to our proposed model can interact directly with one another.[22] The presumed antiferromagnetic behavior[20,21] then may arise by direct metal–metal interaction and/or by super-exchange *via* the bridging halogen atoms.

Of significance would be a measurement of electrical conductivity of pure single crystals (attempts to prepare suitable crystals for X-ray diffraction as yet have been unsuccessful) to determine the metallic nature of these compounds. Also, a low-temperature neutron diffraction study is needed to elucidate the atomic magnetic moment orientation of these presumed antiferromagnetic substances.

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[22] This bonding description also is applicable to Holze's $(Zr_2X_6)_n$ model[3,7] of alternating short and long interatomic distances. The local point group symmetry about each zirconium is decreased to C_{3v} for which the s, p_z, and d_{z^2} orbitals transform as A_1, and the three pairs (p_x, p_y), ($d_{x^2-y^2}$, d_{xy}), and (d_{xz}, d_{yz}) as E. Similarly, after σ-bonding the three orbitals remain on each zirconium with the symmetry $A_1 + E$. The nonequivalent bond distances will result in the energy levels splitting into gaps of bonding and antibonding states; if the dimeric $(Zr_2X_6)_n$ units are sufficiently separated from one another, the interaction of the zirconium atoms can be considered as distinct pairs. Since for a given (Zr_2X_6) unit the axially symmetric A_1 atomic orbitals presumably interact with each other more strongly than the degenerate orbitals making up the E representation, the two coupling electrons can be assigned to the totally symmetric bonding MO with the resulting formation of a direct metal–metal bond. This electron coupling in pairs is similar to that found for α-NbI_4 and TaI_4 which are diamagnetic.[23] The structure of solid α-NbI_4 and the isomorphous TaI_4 consists of infinite chains formed by MI_6 octahedra sharing two opposite edges; the metal atoms are shifted from the centers of the iodine octahedra toward one another in pairs to give a resulting metal–metal distance of 3.31 Å.[23]

[23] L. F. Dahl and D. L. Wampler, *Acta Cryst.*, **15**, 903 (1962).

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY
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The Role of the Monofluoroiron(III) Ion in the Iron(II)–Iron(III)–Fluoride Ion Isotope Exchange Reaction

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The iron(II) + iron(III) exchange rate was measured in NaF–$NaClO_4$–$HClO_4$ media at constant pH and ionic strength. The iron(II) concentration was increased so as to make the isotope exchange rate comparable to the rate of formation of the inner coordination shell complex FeF^{+2}. The observed isotope exchange rate was dependent on the rate of formation of FeF^{+2} in the manner expected if the activated complex $[Fe_2F^{+4}]^*$ was formed from Fe^{+2}(aq) and FeF^{+2}(aq).

A considerable number of anionic catalysts for the iron(II) + iron(III) isotope exchange reaction have been reported.[2] In each of these cases it has been postulated that isotope exchange occurs between Fe^{+2} and FeX_n^{+3-nq}, the latter species being a complex between Fe^{+3} and the anion X^{-q} which is formed reversibly and rapidly compared to the rate of isotope exchange. As a result of the postulate the rate of the isotope exchange reaction is written as

$$R = \left\{k_0 + \frac{k_hK_h}{[H^+]} + k_1K_1[X^{-q}] + k_2K_1K_2[X^{-q}]^2 + \ldots\right\}[Fe^{+2}][Fe^{+3}] \qquad (1)$$

where k_0, k_h, k_1, k_2 are the rate constants for isotope exchange between Fe^{+2} and Fe^{+3}, $Fe(OH)^{+2}$, FeX^{+3-q}, FeX_2^{+3-2q}, respectively, K_h is the acid dissociation constant of aquo ferric ion, and K_1 and K_2 are the stepwise formation constants of the Fe(III)–X^{-q} complexes. The products k_1K_1, $k_2K_1K_2$, . . . in (1) are obtained from the variation of observed rate constants with change of X^{-q} concentration. From these products values of k_1, k_2, . . . are calculated using independently determined values of K_1, K_2, . . . for the inner coordination sphere complexes of Fe(III). The theories concerning mechanisms of electron transfer use these rate constants without it being known whether or not the rate constant values are valid. If, for example, the exchange path involving one Fe^{+2}, one Fe^{+3}, and one X^{-q} in the activated complex was a reaction between FeX^{+2-q} and Fe^{+3} or between Fe^{+2} and an outer-sphere complex, $Fe(H_2O)_6X^{+3-q}$, of $Fe(H_2O)_6^{+3}$ and X^{-q}, then the values of K_1 and k_1 would be very different. Hence, it is very important to obtain evidence of a rate-determining isotope exchange reaction between Fe^{+2} and FeX_n^{+3-nq}. In the work reported here we have obtained excellent evidence that the

