The value 6.54, obtained from the extrapolated data, is believed to be the best as yet available for the thermodynamic equilibrium constant for silver–sodium exchange on this resin.

TABLE II

Ionic strength	0.1 M		0.05 M		0.01 M		0 M	
N_{AgRes}	f_{NaRes}	f_{AgRes}	f_{NaRes}	f_{AgRes}	f_{NaRes}	f_{AgRes}	f_{NaRes}	f_{AgRes}
0.0	1.000	0.382	1.000	0.532	1.000	0.564	1.000	0.544
.1	0.974	.699	0.990	.668	0.990	.687	0.992	.670
.2	.942	.840	.961	.801	.964	.802	.965	.790
.3	.918	.911	.928	.892	.933	.885	.934	.875
.4	.895	.953	.903	.939	.897	.924	.908	.927
.5	.876	.977	.883	.968	.883	.962	.878	.961
.6	.863	.990	.869	.982	.859	.989	.861	.983
.7	.854	.997	.855	.991	.846	.997	.849	.992
.8	.848	1.000	.846	.996	.840	.999	.836	.998
.9	.846	1.000	.835	.999	.835	1.000	.828	1.000
1.0	.846	1.000	.826	1.000	.832	1.000	.823	1.000

This value may be compared with two others for the same equilibrium quotient. The data of Bonner and Rhett[6] for resins of 8 and 16% divinylbenzene content yield, by linear interpolation (a procedure which appears justifiable in view of experimental results in the sodium–hydrogen system), a figure of 5.86 for 10.5% divinylbenzene; corrected for the activity coefficient ratio at 0.1 M ionic strength, this becomes 6.08. The value calculated from the ratio of equilibrium constants for silver–hydrogen and sodium–hydrogen exchanges,[13] previously determined in this Laboratory for the same sample of Dowex 50, is 7.31. In view of the wide diversity of their sources, the approximate concordance of the three values is not without interest.

Acknowledgment.—The authors wish to express their appreciation of a grant from the Office of Ordnance Research, U. S. Army, and of a fellowship from E. I. du Pont de Nemours and Co., which made this work possible.

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[13] A. W. Davidson and W. J. Argersinger, Jr., *Ann. N. Y. Acad. Sci.*, **57**, 105 (1953).

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY OF NUCLEAR STUDIES, CORNELL UNIVERSITY]

The Exchange Reaction between Chromous and Chromic Ions in Perchloric Acid Solution

BY ANNE ANDERSON[1] AND NORMAN A. BONNER[2]

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The rate of the chromium(II)–chromium(III) exchange reaction has been measured in perchloric acid solutions and shown to be first order in chromous ion and first order in chromic ion. In 1.00 f $HClO_4$ the second-order rate constant is 0.440 f^{-1} hr.$^{-1}$ at 24.5°, and the experimental activation energy is 22 ± 2 kcal./mole. If the data obtained by varying the hydrogen ion concentration at approximately constant ionic strength are interpreted in terms of exchange reactions between Cr^{++} and the species Cr^{+++} and $Cr(OH)^{++}$, the second-order rate constants at 24.5° are $\leq 0.07 f^{-1}$ hr.$^{-1}$ and $\simeq 2.5 \times 10^3 f^{-1}$ hr.$^{-1}$, respectively. No catalysis by chloride ion was observed. The separation method used was a novel one based on the fact that chromous ion could be converted to a chromic complex which did not exchange with, and could be separated from, $Cr(H_2O)_6^{+++}$.

Rates of the exchange reactions between only a few simple, hydrated +2 and +3 ions have been measured. The Fe(II)–Fe(III) reaction has been studied in some detail,[3] and preliminary data on the kinetics of the Co(II)–Co(III) reaction have been obtained.[4] The two reactions appear to be very similar in rate and general behavior. King and Garner[5] have obtained evidence indicating that the V(II)–V(III) reaction rate may be of the same order of magnitude as the iron and cobalt reactions.

Meier and Garner[6] have found that in contrast to the above reactions, the Eu(II)–Eu(III) reaction is quite slow. Plane and Taube[7] have reported that the Cr(II)–Cr(III) reaction is also slow.

This paper describes some preliminary studies of the kinetics of the Cr(II)–Cr(III) reaction in perchloric acid solution using a simpler and more direct procedure than that of Plane and Taube.

