The sample is introduced through the sidearm and the cell is evacuated and sealed, leaving 2–3 cm. of sidearm. A blank spectrum, with the cell in its oven, is taken at room temperature: typically such a cell has a transmission *vs.* air greater than 80% to 3.5 μ, 50% to 4.5 μ, and dropping to zero beyond 4.8 μ (*cf.* Fig. 2). The oven is then heated to 10–20° higher than the desired temperature, whereupon the compound sublimes into the cool sidearm. The vapor pressure in the cell is then controlled by the temperature of a small Nichrome-wound glass tube placed over the sidearm.

Infrared Spectra.—Spectra were taken with a Perkin-Elmer Model 21 double-beam recording spectrophotometer with NaCl prism, programmed for maximum resolution (increased source intensity, decreased slit width, expanded scale, and slow scanning). Each spectrum was calibrated against the 3.267 and 3.303 μ bands of Baird polystyrene calibration film. The values quoted are thus internally consistent and accurate to ±5 cm.$^{-1}$. Repetition of these glass cell spectra using LiF optics, as well as the remainder of the infrared spectra of these compounds in an improved hot gas cell, will be reported later. The gas-phase infrared spectrum of C_5H_5Tl in the range 2.0–4.5 μ at 150–249° shows only a single absorption peak at 3101 ± 5 cm.$^{-1}$ (Fig. 2). Slight decomposition, giving a thin black film on the cell, occurred on prolonged heating.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Kinetics of the Silver(I)–Silver(II) Exchange Reaction

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In 5.87 *f* $HClO_4$ the isotopic exchange reaction between Ag^I and Ag^{II} obeys the rate law Rate = $k(Ag^{II})^2$. At 0° the value of *k* is 1020 ± 40 f^{-1} sec.$^{-1}$. The experimental activation energy is 12.5 ± 1.2 kcal. It is proposed that the exchange occurs *via* the reaction $2Ag^{II} \rightleftarrows Ag^I + Ag^{III}$. The exchange rate increases rapidly with decreasing $HClO_4$ concentration. No evidence was found for exchange by direct electron transfer from Ag^I to Ag^{II}, and a limit for the specific rate of this path at 0° is set at <10 *f* sec.$^{-1}$. The rapid-mixing, flow, and quenching techniques used in the measurements of half-times in the range 0.1 to 1 sec. are described.

The silver(I)–silver(II) exchange system was chosen for investigation because the charges of the hydrated cations are lower than those of any other pair of simple hydrated cations previously studied.[2] It was hoped that something of interest could be learned about the importance of coulombic repulsion for such electron-exchange systems.

Perchloric acid solutions were chosen for the reaction media to minimize complex formation. It was necessary to use rather concentrated (∼6 *f*) $HClO_4$ solutions to prevent the rapid reduction of silver(II) by water. Preliminary exchange runs had indicated that the rate of exchange was too large to be measured by conventional techniques, so a rapid-mixing and flow technique first used by Hartridge and Roughton[3] was adapted.

Experimental

Silver Tracer.—The tracer used in these experiments was the 270-day[4] Ag^{110m}, produced by an *n*,γ reaction on silver nitrate, and obtained from the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission. The silver nitrate was dissolved in water, filtered, and before each run an aliquot of the solution was fumed with perchloric acid and diluted with perchloric acid of the desired concentration to form one of the reactant solutions. A four-point decay curve over a period of 600 days showed a half-life of 255 days.

The γ-rays[5] emitted from silver solutions, contained in calibrated six-inch test-tubes, were counted on a scintillation counter having a stilbene crystal.

Chemicals.—Silver(II) solutions were produced by dissolving AgO in 6 *f* $HClO_4$. The AgO was prepared by anodic oxidation of silver nitrate solution.[6] The preparation, analyzed by heating to drive off oxygen and weighing the metallic silver residue, was found to contain 0.99 mole of silver per mole of oxygen atoms. The silver(II) oxide was stable for the duration of the investigation. Because of extensive reduction on solution, silver(II) oxide was also the source of silver(I) in most reaction solutions. For a few runs, silver(I) oxide was also added.