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[2] (a) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952); (b) J. Hudis and A. C. Wahl, *J. Am. Chem. Soc.*, **75**, 4153 (1953); (c) G. S. Laurence, *Trans. Faraday Soc.*, **53**, 1326 (1957); (d) D. Bunn, F. S. Dainton, and S. Duckworth, *ibid.*, **55**, 1267 (1959); *ibid.*, **57**, 1131 (1961); (e) R. A. Horne, *J. Phys. Chem.*, **64**, 1512 (1960); (f) N. Sutin, J. K. Rowley, and R. W. Dodson, *ibid.*, **65**, 1248 (1961); (g) W. L. Reynolds and S. Fukushima, *Inorg. Chem.*, **2**, 176 (1963); (h) K. Bachman and K. H. Lieser, *Z. physik. Chem.* (Frankfurt), **36**, 236 (1963).

isotope exchange reaction involving one fluoride ion does indeed occur between Fe^{+2} and the inner coordination sphere complex FeF^{+2}.

The F^- catalysis of the iron(II) + iron(III) exchange was first investigated by Hudis and Wahl.[2b] At a later date Pouli and Smith[3] measured the rate of formation of FeF^{+2}. We have measured the isotope exchange rate in the presence of F^- under conditions for which the exchange rate and the rate of FeF^{+2} formation were comparable and for which Fe^{+3}, $Fe(OH)^{+2}$, and FeF^{+2} were the main iron(III) species present.

Experimental

Chemicals.—The preparation and standardization of the stock $^*Fe^{+3}$ (labeled iron(III)) solution has been described previously.[2g] Prior to each rate determination a solution of ferric-free ferrous perchlorate was prepared by dissolving iron powder (Baker Analyzed Reagent) in perchloric acid. The reaction was carried out in a bottle fitted with a self-sealing cap in an atmosphere of hydrogen. The presence of ferric ion could not be detected with the thiocyanate test[4a] through about 3 cm. of solution. At the concentration of iron(II) used in this work the solutions were chloride-free. The concentration of the ferrous perchlorate solution was checked spectrophotometrically as the tris-(α,α'-dipyridyl)iron(II) complex.[4b]

Mallinckrodt A.R. sodium fluoride, dried at 150°, was used as the source of fluoride ion. Stock solutions of sodium perchlorate were prepared from G. F. Smith anhydrous sodium perchlorate which was previously dried at 130° and stored over P_2O_5. The sodium perchlorate solutions were free from interfering anions and oxidizing or reducing impurities. Mallinckrodt A.R. perchloric acid (70–72%) was diluted and analyzed with standard sodium hydroxide. The other chemicals used were reagent grade.

Measurement of Isotope Exchange Rate.—A known volume of a mixture of standard ferrous perchlorate and unlabeled ferric perchlorate in a solution of $HClO_4$, $NaClO_4$, and NaF was deaerated for about 1 hr. by passage of water-saturated N_2 gas in an ice–water bath (0°). To start the reaction a known volume of thermostated, deaerated $^*Fe(III)$ solution containing the same concentrations of Fe(III), $HClO_4$, $NaClO_4$, and NaF as the solution in the reaction vessel was added by means of a thermostated pipet. Stirring was accomplished by a vigorous flow of N_2. At a time t, a sample of the reaction mixture was withdrawn by means of a thermostated pipet and delivered into a 25-ml. volumetric flask containing 9 ml. of alcohol, 2 ml. of 0.125 M α,α'-dipyridyl, and 3 ml. of 3 M ammonium acetate. A large concentration of alcohol was necessary to prevent the precipitation of the tris-(α,α'-dipyridyl)iron(II) complex. The solution in the flask was stirred by means of a magnetic stirrer. After the addition of the reaction mixture, 2 ml. of 0.1 M $Al(NO_3)_3$ was added followed by 3 ml. of $NH_4NO_3 + NH_3$ solution to precipitate the Al^{+3} and Fe^{+3}. The solution was then brought to volume and filtered. The radioactivity of 5.00-ml. samples of each filtrate was then determined using the same procedure as that described by Reynolds and Fukushima.[2g]

A plot of log $[(\chi_\infty - \chi)/\chi_\infty]$ *vs.* time, where χ is the radioactivity in counts/min. of the 5.00-ml. portion of filtrate obtained from the sample taken at a time t and χ_∞ is the same quantity for the "infinite time" sample taken after approximately ten half-times of the reaction had elapsed, yielded a straight line. The rate of exchange R was obtained from the slope, α, of the line.