Experimental

Chromium Tracer.—Chromium metal containing 28-day Cr^{51} was obtained from the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission. It was dissolved in HCl and converted to CrO_3 by fuming with perchloric acid. The CrO_3 was dissolved in water, a small amount of ferric chloride added, and ferric hydroxide precipitated by the addition of ammonia. The chromium was then extracted into ethyl ether from acid solution as the blue peroxychromate. After back-extraction into dilute ammonia it was fumed with nitric and perchloric acids to destroy ammonium ion. It was finally diluted with water to a perchloric acid concentration of 1 f and reduced to $Cr(H_2O)_6^{+++}$ with hydrogen peroxide. The excess peroxide was catalytically decomposed on platinum black. The tracer for the exchange experiments was taken directly from this solution. In order to test for undecomposed peroxide, about 1 ml. of the solution was added to a dilute iodide solution and shaken with benzene. No iodine color was observed.

The purified material was checked for radiochemical purity by counting a sample of it in solution on a gamma counter at intervals for 108 days. The half-life observed was 27.6 days. Another sample was converted to $BaCrO_4$ and counted from time to time on an X-ray counter over a period of 68 days. This sample gave a half-life of 27.3 days. Both values are in satisfactory agreement with the published value of 27.8 days.[8]

Specific Activity Measurements.—In runs numbered 2, 5, 6 and 10, the samples whose specific activities were to be measured were converted to chromate by oxidation with

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[1] Department of Zoology, Cornell University, Ithaca, N. Y.

[2] Chemistry Department, University of California Radiation Laboratory, Livermore, Calif. Requests for reprints should be sent to this address.

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

[4] N. A. Bonner and J. P. Hunt, THIS JOURNAL, **74**, 1866 (1952).

[5] W. R. King and C. S. Garner, *ibid.*, **74**, 3709 (1952).

[6] D. J. Meier and C. S. Garner, *J. Phys. Chem.*, **56**, 853 (1952).

[7] R. A. Plane and H. Taube, *ibid.*, **56**, 33 (1952).

[8] W. S. Lyon, *Phys. Rev.*, **87**, 1126 (1952).

peroxydisulfate. Gamma radiation was counted directly from the solutions by putting 10.0 ml. of each sample in a calibrated test-tube in a reproducible position near a brass-wall, flow-type proportional counter. The counting gas was methane at atmospheric pressure. Another aliquot of each sample was diluted to an appropriate volume in a solution 0.05 *f* in NaOH and 0.025 *f* in NH_4OH. The chromium concentrations were determined by measuring the optical density at 370 mμ with a Beckman Model DU spectrophotometer.

The specific activities of all other samples were measured by counting and weighing $BaCrO_4$. The samples were oxidized to chromate with bromate, then precipitated as $BaCrO_4$ from an acetic acid–acetate buffer. After a two-hour digestion the precipitates were filtered on $^7/_8$" circles of Whatman No. 42 filter paper. They were then dried at 110° for an hour and weighed. The filter papers were mounted on cardboard cards under rubber hydrochloride ("Pliofilm"—supplied by the Goodyear Tire and Rubber Co.) of thickness 1 mg./cm.^{2}. The samples were then counted on a flow-type proportional counter with a side window. The window was rubber hydrochloride coated with a conducting layer of "Aquadag." The counting gas was 90% argon–10% methane at atmospheric pressure.

The counting rates were corrected for self-absorption by means of a calibration curve prepared by mounting and counting a set of samples of constant specific activity but differing in weight. The corrections were rather large, and the reproducibility was not better than about 5%, so the specific activity measurements are probably the largest single source of error in the measured exchange rates. These errors were partly compensated for by taking six to eight samples per run, and by taking duplicate samples for the "infinite time" specific activity measurements.

Chemicals.—The inactive chromium perchlorate and the sodium perchlorate were G. F. Smith analytical grade which had been repurified by recrystallization from water.

The hydrogen was electrolytic tank gas passed over a catalyst ("Deoxo") to remove traces of oxygen.

All other chemicals were analytical grade reagents.

