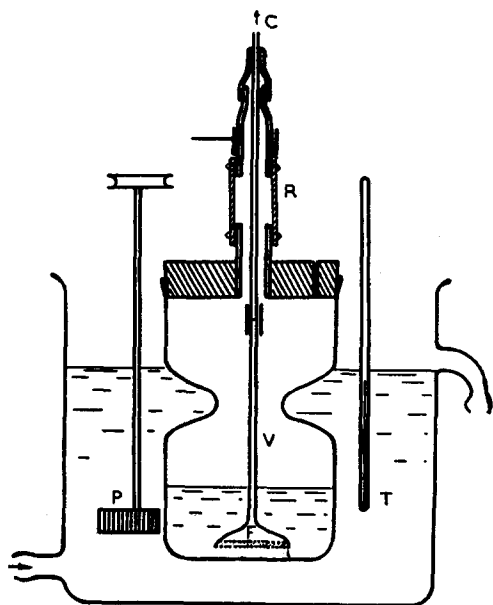


FIG. 1. Shaking arrangement for the exchange experiments. (*F*) Fritted glass filter; (*P*) eccentric pulley for shaking the vessel (*V*); (*R*) rubber tube holding the vessel; (*C*) connection to a liquid jacket counter tube.

¹ A. Langer, J. Phys. Chem. **45**, 639 (1941).

statistical fluctuations in the counting rate was also a few percent because of the relatively low number of counts taken. Since the 45-day silver isotope was predominant, no corrections for decay during a single experiment were necessary.² The measured activities were corrected for the background.

EXPERIMENTAL RESULTS

The first experiments were done with precipitates prepared by shaking them for 5 minutes with the mother liquid after precipitation. Figure 2 shows activity-time curves obtained with the indicated amounts of silver in solution and silver in the precipitate. It can be seen that the original activity (C_0) of the solution rapidly decreases from the beginning of the shaking and becomes almost constant after about one hour. It was found that this final activity (C_∞) as measured by the counting rate and taken proportional to the concentration of the radioactive silver in the solution, corresponds closely to a homogeneous distribution of the radioactive silver through the whole system given by:

$$C_\infty = C_0(M_s/M_t). \quad (1)$$

Where (M_s) is the amount of silver in the solution and (M_t) the total amount of silver present:

$$M_t = M_s + M_p, \quad (2)$$

where (M_p) is the amount of silver in the precipitate. The computed (C_∞)'s are indicated in Fig. 2 with arrows and it can be seen that these values are reached within the limits of the experimental errors. The similarity of the curves shows that the process of exchange is not markedly affected by the ratio of the silver in solution to that in the precipitate if the precipitates are prepared in the same manner and the curves taken under similar conditions.

That one deals here with only an exchange reaction is indicated by the fact that the total concentration of the silver in solution after the shaking with the precipitate is practically unchanged. This was shown by comparison of the titers of the filtered solutions before and after shaking. It was also found that the exchange is reversible in the sense that if the precipitate is made radioactive and the solution used is

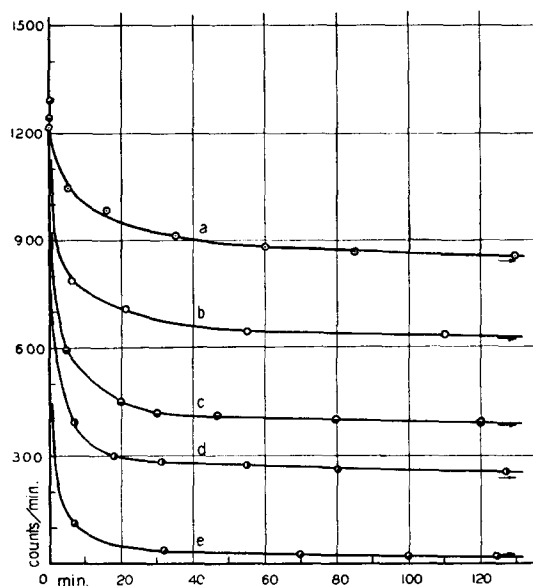


FIG. 2. Radioactive silver exchange—time curves for fresh silver chloride with different amounts of total silver in the precipitate (M_p) and in solution (M_s) at 25°C.

Curve	a	b	c	d	e
M_p mg Ag	10.8	107.9	53.9	107.9	215.8
M_s mg Ag	24.4	104.0	24.4	24.4	3.6

inactive, the activity of the solution increases to a value corresponding to a homogeneous distribution of the radioactive silver.