Mallinckrodt A.R. silver(I) oxide, nitric acid, ammonium thiocyanate, ferric ammonium sulfate, perchloric acid, sodium carbonate and Eimer and Amend sodium perchlorate monohydrate were used without further purification. G. F. Smith *o*-phenanthroline was dissolved in 6 *f* HNO_3 to make a 0.10 *M* solution, which was stored at −18°. Perchloric acid (70%) was diluted with doubly distilled water to the desired concentrations, which were determined by titration with standard sodium hydroxide solution. Reaction solutions containing sodium perchlorate were analyzed for perchlorate ion gravimetrically by weighing slightly soluble tetraphenylarsonium perchlorate.[7]

Silver Analysis.—Silver solutions were analyzed after being counted by titration with 0.01 *f* NH_4SCN solution, ferric ion being the indicator.[8] The blank correction was 0.02 ml., and the error was estimated to be ±0.02 ml. Most exchange runs were at such silver(II) concentrations as to require 0.70 ml. or more of titrant. For a few runs, the amount of titrant required was as little as 0.20 ml., leading to a titration error of 10%. A more sensitive potentiometric titration[8] was attempted, but it was not successful because of end-point drift in the acidic solutions.

The unit of specific activity used throughout these experiments was counts/min./ml. of thiocyanate solution.

Rapid Mixing and Flow Apparatus.—The rapid mixing and flow technique developed by Hartridge and Roughton[3] was used. The apparatus in our experiments is diagrammed in Fig. 1. The two reactant solutions (in 35-ml. reservoirs R and R′) were forced by compressed air (applied through stopcock S_1) up tubes T and T′ into the mixing chamber M. The mixed reaction solution flowed through reaction tube A and tip B, from which it squirted into the quench solution 10 cm. below.

The first ∼4 ml. of reaction solution was intercepted and discarded. It served to cool the walls of the reaction tube and contained any incompletely mixed reaction solution. About 6 ml. of reaction solution was collected in the quench

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(1) This paper was abstracted from the Ph.D. thesis of Barry M. Gordon, Washington University, 1955; Phillips Petroleum Fellow 1953-1955.

(2) B. J. Zwolinski, R. J. Marcus and H. Eyring, *Chem. Revs.*, **55**, 157 (1955).

(3) H. Hartridge and F. J. W. Roughton, *Proc. Roy. Soc.* (*London*), **A104**, 376 (1923).

(4) J. R. Gum and M. L. Pool, *Phys. Rev.*, **80**, 315 (1950).

(5) K. Siegbahn, *ibid.*, **77**, 233 (1950).

(6) A. A. Noyes, D. DeVault, C. D. Coryell and T. J. Deahl, THIS JOURNAL, **59**, 1326 (1937).

(7) H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 186, 305 (1939).

(8) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Rev. Ed., The Macmillan Co., New York, N. Y., 1948, pp. 475, 507.

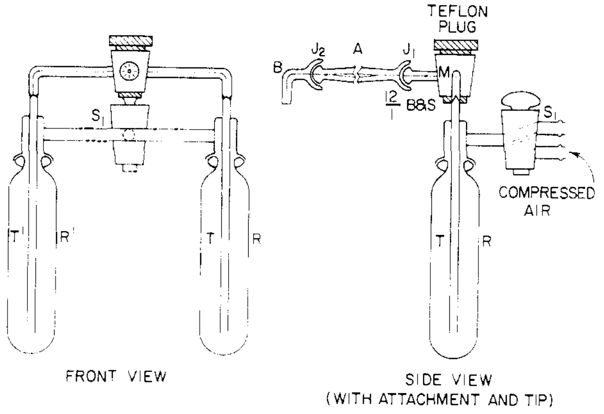

Fig. 1.—Schematic diagram of rapid mixing and flow apparatus.

solution before the flow was stopped by opening stopcock S_1 to the atmosphere, and then quickly closing it to prevent flow of the reaction solution in A and B back into the reservoirs.