Results and Discussion

Provided the rate of formation of the ferric monofluoride complex, at low fluoride concentration, is rapid compared to the rate of the isotope exchange reaction, it can be readily shown[2b] that the apparent rate constant, k_{app}, is related to the rate of exchange R by the expression

$$R = k_{app}[Fe(II)][Fe(III)] \qquad (2)$$

where

$$k_{app} = \frac{k_0 + k_hK_h/[H^+] + k_1K_1[F^-]}{1 + K_h/[H^+] + K_1[F^-]}$$

Values of k_{app} were calculated from the equation

$$k_{app} = -\alpha/\{[Fe(II)] + [Fe(III)]\} \qquad (3)$$

where [Fe(II)] and [Fe(III)] are the total concentrations of ferrous and ferric ion, respectively. The values of k_{app}, the half-time calculated for first-order dependence on [Fe(II)], [Fe(III)], and $[F^-]$ expected on the basis of the work of Hudis and Wahl,[2b] and the actual half-times observed are listed in Table I. It can be seen from the table that, for given values of $[Fe^{+3}]$ and $[F^-]$, k_{app} decreases with increasing values of [Fe(II)] and that the calculated half-times, $t_{1/2}$(calcd.), and the apparent half-times, $t_{1/2}$(app.), are different where the ferrous concentrations used by us are larger than those used by Hudis and Wahl.[2b] At 2.5×10^{-4} M Fe(II), the lowest Fe(II) concentration used in the work reported here, and similar concentrations of ferric and fluoride ions our results are the same as those of Hudis and Wahl[2b] within experimental error. However, we can compare our apparent rate constant with only one rate constant given by Hudis and Wahl[2b] because the latter investigators used larger fluoride concentrations than we did in the remainder of their experiments.

TABLE I

VARIATION OF k_{app} WITH [Fe(II)] AT $[H^+] = 0.400$ M, $\mu = 0.500$, AND 0°

Fe(II) × 10^3, M	$t_{1/2}$(app.), sec.	$t_{1/2}$(calcd.),[a] sec.	k_{app}, l./mole sec.
0.250	1020	935	2.60 ± 0.07[b]
0.500	555	478	2.44 ± 0.04[b]
0.750	389	321	2.34 ± 0.05[b]
1.00	303	242	2.26 ± 0.04[b]
1.50	218	162	2.10 ± 0.06[b]
2.00	172	122	2.00 ± 0.05[b]
3.00	123	81	1.87 ± 0.08[b]
0.500	647	611	2.10 ± 0.02[c]
1.00	350	309	1.96 ± 0.04[c]
1.01	343	305	1.98 ± 0.02[d]
1.50	247	206	1.86 ± 0.03[c]
2.00	196	155	1.76 ± 0.05[c]
2.50	161	124	1.72 ± 0.05[c]
3.00	135	104	1.70 ± 0.07[c]
4.00	104	78	1.66 ± 0.07[c]

[a] $t_{1/2}$ (calcd.) has been corrected for differences in [Fe(II)] + [Fe(III)]. [b] 1.00×10^{-5} M Fe^{+3}, 4.584×10^{-4} M NaF, 1.95×10^{-6} M FeF^{+2}, 2.00×10^{-6} M F^-. [c] 0.912×10^{-5} M Fe^{+3}, 2.292×10^{-4} M NaF, 0.88×10^{-6} M FeF^{+2}, 1.00×10^{-6} M F^-. [d] 0.985×10^{-5} M Fe^{+3}, 2.296×10^{-4} M NaF, 0.96×10^{-6} M FeF^{+2}, 1.00×10^{-6} M F^-.

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(3) D. Pouli and W. MacF. Smith, *Can. J. Chem.*, **38**, 567 (1960).