That the exchange of the silver ions in the solution with the silver in the precipitate must be continuous was indicated by experiments in which a new radioactive solution was added to the solution which was already in exchange equilibrium with the precipitate. It was found that after about the same time as before a new equilibrium was established. Repeated addition of the radioactive silver solution gave again an homogeneous distribution.

Experiments were made to determine whether different treatments of the precipitates, which could change the crystal size by way of recrystallization, have any influence on the exchange rate. Precipitates obtained from 10 ml 0.1 *M* sodium chloride with 10.1 ml of 0.1 *M* silver nitrate had the following treatments: (a) shaken in the mother liquid for five minutes; (b) shaken for one hour; (c) shaken for one day; (d) after addition of 10 ml concentrated nitric acid to the mother liquid, boiled for five minutes; (e) boiled for one hour; (f) boiled in concentrated nitric acid for three hours; (g) recrystallized from

² T. Enns, Phys. Rev. **56**, 872 (1939).

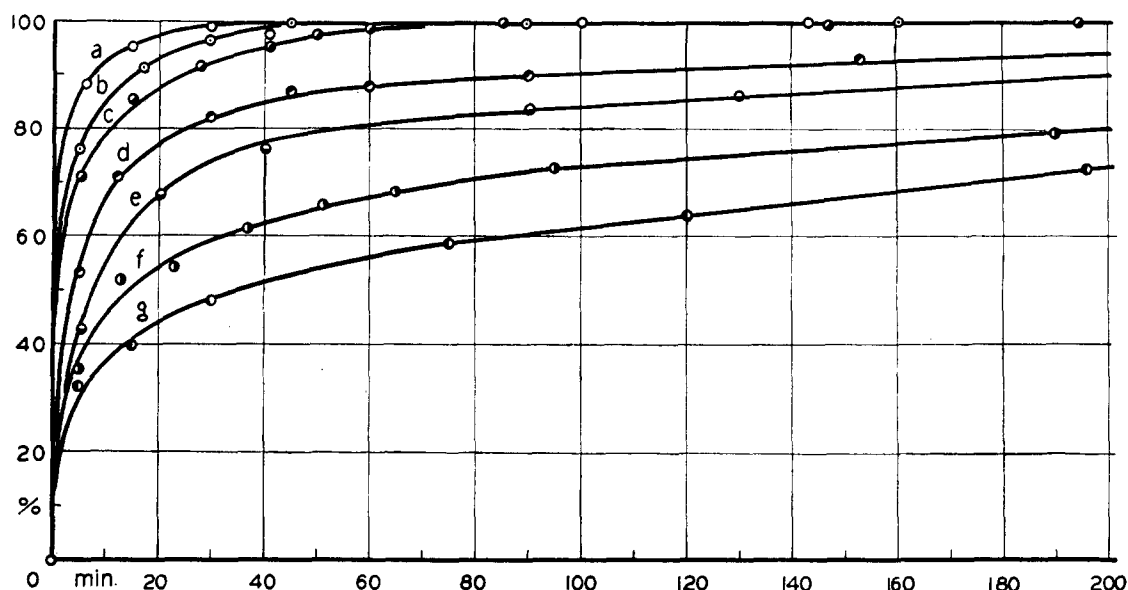


FIG. 3. Radioactive silver exchange—time curves for silver chloride of different origin; $M_p = 107.9$ mg Ag, $M_s = 24.4$ mg Ag, temperature = 25°C , curves *a, b, c*, shaken with the mother liquid, *d, e, f*, boiled with nitric acid, *g* recrystallized from ammonia.

ammonia by slowly heating and stirring. The results obtained with these different precipitates are given in Fig. 3. In order to eliminate differences in the exchange-time curves, resulting from different initial strength of the radioactive solution, all the activity measurements are expressed by the fraction

$$\alpha = \frac{C_0 - C_t}{C_0 - C_\infty} \times 100, \quad (3)$$

where (C_t) is the radioactivity after the time (t) and (C_∞) as computed from Eq. (1). It can be seen that (α) expresses in percent the completeness of exchange. These time-exchange curves indicate that there is a difference in exchange rate for silver chloride precipitates having different treatment. The fresh silver chloride and even that shaken in the mother liquid for one day was in complete equilibrium after about 1 hour, whereas the precipitate recrystallized from ammonia was only 50 percent exchanged in the same time. Microscopic measurements showed that the mean crystal diameter of the fresh precipitates was of the order of 10^{-4} cm and that the crystallites are of a fairly uniform size and a round appearance. The crystals recrystallized from ammonia were