The time of reaction was calculated by division of the flow rate into the volume through which the reaction solution passed. Times were varied by replacement of tube A (connected by ball joints J_1 and J_2) with other tubes of different volumes. The reaction tubes were designed to avoid streamline flow, eddying on the surface, and large changes in flow rate. The smaller tubes were made of 1 mm. capillary, the same as the connecting tubes; the larger tubes were 2 and 3 mm. maximum inside diameter expanded in conical sections (diffusers) from 1 mm. ends. The optimum diffuser angle to prevent eddying on the surface is seven degrees.[9] Linearity of the exchange curves was used as the criterion for uniform flow through the tubes. Eddying would result in an upward curvature, and this curvature was observed in experiments run with reaction tubes having diffuser angles of fifteen degrees

To keep the flow rate approximately constant at the same driving pressure (10.5 lb./in.^{2}), the orifice of tip B was restricted to 0.5 mm. in diameter so as to be the principal resistance to flow. The actual flow rate of 6 *f* $HClO_4$ through each reaction tube was determined for the various experimental conditions. It was found to be close to 2 ml./sec. for all reaction tubes.

The mixer M was on the surface of the Teflon plug. Its design was similar to one described by Millikan.[10] Two tangential inlet capillaries provided a swirling motion to minimize streamlined flow. The mixing efficiency was found to be >98% from the loss of color observed when a 0.1 *f* NaOH solution containing phenolphthalein was mixed with a hydrochloric acid solution 1% more concentrated.[3] The time required for this complete mixing was found to be <0.004 sec. (*i.e.*, within 1 cm. of the mixing chamber) from thermocouple measurements of the temperature rise at various distances from the chamber when 4 *f* NaOH and 4 *f* HCl were mixed.[11]

An over-all test of the rapid mixing and flow apparatus was its use in the measurement of the rate of a reaction with known kinetics. The reaction was the manganate–permanganate exchange reaction, which had been found by Sheppard and Wahl[12] to obey a second-order rate law having a rate constant of 710 ± 30 M^{-1} sec.$^{-1}$ at 0.1° in 0.16 *f* NaOH. Three runs made by Sheppard[12] using the rapid mixing and flow apparatus under the above conditions, with variation of the reactant concentrations, gave rate constant values of 680, 700 and 750 M^{-1} sec.$^{-1}$.

Separation of Reactants.—The quenching procedure was to run about 6 ml. of reaction solution into 2 ml. of a 0.10 *M* *o*-phenanthroline solution in 6 *f* HNO_3. A precipitate of the perchlorate salt of the *o*-phenanthroline complex of silver(II) formed immediately.

The exchange between silver(I) and the silver(II)-phenanthroline complex ion was investigated, and under the conditions of the quenching procedure it was shown to have a half-time in excess of 10 sec. Heterogeneous exchange between silver(I) and the $Ag(phen)_2(ClO_4)_2$ precipitate was very slow; negligible exchange occurred during the time the precipitate was in contact with the solution.

Procedure.—A weighed amount of silver(II) oxide was dissolved with vigorous shaking in approximately 80 ml. of 6 *f* $HClO_4$ solution cooled to −18°. Oxygen gas was evolved since most of the silver(II) oxide was reduced to silver(I). The resulting pink silver(I)–silver(II) solution was one reactant solution, the silver(I) tracer solution was the other. For the 0°-degree work the reservoirs joined to the mixer were immersed into a water–ice-bath, and the experiments carried out in a refrigerated room (0 to 3°). The successive reactions were quenched in 40-ml. conical-tipped centrifuge tubes, which were placed in an ice-bath to await centrifugation after the reactions for all six or more times had been run. The silver(I) solutions were set aside for analysis. The precipitates were dissolved in 10 ml. of 6 *f* HNO_3, and the resulting solutions counted and analyzed. Also, 5 ml. of reaction solution from each set of reservoirs was diluted, counted and analyzed.