(4) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, D. Van Nostrand Co., New York, N. Y., 1949: (a) p. 307; (b) p. 316.

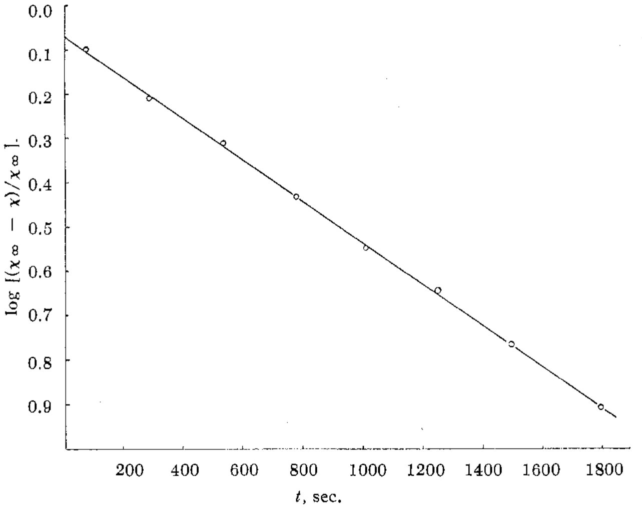

Fig. 1.—Plot of log $[(\chi_\infty - \chi)/\chi_\infty]$ *vs.* time: [Fe(II)] = 5.00 × 10^{-4} *M*, [Fe(III)] = 1.00 × 10^{-5} *M*, $[F^-]$ = 1.00 × 10^{-6} *M*, $[H^+]$ = 0.400 *M*, μ = 0.500, 0°.

It has already been mentioned that under the experimental conditions used in this work the rate of isotope exchange is comparable with the rate of formation of the FeF^{+2} complex. Also at low F^- concentrations only FeF^{+2} is formed.[5] Hence the following reactions must be considered.

$$^*Fe^{+3} + Fe^{+2} \xrightarrow{k_0} {}^*Fe^{+2} + Fe^{+3} \qquad (4)$$

$$^*Fe(OH)^{+2} + Fe^{+2} \xrightarrow{k_h} {}^*Fe^{+2} + Fe(OH)^{+2} \qquad (5)$$

$$^*FeF^{+2} + Fe^{+2} \xrightarrow{k_1} {}^*Fe^{+2} + FeF^{+2} \qquad (6)$$

$$^*Fe^{+3} + F^- \xrightarrow{k_1'} {}^*FeF^{+2} \qquad (7)$$

$$^*Fe^{+3} + HF \xrightarrow{k_2'} {}^*FeF^{+2} + H^+ \qquad (8)$$

In this set of postulated reactions we are, at constant pH, concerned with three rates of reactions which are of comparable magnitudes. These three rates may be written as

$$R_1 = k_1[Fe^{+2}][FeF^{+2}] \qquad (9)$$

$$R_2 = (k_1' + k_2'[H^+]/K_{HF})[Fe^{+3}][F^-] \qquad (10)$$

$$R_3 = (k_0 + k_hK_h/[H^+])[Fe^{+3}][Fe^{+2}] \qquad (11)$$

Let $A = [Fe^{+2}] + [^*Fe^{+2}]$; $B = [Fe^{+3}] + [FeOH^{+2}] + [^*Fe^{+3}] + [^*FeOH^{+2}]$; $C = [FeF^{+2}] + [^*FeF^{+2}]$; S_a^0, S_b^0, S_c^0 = specific activities of Fe^{+2}, Fe^{+3} + $FeOH^{+2}$, FeF^{+2}, respectively, at time $t = 0$; and S_a^∞ = specific activity of Fe^{+2} at equilibrium. Abell, Bonner, and Goishi[6] have shown that for systems of this type the exchange equation in its general form is

$$1 - F = Q_1e^{-(q+p)t} + Q_2e^{-(q-p)t} \qquad (12)$$

where

$$F = \chi/\chi_\infty$$

$$2q = \left(\frac{A + C}{AC}\right)R_1 + \left(\frac{B + C}{BC}\right)R_2 + \left(\frac{A + B}{AB}\right)R_3$$