much larger, more plate-like in shape, and not as uniform in size. Because it was difficult to estimate the average size of all the precipitates used, dye absorption measurements on the crystal surface were made in order to determine the surface area which is related to the crystal size. For this reason the precipitates shaken with the radioactive silver were centrifuged, washed twice with 20 ml water, and partly dried. After that, 10 ml of 0.01 percent methylene blue chloride solution were added and the precipitate shaken with the dye for two hours, then the solution was centrifuged and the clear solution compared with the original one by means of a visual photometer. At the same time a similar experiment was done with a precipitate which had not been shaken with the radioactive silver solution. The two methods checked to within 10 percent. Because only small amounts of dye were adsorbed on aged precipitates, the accuracy of measurements is about of that order of magnitude. This indicates that no substantial surface change took place during the experiments. It was found in general that with decreasing amounts of adsorbed dyes the time to reach a given percentage of exchange increases rapidly (see Fig. 4).

To see whether the coating of the precipitate surface with an adsorbed dye prevents the silver

in solution from exchanging with the precipitate, the five-minute old silver chlorides were shaken with one percent solutions of the following dyes in water: fluorescein, eosin, methylene blue, and wool violet. After 30 minutes of shaking the precipitate was centrifuged and then shaken with the radioactive silver solution as described before. Figure 5 indicates that the coatings with the dyes used had almost no effect on the rate of exchange and could not prevent an homogeneous distribution of the radioactive silver. The points obtained give also an indication of the reproducibility of the precipitates and of the measurements.

In Fig. 6 the influence of the temperature on the speed of exchange is given. All the precipitates were prepared from 10 ml 0.1 *M* sodium chloride with 1 ml concentrated nitric acid and 10.1 ml 0.10 *M* silver nitrate boiled with the mother liquid for 30 minutes and shaken for 3

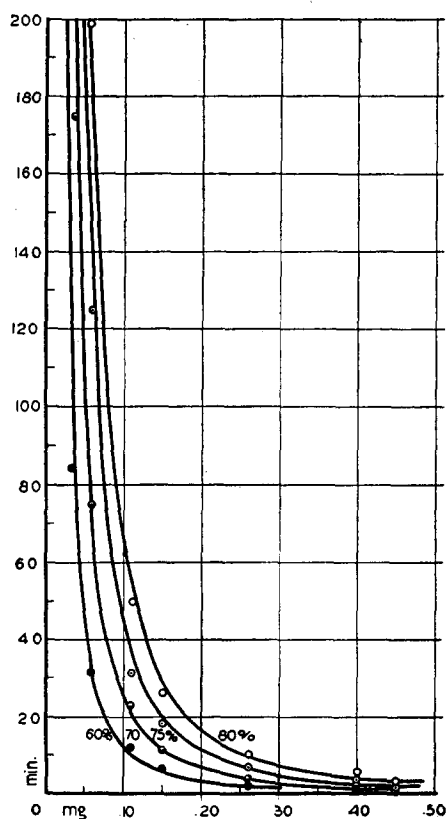


FIG. 4. Curves indicating the relation between the amount of adsorbed methylene blue in mg of dye per millimole of silver chloride and the time to obtain an indicated fraction of radioactive exchange.

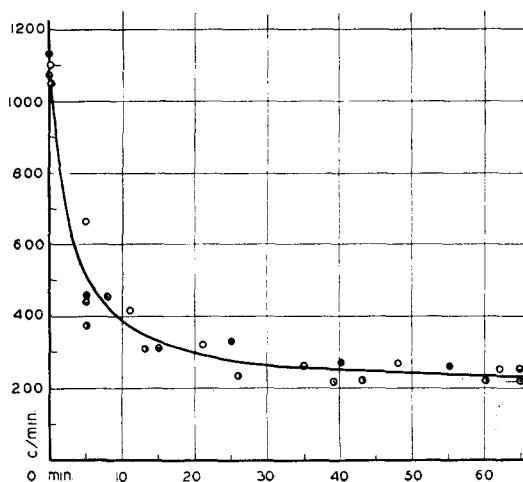


FIG. 5. Radioactive silver exchange-time curves for fresh silver chloride with dye coated surface. \circ = methylene blue; \circ = fluorescein; \bullet = wool violet 5BN; \bullet = Eosin; \bullet = without dye.
 $M_p = 109.7$ mg Ag; $M_s = 24.4$ mg Ag at 25°C.

days at room temperature. This treatment was used to minimize the influence of temperature on the crystal size during the shaking with the radioactive silver nitrate. From this figure it can be seen that the speed of exchange increases markedly with the temperature. Previous experiments with a standard radioactive silver solution showed that the effect of temperature on the counting rate is negligible.