Separation Method.—Because chromous ion is rapidly oxidized by air, the direct separation of chromous and chromic ions is difficult. We were able to avoid this difficulty by the rather novel method of converting the chromous ion to a chromic complex before the separation. The complex had to be one which did not exchange rapidly with $Cr(H_2O)_6^{+++}$ and which could be separated from $Cr(H_2O)_6^{+++}$. A Cr(III)-oxalate complex turned out to be a convenient one to use. This solution to the problem was possible because of the slowness of Cr(III) substitution reactions in general.[9]

The procedure was to blow a sample of the exchange mixture out of the apparatus into an equal or larger volume of 0.4 *f* oxalic acid. The aquo complex is unaffected by this treatment. The chromous ion, however, in the presence of air and oxalic acid is largely converted to a Cr(III)-oxalate complex. The reactions occurring here are not at all clear and would be an interesting subject for further study. In order to separate the two Cr(III) species, two grams of Dowex-50 cation-exchange resin in the acid form was added and the mixture stirred for at least two minutes. The aquo complex was taken up quantitatively by the resin, while the oxalate complex (presumably being an anion) stayed in solution. The resin was filtered off and washed with several small portions of water. The filtrate and washings (which contained most of the chromium that had originally been in the form of chromous ion and none that had been in the form of chromic ion) were then treated as described under "Specific Activity Measurements."

The observed zero time exchange was less than 1% with this procedure.

Since up to 30% (but usually less) of the chromous ion was oxidized to a Cr(III) species during the course of a run, and since the separation procedure gave a "chromous" fraction essentially free of chromic ion (but not *vice versa*), it was decided to follow the specific activity of the chromous ion and add tracer as chromic ion. Experiment No. 15 was done with chromous tracer to be sure that nothing unusual was occurring.

Procedure for Exchange Runs.—The apparatus used for carrying out the exchange runs is shown in Fig. 1. All connections were glass with the exception of a length of rubber tubing between the hydrogen tank and stopcock C.

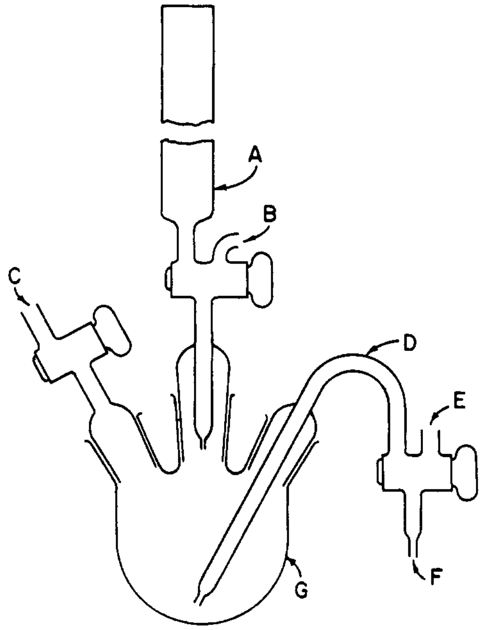

Fig. 1.—Apparatus for exchange runs.

To start an ordinary run, all reagents except the solution containing the chromous ion were put into the flask (G). (In all runs except No. 15 the tracer was added at this point. In run No. 15, the tracer was added as Cr^{++} through the Jones reductor (A).) The apparatus was assembled with a plug in place of the reductor, and evacuated through the hydrogen inlet (C). It was allowed to stand under vacuum, with occasional pumping, while the Jones reductor was being assembled. The reductor was filled with a solution of chromic perchlorate in 0.2 *f* perchloric acid. (In runs 16 and 17 the HCl to be added was also present.) The apparatus was then filled with hydrogen through the sample outlet (F), the pump was disconnected, and the hydrogen tank attached to stopcock C. With stopcock C open and the reduction valve set for about 6 pounds pressure, the plug was removed from the center neck of the flask and the Jones reductor put in place. The pump was attached to outlet B and the system was alternately evacuated and filled with hydrogen several times. The apparatus was tilted while hydrogen was being admitted in order to prevent solution from getting into the sample outlet before the chromous solution was added. After a final evacuation, the required volume of solution was added from the Jones reductor. (The volume being added was somewhat uncertain because of hydrogen evolution from the reductor. This uncertainty is the cause of the deviation from 1 *f* of the perchloric acid concentration in many of the runs. In addition, the hydrogen ion concentration of the solution in the reductor was reduced by an unpredictable amount.) The contents of the flask were swirled to mix them, hydrogen was admitted to a pressure of about 6 pounds per square inch above atmospheric pressure, and the apparatus immersed in a constant temperature bath. The temperature was known to ±0.1° and was kept constant to ±0.02°.