Concentrations were corrected for the differences in densities of the solution at reaction temperature and room temperature, the corrections being 2.6% for the runs at −14.8° and 1.5% for the runs at 0°.

The fraction exchange was calculated by dividing the specific activity of a silver(II) sample by the average of the specific activity values determined for the reaction mixture. Several checks had shown that the specific activity of the reaction mixture and the silver(II) "infinite-time" specific activity were equal. The data were plotted as illustrated in Fig. 2, and the half-times were read from the plots. As can be seen the intercepts at time zero are considerably less than one. This "zero-time" exchange must be due to exchange occurring during the quenching process (separation-induced exchange); fortunately, it was reproducible for a given set of conditions as shown by the linearity of the exchange curves.

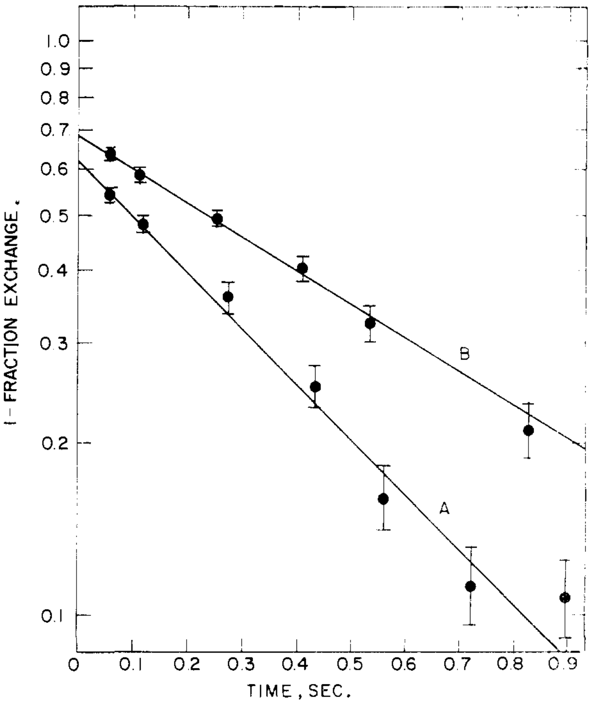

Fig. 2.—Typical exchange curves: curve A is for the tenth experiment listed in Table I; curve B is for the fifteenth. The errors shown correspond to 3% of the fraction-exchange values.

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[9] R. C. Binder, "Advanced Fluid Dynamics and Fluid Machinery," Prentice-Hall, Inc., New York, N. Y., 1951, p. 107.

[10] G. A. Millikan, *Proc. Roy. Soc.* (*London*), **A155**, 277 (1936).

[11] F. J. W. Roughton and G. A. Millikan, *ibid.*, **A155**, 258 (1936).

[12] J. C. Sheppard and A. C. Wahl, THIS JOURNAL, **79**, 1020 (1957).

At the higher Ag^{II}/Ag^{I} ratios the rate of reduction of silver(II) by water was sufficiently rapid that the ratio changed appreciably during the course of a run. For example, at 0° during the ~20 min. required to make the usual 7-point run, the Ag^{II}/Ag^{I} ratio starting at a value of 0.226 decreased 20%, starting at a value of 0.180 it decreased 6%, and starting at a value of 0.117 no decrease was observed. This behavior is consistent with the observations of Noyes, Coryell, Stitt and Kossiakoff[13] that in nitric acid solution the rate of reduction of silver(II) increased rapidly with increasing silver(II) concentration and decreased with increasing silver(I) and nitric acid concentrations.

To minimize the effect of changing reaction conditions, runs at the higher Ag^{II}/Ag^{I} ratios were made with only three points, the first with a reaction time corresponding to about two half-times, the second with the shortest possible reaction time, 0.061 second, and the third a repeat of the first. The fraction-exchange values for the first and third points were averaged, and the Ag^{II}/Ag^{I} ratio for the second was used.