DISCUSSION

To explain the exchange of the silver ions in solution with the silver in the precipitate quantitatively, let us assume that the crystals are spherical and that in addition to a rapid surface exchange, the distribution of the radioactive silver inside the crystal lattice will take place by diffusion. Although the surface exchange is governed also by a diffusion process through the adsorbed layer of solution, this process will probably be very rapid because of the vigorous shaking of the liquid and will be neglected in further considerations. If, therefore, only diffusion into the solid is the main factor governing the exchange process, then the problem of the radioactive exchange in such a simple case is exactly analogous to the cooling of a hot stirred liquid, insulated from outside, in which is immersed a given mass of cold spheres. Experiments done jointly with Dr. Kauzmann have

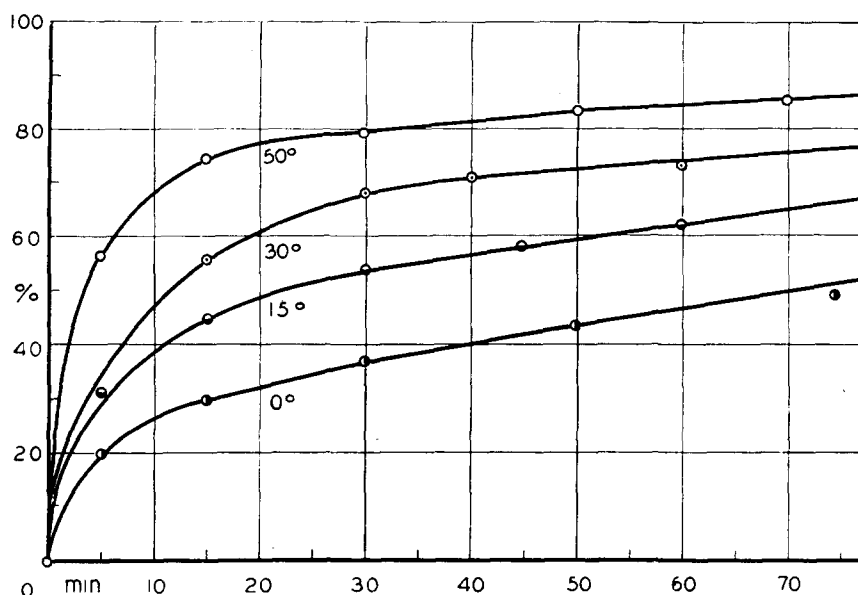


FIG. 6. Radioactive silver exchange curves for silver chloride at 0°, 15°, 30°, and 50°C; $M_p = 107.9$ mg Ag, $M_s = 24.4$ mg Ag.

shown that the cooling-time curve of stirred carbon tetrachloride in a Dewar flask containing a steel ball previously cooled in ice water resembles very closely the radioactive exchange curve. For a given mass of solid and liquid, different rates of cooling can be obtained by subdividing the solids into spheres of different sizes.

Assuming such a diffusion, that concentric surfaces have the same concentration, then this problem may be treated quantitatively by solving the differential equation for Fick's law for a sphere

$$\frac{\partial(rc)}{\partial t} = D_T \frac{\partial^2(rc)}{\partial r^2}. \quad (4)$$

The solutions of this differential equation are known to be of the form³

$$rc = [A \sin \mu r + B \cos \mu r] \exp(-\mu^2 D_T t). \quad (5)$$

Since at the start of the experiment we have no radioactive atoms in the solid, and assuming that the distribution of the radioactive atoms at the surface of the solid is the same as that in the stirred liquid (C_l),

$$C_s(a, t) = C_l(t)$$

³ H. S. Carslaw, *The Conduction of Heat* (Macmillan, 1921), p. 135; R. M. Barrer, *Diffusion in and Through Solids* (Macmillan, 1941), p. 11.

as a boundary condition, where (a) is the radius of the sphere it can be shown⁴ that $C_l(t)$ can be expressed as:

$$C_l(t) = \sum_{n=0}^{\infty} A_n \exp \left[-k_n \frac{D_T t}{a^2} \right], \quad (6)$$

where D_T is the diffusion coefficient at the temperature T of the experiment and A_n and k_n are constants. In general, the concentration of the radioactive material in the liquid at any time (t) after the start of the diffusion process can therefore be expressed as:

$$C_l(t) = f(D_T t/a^2). \quad (6a)$$

The exchange fraction (α) is given in terms of (C_l) by Eq. (3). This means that for a given mass of solid and a given value of (α) the quantity

$$D_T t/a^2 = \text{const.} \quad (7)$$

for uniform spheres of any size.