The time origin for the exchange experiments at 24.5 and at 0° was taken as the time when approximately half of the chromous solution had been admitted. For the 34.5° run the time origin was taken as the time at which the flask was put into the thermostat. In the 0° run the solution in the flask was pre-cooled, but the solution in the reductor was not.

In taking a sample, the flask was removed from the water-bath, tip F was washed by running water through E, and the end of the sample outlet tube was dipped under the surface of a 0.4 *f* oxalic acid solution in a small beaker. The required amount of solution was removed from the flask by opening the stopcock on the outlet tube, the pressure in the flask forcing the solution out. The volume of solution withdrawn was not controlled accurately, but the sample size

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[9] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

was measured by weighing the beaker before and after the sample was taken. The solution in the beaker was stirred fairly vigorously while the sample was being taken. Each sample was then treated as described under "Separation Method."

At the completion of the run, samples were taken for measurements of acid concentration, total chromium concentration, "infinite time" specific activity, and for any other analyses necessary.

Acid concentration was determined by titration with 0.1 *f* NaOH, using methyl orange as indicator. The end-point was determined by comparison with a color standard containing the same amount of methyl orange and chromium as the sample and buffered at *p*H 4 with potassium acid phthalate. At this *p*H hydrolysis of Cr(III) does not interfere with the titration.

The "infinite time" specific activities were determined (usually in duplicate) by converting a sample of the unseparated exchange mixture to chromate and measuring the specific activity in the same way as the samples.

The total chromium concentration in the exchange mixture was determined by converting a sample to chromate and measuring the optical density as described under "Specific Activity Measurements."

It should be noted that all exchange mixtures contained at least half as many gram-ions of Zn^{++} as of Cr^{++}.

Results

The exponential exchange law[10] as applied to the Cr(II)–Cr(III) exchange is

$$Rt = \frac{-(Cr^{II})(Cr^{III})}{(Cr)_T} \ln(1 - F) \qquad (1)$$

where R is the constant rate at which Cr(II) becomes Cr(III) and Cr(III) becomes Cr(II), $(Cr)_T$ is the total chromium concentration, and F is the fraction exchange attained at time t, determined in our experiments as the specific activity of the Cr(II) fraction at time t divided by the "infinite time" specific activity.

$$F = S_t/S_\infty$$

The specific activity at infinite time is, of course, equal to the average specific activity of all the chromium in the mixture.

If the exchange is first order in Cr(II) and first order in Cr(III), then $R = k_m(Cr^{II})(Cr^{III})$, where k_m is the specific rate constant for a given temperature and given concentrations of all other substances taking part in the reaction. The half-time, $t_{1/2}$, the time required for $(1 - F)$ to decrease by a factor of two, is related to k_m by

$$k_m = \frac{0.693}{t_{1/2}(Cr)_T} \qquad (2)$$

In the present experiments semi-logarithmic plots of $(1 - F)$ *vs.* t gave straight lines within experimental error (3 to 5%) as required by equation 1. Short time experiments indicated that the separation procedure caused less than 1% apparent exchange, so all exchange curves were drawn through $(1 - F) = 1$ at $t = 0$. Figure 2 shows some typical exchange curves.

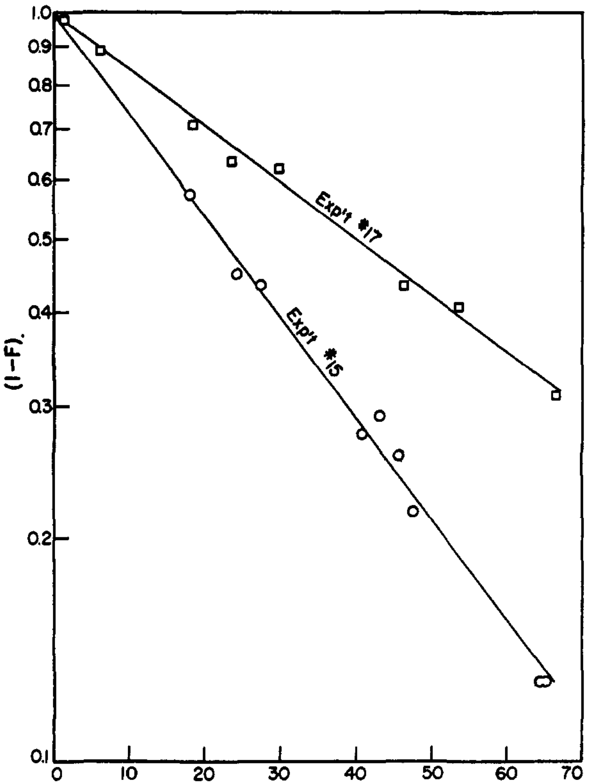

Fig. 2.—Typical exchange curves.