Experiments at 11.4° were performed in the same manner as those at 0°. Runs at −14.8° were performed with the apparatus described by Sheppard and Wahl.[12] This apparatus consisted of electronically operated solenoidal valves which controlled the mixing of the reactant solutions and the subsequent addition of the quenching solution. The apparatus was adapted for reaction times >1 sec. The consistency of these data with those obtained at 0 and 11.4° was further evidence that the rapid-mixing and flow technique was sound.

TABLE I

RATE DEPENDENCE ON REACTANT CONCENTRATIONS AND ON TEMPERATURE (5.87 f $HClO_4$)

$(Ag^{I}) + (Ag^{II})$, $f \times 10^3$	$\frac{(Ag^{II})}{(Ag^{I})}$	$t_{1/2}$, sec.	k', f^{-1} sec.$^{-1}$	k_1, $^{-1}$ sec.$^{-1}$
		0.2°		
2.87	0.286	0.765	320	1100
5.08	.365	.347[a]	390	1080
5.10	.425	.335[a]	410	960
5.14	.310	.416[a]	320	1040
9.04	.325	.264[a]	290	890
9.12	.312	.253	300	960
9.47	.253	.339	220	850
11.28	.131	.485	130	970
11.64	.211	.285	210	990
12.41	.169	.320	175	1030
16.91	.092	.445	92	1000
18.86	.072	.507	72	1010
25.44	.054	.540	50	930
31.46	.040	.600	37	920
			Av.[b]	1020 ± 40
		11.4°		
3.78	0.123	0.520	350	2870
5.27	.175	.245[a]	540	3070
5.87	.160	.265[a]	450	2830
6.18	.145	.280	400	2760
7.45	.128	.235[a]	400	3090
7.77	.197	.163[a]	550	2780
9.99	.088	.285	240	2770
18.00	.050	.265	145	2910
			Av.[b]	2740 ± 60
		−14.8°		
5.45	0.210	2.02	63	300
8.55	.092	2.70	30	326
9.03	.085	2.85	27	316
15.66	.057	2.69	16	289
			Av.[b]	300 ± 13

[a] Three-point runs. [b] From least-squares analysis.

Results

If the exchange reaction obeyed the rate law Rate = $k'(Ag^{I})(Ag^{II})$, as would be expected if the rate step involved the transfer of an electron from silver(I) to silver(II), the rate constant k' would be related to the half-time $t_{1/2}$ by the expression[14]

$$k' = \frac{\ln 2}{t_{1/2}[(Ag^{I}) + (Ag^{II})]} \qquad (1)$$

This expression is not valid as is shown in Table I by the variation of k' with reactant concentrations.

The more general rate law Rate = $k(Ag^{I})^a \cdot (Ag^{II})^b$ is related to the half-time by the expression

$$k = \frac{\ln 2}{t_{1/2}\,[(Ag^{I}) + (Ag^{II})]}\,(Ag^{I})^{1-a}(Ag^{II})^{1-b} \qquad (2)$$

A good fit of the data was obtained for $a = 0$ and $b = 2$, *i.e.*

$$\text{Rate} = k_1(Ag^{II})^2 \qquad (3)$$

$$k_1 = \frac{\ln 2}{t_{1/2}\,[(Ag^{I}) + (Ag^{II})]} \times \frac{(Ag^{I})}{(Ag^{II})} \qquad (4)$$

as shown by the linearity of the plots in Fig. 3.