The radii of the spherical particles in any precipitate are correlated to the surface as found from the dye absorption measurements as follows. Since in all of these measurements the same amount of solid silver chloride was used,

⁴ For more details: H. W. March and W. Weaver, *Phys. Rev.* **31**, 1072 (1928); R. E. Langer, *Tohoku Math. J.* **35**, 260 (1932).

a change in the area of surface must be accompanied by a change in the size and in the number of the spheres. It is easily shown, assuming the crystal to be uniform, that the surface (S) which we can assume to be proportional to the amount of dye adsorbed is related to the radius (a) by:

$$S = K/a. \quad (8)$$

Thus we have for a given value of (α) at a given temperature substituting (8) into (7) the quantity

$$S^2t = \text{const.} \quad (9)$$

That is, for a given amount of precipitate, the product of the square of the surface (expressed, for example, in the amount of large dye molecules adsorbed uniformly only on the surface) and the time required for the same precipitate to arrive at a given fraction of complete exchange with the "tagged" atoms should be constant. In Fig. 4 are indicated the points obtained by plotting the time to reach a given (α) taken from Fig. 3 against the amount of dye adsorbed on the precipitate used. These points fall close to the solid curves which were calculated for $S^2t = \text{constant}$. This quite close agreement, in spite of the necessary assumptions, indicates that simple considerations of crystal size and diffusion rate are sufficient to account for the large variations in the exchange rates with aged silver chloride.

The influence of temperature can also be easily explained. Since the diffusion coefficient for silver ions moving through the silver chloride lattice doubtless changes with changing temperature according to the known relation

$$D_T = D_0 \exp(-Q/RT), \quad (10)$$

where (Q) is the activation energy for the ionic movement, (R) the gas constant, and (T) the absolute temperature. A plot of ($\ln D$) versus ($1/T$) should give a straight line with a slope of ($-Q/R$). But from Eq. (7) we can see that as long as the particle size is constant, the time (t) for a given fraction of exchange (α) to be reached should be inversely proportional to the diffusion constant. Dye absorption measurements indicate

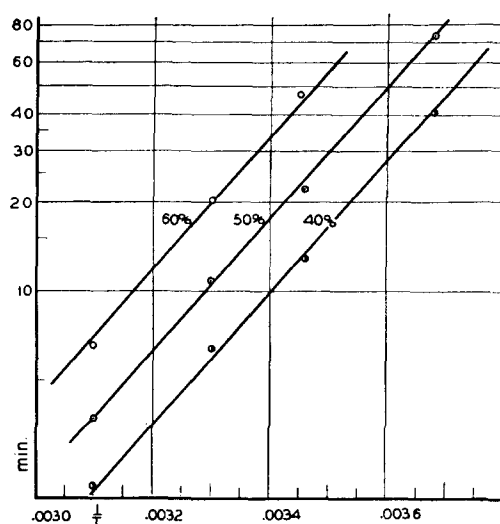


FIG. 7. Time of exchange plots, for a given exchange, versus the reciprocal of the absolute temperature on a semi-logarithmic scale.

that for the precipitates used in the exchange measurements at different temperatures, the surface and hence the particle size is roughly constant. In Fig. 7 are given semi-logarithmic plots of the times to reach various fractions of exchange against ($1/T$). The fact that the slopes of these straight lines are the same is also an evidence for the interpretation proposed here. The slopes of these lines indicate a rather low activation energy for the movement of silver ions through the silver chloride lattice.

The value thus obtained, approximately 10 kcal., seems to be at least of the right order of magnitude as compared with 18.5 kcal. derived from conductivity measurements of Koch and Wagner.⁵ However, much more carefully planned experiments with radioactive silver must be made before any definite value of Q for the flow of the silver ions only can be given.

It is a pleasure to thank Dr. E. U. Condon for his interest in this work and for help in deriving the mathematical expression for the diffusion equation.

⁵ E. Koch and C. Wagner, *Zeits. f. physik. Chemie*, **B38**, 295 (1937); N. F. Mott and R. W. Gurney, *Electronic Process in Ionic Crystals* (Oxford, 1940) p. 47.