Order of the Reaction.—Table I summarizes the data obtained from experiments in which the chromium concentrations and total acid concentration were varied. The perchloric acid concentration was difficult to adjust exactly because of the method used to make up the exchange mixtures, so experiments 8 and 9 were purposely carried out at acid concentrations rather far from 1 *f*. For experiments 1 through 9, k_m was plotted *vs.* perchloric acid concentration. A straight line was drawn through the points and each individual value of k_m was then corrected to 1 *f* $HClO_4$ on the basis of the line. The results are listed under the column headed "k_c." This arbitrary correction takes care of changes in the activity coefficients of Cr^{++} and Cr^{+++} as well as the variations in the concentrations of H^+ and ClO_4^-.

TABLE I

VARIATION OF EXCHANGE RATE WITH CONCENTRATIONS OF CHROMIUM AND $HClO_4$, 24.5°

Expt. no.	$(Cr)_T$, *f*	$\frac{(Cr^{++})}{(Cr^{+++})}$	(H^+), *f*	$t_{1/2}$, hr.	k_m, f^{-1} hr.$^{-1}$	k_c, f^{-1} hr.$^{-1}$
1	0.0117	17	0.990	138	0.431	0.430
2	.0221	1	~1	69.7	.450	...
3	.0312	0,5	1.004	50	.445	.446
4	.0364	30	0.907	42.5	.448	.430
5	.0407	1.5	0.932	37.9	.450	.435
6	.0410	1	1.03	38.1	.443	.446
7	.1068	2	0.946	14.1	.460	.450
8	.0405	3	0.575	32.6	.525	.438
9	.0417	3	1.663	56.2	.296	.436
10	.0244	1	~0.2	16	1.8	...

The total chromium concentration was varied from 0.0117 to 0.1068 *f*, and the ratio of Cr(II) to Cr(III) concentrations from 30 to 0.5. The constancy of k_c for these experiments indicates that the exchange rate is indeed first order in (Cr^{II}) and first order in (Cr^{III}). The best value for the rate constant at 1.00 *f* $HClO_4$ is 0.440 f^{-1} hr.$^{-1}$. This is

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[10] See for example A. C. Wahl and N. A. Bonner (editors), "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 1 by O. E. Myers and R. J. Prestwood, p. 9.

in reasonably good agreement with the value of 0.168 obtained by Plane and Taube[7] under somewhat different conditions.

Dependence on Acid Concentration.—Table II summarizes the data obtained from experiments in which the perchloric acid was partly replaced by sodium perchlorate, the sum of the two concentrations being kept as close to 1.00 *f* as possible.

TABLE II

VARIATION OF EXCHANGE RATE WITH ACID CONCENTRATIONS, 24.5°, ($HClO_4$) + ($NaClO_4$) = 1.0 *f*

Expt. no.	(H^+)	($HClO_4$) + ($NaClO_4$)	(Cr)T	$t_{1/2}$, hr.	k_m
11	0.213	1.01	0.0436	8.55	1.86
12	.278	1.02	.0365	11.7	1.62
13	.371	1.03	.0403	16.0	1.07
14	.512	0.990	.0421	22.2	0.741

When the rate constants obtained from these experiments (plus the constant for 1.00 *f* $HClO_4$) are plotted *vs.* the reciprocal of the hydrogen ion concentration as in Fig. 3, something which can perhaps best be described as a straight line is obtained. The experimental errors are too large to define the intercept accurately, but it is certainly small. The intercept is less than 15% of the value of k_c at 1 *f* hydrogen ion.

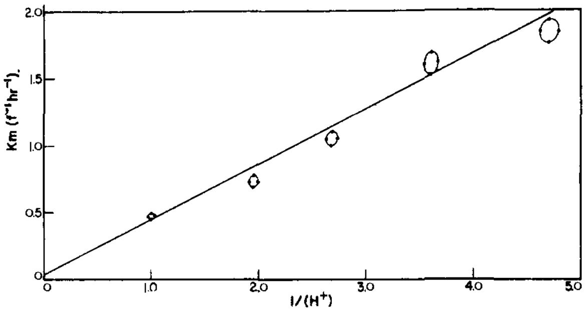


Fig. 3.—Dependence of exchange rate on acid concentration, 24.5° ($HClO_4$) + ($NaClO_4$) = 1.0 *f*.