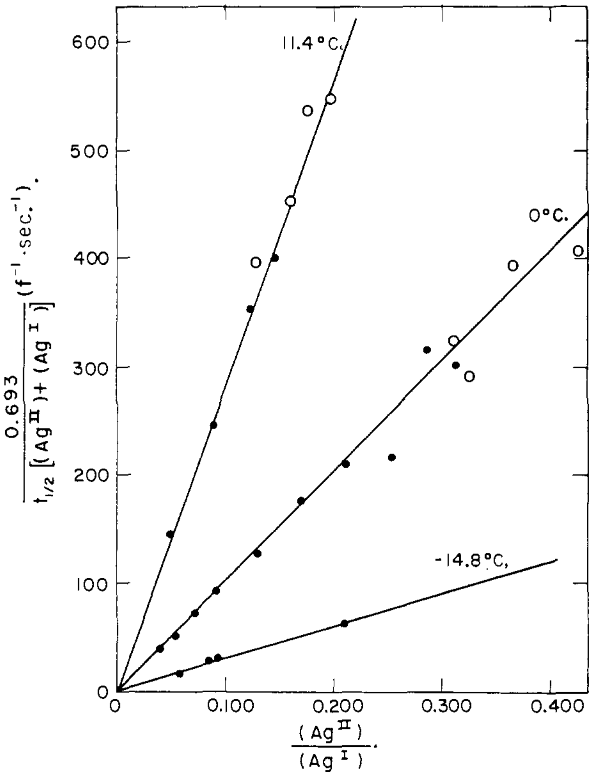

Fig. 3.—Plots of exchange data according to equation 4: ●, normal 6 and 7-point runs; ○, 3-point runs.

The possible contribution of an additional term of the form $k_2(Ag^{I})(Ag^{II})$ in the rate law was considered, but as can be seen from the relationship

$$\frac{\ln 2}{t_{1/2}\,[(Ag^{I}) + (Ag^{II})]} = k_1\frac{(Ag^{II})}{(Ag^{I})} + k_2 \qquad (5)$$

and the intercepts of the lines at the origin in Fig. 3, the contribution is negligible.

From the slope of the log k_1 *vs.* $1/T$ plot (not shown) the experimental activation energy of 12.5

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(13) A. A. Noyes, C. D. Coryell, F. Stitt and A. Kossiakoff, THIS JOURNAL, **59**, 1316 (1937).

(14) O. E. Myers and R. J. Prestwood, "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Bonner, editors, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 11.

± 1.2 kcal./mole was obtained. From this value an experimental entropy of activation value of −1 cal./deg./mole was calculated. Neither of these values is considered theoretically significant since hydrolysis reactions probably precede the rate step, and, therefore, the values include, respectively, the heat and entropy of hydrolysis.

Investigation of rate dependence on the hydrogen ion concentration was difficult because the rate of reduction of silver(II) increased as the hydrogen ion concentration decreased. The data that were obtained are listed in Table II. Over the limited range studied the data are consistent with an inverse 4th power dependence on the hydrogen ion concentration.

TABLE II

RATE DEPENDENCE ON HYDROGEN ION CONCENTRATION

(0.2°, ionic strength adjusted to 5.87 with $NaClO_4$)

$(HClO_4)$, f	$(Ag^I) + (Ag^{II})$, $f \times 10^3$	$\frac{(Ag^{II})}{(Ag^I)}$	$t_{1/2}$, sec.	k_1, f^{-1} sec.$^{-1}$	$k_1(H^+)^4$, f^3 sec.$^{-1}$ $\times 10^{-6}$
5.89	(From Table I)			1020	1.21
4.90	7.97	0.063	0.78	1770	1.06
4.92	4.82	.190	.40	1890[a]	
4.40	10.31	.055	.395	3090[b]	1.16
3.94	8.39	.033	.50	5000	1.19
3.94	8.44	.050	.36	4560[b]	
3.94	8.85	.035	.43	5200	

[a] No $NaClO_4$ added, $\mu = 4.92$. [b] Aqueous $NaClO_4$ was prepared from $NaCO_3 + HClO_4$; solid $NaClO_4 \cdot H_2O$ was used in the other runs.

Our rate data are summarized in Table III. For the 5.87 f $HClO_4$ solutions the values of k_1, the slopes of the lines in Fig. 3, were obtained by least-squares analysis of the data. The values obtained from the analysis for the intercepts, k_2, are also listed; all are zero within the estimated uncertainty.