$$p = +(q^2 - r)^{1/2}$$

$$r = (R_1R_2 + R_1R_3 + R_2R_3)\frac{A + B + C}{ABC}$$

$$Q_1 = \frac{1}{2pA}\left[-A(q - p) + \frac{(R_1 + R_3)S_a^0 - R_1S_c^0 - R_3S_b^0}{S_a^0 - S_a^\infty}\right]$$

$$Q_2 = 1 - Q_1$$

Equation 12 predicts that, in general, a plot of ln $(1 - F)$ against t should yield a curve composed of two straight lines,[6] and a system of this type has already been observed.[7] However, in our case it is readily seen that

$$Q_2e^{-(q-p)t} \gg Q_1e^{-(q+p)t}$$

if the values $(k_0 + k_hK_h/[H^+])$ = 1.50 M^{-1} sec.$^{-1}$, k_1 = 9.7 M^{-1} sec.$^{-1}$, and K_1 = 9.7 × 10^4 M^{-1} for the conditions given in Table I are adopted from the work of Hudis and Wahl[2b] and if the values k_1' = 1.44 × 10^2 M^{-1} sec.$^{-1}$ and k_2' = 2.68 M^{-1} sec.$^{-1}$ obtained by extrapolating the data of Pouli and Smith[3] to 0° are used where necessary. The acid dissociation constants K_{HF} = 1.76 × 10^{-3} and K_{HF_2} = 0.28 were computed by Hudis and Wahl[2b] from the data of Broene and DeVries.[8] Therefore eq. 13 is applicable (except perhaps for very accurate measurements near the start of the exchange reaction) as can be seen in Fig. 1.

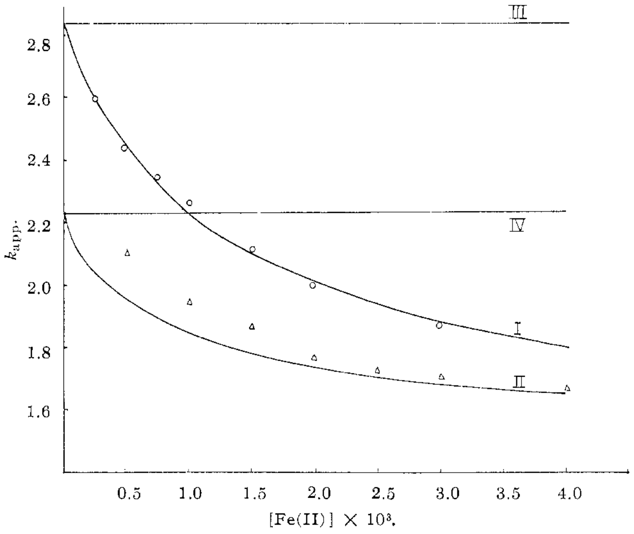

Fig. 2.—Variation of k_{app} with [Fe(II)]. I: Theoretical curve for $[Fe^{+3}]$ = 1.00 × 10^{-5} *M*, $[FeF^{+2}]$ = 1.95 × 10^{-6} *M*, $[F^-]$ = 2 × 10^{-6} *M*, $[H^+]$ = 0.400 *M*, μ = 0.500, 0°; ○, experimental points under the same conditions. II: Theoretical curve for $[Fe^{+3}]$ = 9.12 × 10^{-6} *M*, $[FeF^{+2}]$ = 0.88 × 10^{-6} *M*, $[F^-]$ = 1 × 10^{-6} *M*, $[H^+]$ = 0.400 *M*, μ = 0.500, 0°; △, experimental points under the same conditions. III: Same as I assuming that formation of FeF^{+2} is not a rate-determining step. IV: Same as II assuming that formation of FeF^{+2} is not a rate-determining step.

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[5] H. W. Dodgen and G. K. Rollefson, *J. Am. Chem. Soc.*, **71**, 2600 (1949).

[6] D. F. Abell, N. A. Bonner, and W. Goishi, *J. Chem. Phys.*, **27**, 658 (1957).

[7] N. A. Bonner and W. Goishi, *J. Am. Chem. Soc.* **83**, 85 (1961).