Dependence on Other Variables.—Table III summarizes the data obtained from a variety of miscellaneous experiments.

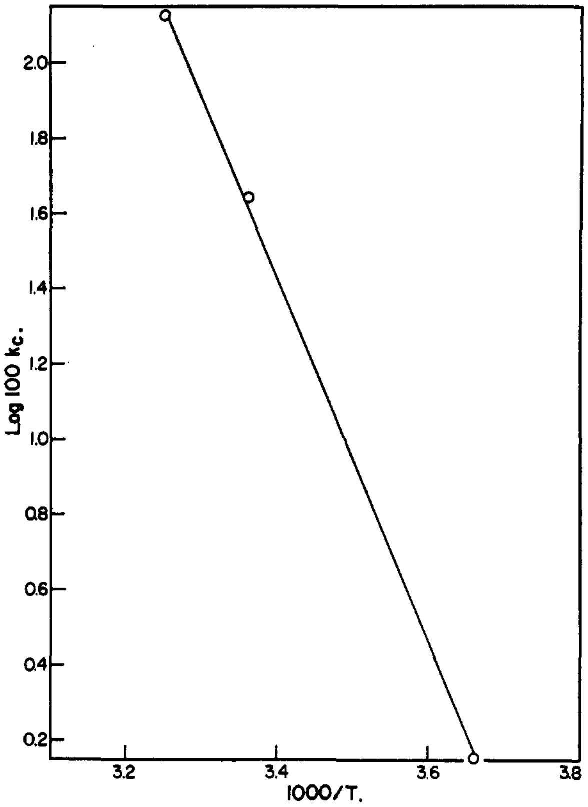


Fig. 4.—Temperature dependence of over-all rate constant.

In experiment 18 the initial ratio of chromous concentration to chromic concentration was about 15:1. After about 30% exchange had occurred, enough air (25 ml.) was admitted through the sample outlet to oxidize about half of the chromous ion. The resulting exchange curve had a slightly unusual shape, but the net effect was not large. If a straight line was drawn through the points obtained, the half time was, within experimental error, the same as would have been predicted if air had not been added. This experiment indicates that accidental admission of small amounts of air would have a negligible effect on the measured rates.

TABLE III

EFFECTS OF OTHER VARIABLES

Expt. no.	(Cr)T	(H^+)	$t_{1/2}$, hr.	k_m	k_c	Other conditions
15	0.0375	0.905	44 ± 10	0.42 ± 0.1	0.40 ± 0.1	Cr(II) tracer
16	.0365	.905	43.1	0.440	0.423	0.01 *f* HCl
17	.0340	.898	40	0.510	0.488	0.226 *f* HCl
18	.0384	.919	37.5	0.481	0.454	Cr(II) partially oxidized by air during run
19	.0369	.885	1250	0.0150	0.0143	0°
20	.0376	.969	13.5	1.36	1.34	34.5°

Experiments 19 and 20, combined with the best value of k_c for experiments at 24.5°, give an experimental activation energy of 22 ± 2 kcal./mole.

Experiments 16 and 17 were carried out in order to determine the effect of chloride on the exchange rate. There seems to be no appreciable effect. The rate constant in the presence of 0.226 *f* HCl in 1 *f* acid is only 12% higher than the value in the absence of chloride.

No experiments were carried out specifically to measure the effect of light and surface type and area on the rate. However, it seems unlikely that either has an appreciable effect. The experiments were done in three similar, but different, flasks and were run under varying conditions of illumination. If either surface or light had a large effect it seems unreasonable to expect that the measured rate constants would be as constant as they are.

It also seems unlikely that ionization of the solution caused by the tracer had any effect on the rate. Experiments 2, 5, 6 and 10 (the ones in which gamma counting was used) had about 30 times as much Cr^{51} present as did the remainder of the experiments. These experiments are completely consistent with the rest of the set.

Discussion

It appears that under the conditions used in these experiments the data can be represented in the form

$$R = (Cr^{II})(Cr^{III})[k_1 + A/(H^+)] \qquad (3)$$

where k_1 is much smaller than A.