TABLE III

SUMMARY OF RATE DATA

Temp., °C.	$(HClO_4)$, f	k_1, f^{-1} sec.$^{-1}$	k_2, f^{-1} sec.$^{-1}$
−14.8	5.87	300 ± 13	1 ± 10
0.2	5.87	1020 ± 40	−3 ± 10
	4.90	1800 ± 200	
	4.40	3100 ± 310	
	3.94	4900 ± 240	
11.4	5.87	2740 ± 60	8 ± 10

Discussion

A brief review of the work of Noyes[6,13,15,16,17] and co-workers concerning the silver(I)–silver(II) system will be helpful. They studied the oxidation of silver(I) in nitric acid solution by ozone and the oxidation of water by silver(II) in nitric acid solution. The kinetic studies indicated that silver(III) is an intermediate in both reactions. However, magnetic susceptibility and electrode potential measurements indicated that essentially all silver of oxidation state greater than +1 was in the +2 state, so the silver(III) must be present only in very small concentration. To account for their observations Noyes[13,15,16] and co-workers proposed the following rapid reversible equilibrium lying far to the right.

$$Ag^{III} + Ag^{I} \rightleftharpoons 2Ag^{II} \qquad (6)$$

The experimentally determined rate law, rate $= k_1(Ag^{II})^2$, for the isotopic exchange reaction in 6 f $HClO_4$ is consistent with the view that the isotopic equilibration occurs through reaction 6 and that the rate of exchange is the rate of this reaction at equilibrium.

The large inverse dependence of the exchange rate on the perchloric acid concentration is analogous to the large inverse dependence on nitric acid concentration for the rate of reduction of silver(II) by water and suggests that hydrolyzed forms of silver(II) are involved in the rate step of the disproportionation reaction.

$$Ag^{++} + xH_2O \rightleftharpoons Ag(OH)_x^{+(2-x)} + xH^+ \quad \text{(rapid equilibrium)}$$

$$2Ag(OH)_x^{+(2-x)} \rightleftharpoons \begin{bmatrix}\text{activated} \\ \text{complex}\end{bmatrix} \rightleftharpoons Ag^{III} + Ag^{I} \quad \text{(rate determining)}$$

The experimental value of −4 for the acid dependence would make $x = 2$ and result in a neutral activated complex. Such extensive hydrolysis even for the formation of low-concentration intermediates in these highly acidic solution is very surprising. The value of −4 might well be in error by as much as one unit since the acid dependence could be measured only over a limited range, but this is not of much help. It is, of course, possible that the rate law determined in 5.87 f $HClO_4$ is not valid at the lower acid concentrations so that the calculations of the rates from the measured half-times are incorrect. It is also possible that for these concentrated electrolyte solutions the usual procedure of maintaining a constant ionic strength by replacement of H^+ by Na^+ does not keep constant the activity coefficients of all species concerned. If this were true the increasing rate with decreasing acid concentration could be due to more complex effects than the decrease in hydrogen-ion concentration. It may be noted in Table II that for 4.9 f $HClO_4$ the rate was the same whether or not sodium perchlorate was added.

The specific rate for the direct electron transfer from Ag^+ to Ag^{++} has been shown to be < 10 f sec.$^{-1}$. This is at most only an order of magnitude greater than the specific rate for electron exchange between Fe^{++} and Fe^{+++} (0.9 f sec.$^{-1}$, 0°, 0.5 f $HClO_4$),[18] a difference too small for coulombic repulsion to be the principal deterrent to electron transfer for both reactions.

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[15] A. A. Noyes, J. L. Hoard and K. S. Pitzer, THIS JOURNAL, **57**, 1221 (1935).

[16] A. A. Noyes, K. S. Pitzer and C. L. Dunn, *ibid.*, **57**, 1229 (1935).

[17] A. A. Noyes and A. Kossiakoff, *ibid.*, **57**, 1238 (1935).

[18] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).