[8] H. H. Broene and T. DeVries, *ibid.*, **69**, 1644 (1947).

$$\ln (1 - F) = \ln Q_2 - (q - p)t \qquad (13)$$

Hence

$$k_{\text{app}} = -(q - p)/(A + B + C) \qquad (14)$$

In eq. 14 $(q - p)$ is a function of Fe(II) concentration. The theoretical variation of k_{app} with [Fe(II)] at two F^- concentrations was calculated using the theoretical value of $(q - p)$ (as distinguished from the experimental slope) and the results have been plotted as the solid curves I and II in Fig. 2. It is seen that the experimental variation of k_{app} with Fe(II) concentration is in good agreement with the theoretical curve derived on the basis of the postulated reactions in eq. 4–8. Thus it can be concluded that FeF^{+2} is formed as an intermediate and that isotope exchange occurs between Fe^{+2} and FeF^{+2} rather than between FeF^+ and Fe^{+3} or between Fe^{+2} and an outer coordination sphere complex of Fe^{+3} and F^-. The results do not allow us to distinguish between the bridge or outer-sphere mechanisms of electron transfer.

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Exchange of Ammonia between Hexaamminechromium(III) Salts and Solvent Ammonia. II[1]

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New rate data are reported for the homogeneous ammonia exchange between $Cr^{III}(NH_3)_6$ and liquid ammonia mainly in a perchlorate medium. It is suggested that species such as $Cr(NH_3)_5(NH_2)(ClO_4)^+$ are responsible for the exchange. Further ion association decreases the exchange rate. An apparent activation energy of *ca.* 33 kcal./mole was found. Light appears to speed up the exchange. Addition of benzene to the ammonia causes a reduction in rate. At −50°, six ammonia molecules per chromium atom are "held back."

Introduction

We have extended the research reported previously[3] on the $Cr^{III}(NH_3)_6$ exchange system. The former work dealt mainly with nitrate salts, and here we present new data using perchlorate salts which show significant differences in behavior.

Experimental

The procedures and methods used were those described earlier.[3] Anhydrous $NaClO_4$ was prepared by the method of Willard and Smith.[4] Anhydrous $CrCl_2$ was prepared by the method of Schlesinger and Hammond.[5] Care was taken to maintain anhydrous conditions and the runs were made in the dark except for some experiments designed to test these factors.

Results and Treatment of Data

We have not been able to determine the holdback of NH_3 by the Cr(III) ammine species (using nitrate or perchlorate salts) in liquid ammonia at room temperature, but at −50° $Cr(NH_3)_6(NO_3)_3$ is quite soluble and some experiments were performed at this temperature. The procedure was analogous to that used by Hunt and Taube[6] for the $Cr(H_2O)_6{}^{3+}$ system modified because of the properties of liquid ammonia. Solutions of $Cr(NH_3)_6(NO_3)_3$ in ammonia of normal isotopic composition (*ca.* 2 *M* in salt) were mixed with liquid ammonia containing *ca.* 1.7 times the normal amount of N^{15}. Solvent was evaporated after 2 and 15 min. intervals, trapped, and converted to N_2 in the usual way. The fractionation on evaporation is small (*ca.* 0.1%). The number of ammonia molecules held back was found to be 6 ± 0.2 per Cr. Since outer-sphere ammonia thus shows no measurable holdback at −50°, it seems likely that the holdback is also 6 NH_3/Cr at room temperature. The data below have been treated on this basis. We have confirmed previous observations that packing with glass helices had no effect on the rate. Addition of mercury, which could be a contaminant, also produced no change in exchange rate.

The McKay plots of the exchange data were quite good with the lines passing through the origin. The precision of the data appears to be ±5 to 10%. Values for *R* (the total exchange rate) were calculated from the relation

$$R = 6[\mathrm{Cr}][\mathrm{NH_3}]/(6[\mathrm{Cr}] + [\mathrm{NH_3}]) \times (0.693/t_{1/2}) \cong 6 \times 0.693[\mathrm{Cr}]/t$$

In the earlier work[3] it was found that the exchange rate was dependent on the concentration of "inert salt" present. This fact raised the question as to how to best control what might be termed "medium effects." The ionic strength is not a useful variable in these experiments because the low dielectric constant of the

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[1] Supported by United States Atomic Energy Commisson AT(45-1)-1031.

[2] To whom inquiries may be addressed.

[3] T. W. Swaddle, L. F. Coleman, and J. P. Hunt, *Inorg. Chem.*, **2**, 950 (1963).

[4] H. H. Willard and G. F. Smith, *J. Am. Chem. Soc.*, **44**, 2817 (1922).

[5] H. I. Schlesinger and E. S. Hammond, *ibid.*, **55**, 3971 (1933).

[6] J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).