The simplest and most obvious interpretation is that the exchange reaction can proceed by two paths, one acid independent and one involving a hydrolysis product whose concentration is inversely proportional to the hydrogen ion concentration. This rests on the assumption that the chromium activity coefficients are constant at constant ionic strength. The assumption is not necessarily a good one, but if the variation is not too large the above interpretation is reasonable.

If one assumes that the chromous ion does not hydrolyze under the conditions of these experiments, the rate law may be written

$$R = k_1(Cr^{++})(Cr^{+++}) + k_2(Cr^{++})(CrOH^{++}) \qquad (4)$$

The value of the equilibrium constant for the hydrolysis reaction of Cr^{+++}

$$Cr^{+++} + H_2O = CrOH^{++} + H^+$$

is $K = 1.5 \times 10^{-4}$ at ionic strength zero.[11]

Combining the expression for the equilibrium constant with equation 4 we get

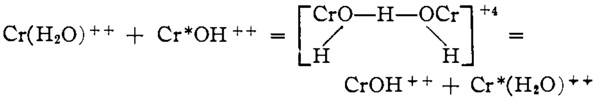
$$R = (Cr^{++})(Cr^{+++})\left[k_1 + \frac{k_2K}{(H^+)}\right] \qquad (5)$$

If hydrolysis proceeds to a sufficiently small extent, the total concentration of chromic species will be very nearly equal to the concentration of Cr^{+++}, and equation 5 is the same as the observed relationship (3). The chromic hydrolysis constant is small enough so that the above assumption is a good one.

For the present experiments, then

$$k_1 \leq 0.07 f^{-1}\text{hr.}^{-1} \text{ and } k_2 \cong 2.5 \times 10^3 f^{-1}\text{hr.}^{-1}$$

The large value of k_2 as compared with k_1 is consistent with (but not proof of) an atom transfer mechanism for the acid dependent path involving a symmetrical transition state



$$Cr(H_2O)^{++} + Cr^*OH^{++} = \left[\begin{matrix} CrO-H-OCr \\ / \qquad\quad \backslash \\ H \qquad\qquad H \end{matrix}\right]^{+4} = CrOH^{++} + Cr^*(H_2O)^{++}$$

Each chromium atom is presumed to have five more water molecules attached, but not shown in the above formulation. In this mechanism a hydrogen atom from the hydration sphere of the chromous ion is transferred to the OH group of a hydrolyzed chromic ion. This mechanism might be expected to be faster than an acid-independent one involving electron transfer through both hydration spheres or hydrogen atom transfer from a hydrated chromous ion to a hydrated chromic ion.

The above type of mechanism has been proposed for the Fe(II)–Fe(III) exchange by Dodson[12] and by Hudis and Wahl.[13]

In view of the fact that the Fe(II)–Fe(III) and Eu(II)–Eu(III) reactions are catalyzed by chloride, the lack of chloride catalysis of the Cr(II)–Cr(III) reaction is interesting.[14] Taube, Myers and Rich[15] have shown that catalysis by ions such as chloride can be brought about by the anion acting as a bridge and being transferred from one cation to the other in the process of the reaction. For the Cr(II)–Cr(III) exchange reaction the transition state would be

$$[(H_2O)_5Cr—Cl—Cr(H_2O)_5]^{+4}$$

This path is not available, however, because the chromic species is $Cr(H_2O)_6^{+++}$ and the water molecules in this complex are not labile.[16] Hence a chloride cannot reach the chromium. One would thus expect no chloride catalysis on the basis of this picture, but the exchange between Cr^{++} and $Cr(H_2O)_5Cl^{++}$ should be faster than the exchange between Cr^{++} and $Cr(H_2O)_6^{+++}$. Furthermore, no net change in the system $Cr(H_2O)_5Cl^{++}$–Cr^{++} should occur. If, however, the mechanism does not involve transfer of chlorine atoms, $Cr(H_2O)_5Cl^{++}$ should be converted to $Cr(H_2O)_6^{+++}$ and free chloride ion released to the solution as exchange occurs.

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[11] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, p. 247.

[12] R. W. Dodson, discussion following paper of note 3.

[13] J. Hudis and A. C. Wahl, THIS JOURNAL, **75**, 4153 (1953).

[14] It should be noted that Plane and Taube (note 7) found a large chloride catalysis. There is no obvious explanation for this discrepancy.

[15] H. Taube, H. Myers and R. Rich, THIS JOURNAL, **75**, 4118 (1953).

[16] J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951); *ibid.*, **18**, 757 (1950).