4. The magnetic susceptibility of each compound was measured at 25.3° and found to be 2340×10^{-6}, 4180×10^{-6} and 2470×10^{-6} per mole for VCl_4NO, V_2Cl_7NO and $V_2Cl_8(NO)_5$, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON UNIVERSITY]

The Kinetics of the Thallium(I)–Thallium(III) Exchange Reaction

BY RENÉ J. PRESTWOOD[1] AND ARTHUR C. WAHL

Harbottle and Dodson[2] and the authors[3] have previously reported that the rate of the exchange reaction between thallium(I) and thallium(III) in acid solution is measurable. Harbottle and Dodson found that in perchloric acid the rate was proportional to the first power of the concentration of each reactant. They also found that the rate increased when lithium perchlorate was added, varied when the acid concentration was varied, being a maximum at about 1 f., and was greater in hydrochloric acid than in perchloric acid. The authors found the rate was greater in nitric acid than in perchloric acid, increased with increasing nitric acid concentration (1.0–1.5 f.) and decreased with increasing perchloric acid concentration (1.5–3.5 f.). This paper describes our studies of the kinetics of the thallium(I)–thallium(III) exchange reaction.

Experimental

Radioactivity.—The 3.5-year Tl^{204} was used as tracer in all experiments. Part of the Tl^{204} was produced by the n,γ reaction and was obtained from the Clinton Laboratories on allocation from the U. S. Atomic Energy Commission; part was produced by the d,p reaction in the Washington University cyclotron. The activity produced in the cyclotron was purified by solution of the bombarded metal in dilute nitric acid, oxidation with aqua regia, ether extraction of thallium(III) chloride from 6 f. hydrochloric acid containing lead(II) carrier, precipitation of thallium(III) hydroxide from copper(II) and zinc(II) carriers with ammonium hydroxide, solution of the hydroxide in nitric acid, reduction with sulfite, precipitation of added iron(III) carrier with ammonium hydroxide, oxidation of the supernatant with aqua regia, and reprecipitation and solution of thallium(III) hydroxide. Thallium(III) oxide was purified prior to irradiation in the Oak Ridge pile by solution of thallium metal in dilute nitric acid, precipitation of thallium(I) chloride, oxidation with aqua regia, ether extraction of thallium(III) chloride from 6 f. hydrochloric acid, and precipitation and reprecipitation of thallium(III) hydroxide with ammonium hydroxide. The hydroxide was dried at 150–200°. The irradiated thallium(III) oxide was dissolved in nitric acid, the solution oxidized with aqua regia to be certain all the Tl^{204} was in the plus three oxidation state, and thallium(III) hydroxide precipitated and dissolved in the appropriate acid. The specific activity of this thallium was the same as that of an aliquot further purified from added lead and mercury carrier. Aluminum absorption curves of the radiation from either n,γ or d,p produced Tl^{204} agreed with the curve reported by Fajans and Voight.[4] The initial half-thickness was 30 mg. per cm.², the range 310 mg. per cm.², the beta to gamma ratio about 10^4.

Chemicals.—With the exception of the materials used in the preliminary studies of separation methods, all reaction mixtures were made up from the following solutions.

0.100 f. thallium(I) perchlorate (inactive)
0.100 f. thallium(III) perchlorate (radioactive) in 2.50 f. perchloric acid
5.00 f. perchloric acid
5.00 f. sodium perchlorate
5.00 f. sodium nitrate

Thallium(I) perchlorate was prepared by evaporation of a perchloric acid solution of Fisher pure thallium(I) nitrate and recrystallization of thallium(I) perchlorate three times from water. The thallium(III) perchlorate solution was prepared by solution of a mixture of active and inactive thallium(III) oxide in 9.3 f. perchloric acid and dilution. The inactive thallium(III) oxide was prepared by the method used to purify the oxide prior to neutron irradiation. Both thallium perchlorate solutions were assayed for thallium gravimetrically by precipitation of thallium (I) hexachloroplatinate(IV). The excess acid in the thallium(III) perchlorate solution was assayed by addition of excess standard sodium hydroxide, centrifugation of thallium(III) hydroxide, and back-titration with standard acid. Mallinckrodt "Analytical Reagent Grade" 60 or 71% perchloric acid and dried sodium nitrate and G. Frederick Smith anhydrous sodium perchlorate were used to prepare the remaining solutions. Mallinckrodt "Analytical Reagent Grade" ammonium hydroxide, sodium bromide, sodium chromate, sodium cyanide, and hexachloroplatinic acid (10% solution) were used in various solutions employed in the separation of the reactants.

Measurement of Radioactivity.—All precipitates were mounted by filtration on a tared, 18-mm. diameter piece of Whatman No. 42 filter paper, dried at 110°, weighed, mounted on a 2 × 2.5 in. cardboard card with scotch tape placed directly over the sample, and counted on a Geiger-Müller counter. During the filtration the filter paper was clamped between a glass chimney, 2.5 in. high and 14 mm. inside diameter, and a Hirsch funnel, without sides and with its surface ground flat. In order to obtain uniform deposits, the precipitate was allowed to settle on the filter paper before suction was applied. The Geiger counter[5] had an 8 mg./cm.² dural side window, 1.0 in. in diameter. The sample was placed directly below and 0.5 cm. from the window. The counter pulses were fed directly into the discriminator of an Instrument Development Laboratories' Model 161 scaler (scale of 256). The counter was stable, had a 100 v. plateau which was flat within 1% statistical error, and had a background of 50 counts per minute inside a lead shield. The response of the counter was linear to within about 2% up to the maximum counting rate measured (3000 counts per minute).

Since samples of the same weight, composition and

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[1] (a) This paper is a portion of the dissertation presented by René J. Prestwood in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Washington University, June, 1948; (b) Monsanto Fellow, 1948; (c) present address: Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

[2] G. Harbottle and R. W. Dodson, THIS JOURNAL, **70**, 880 (1948).

[3] R. J. Prestwood and A. C. Wahl, *ibid.*, **70**, 880 (1948).

[4] K. Fajans and A. F. Voight, *Phys. Rev.*, **60**, 619 (1941).

[5] The details of the construction and operation of the Geiger counter will be reported in a later publication.

thickness were always compared, and since the scotch tape was of uniform thickness (9 mg./cm.^{2}), no absorption or scattering corrections were made. This procedure appears to be justified because good agreement between duplicate samples was always obtained. For example the average deviation between the measured specific activities (counts per min./mg. Tl_2CrO_4) of duplicate samples, prepared for the determination of the equilibrium specific activities of twenty-five reaction mixtures, was 0.9%, a deviation consistent with known counting and weighing errors.

Procedure.—All components of a reaction mixture except the active thallium(III) solution (*ca.* 10% of the total volume) were mixed, the solution allowed to reach temperature equilibrium in a constant temperature (±0.1°) water-bath, and the thallium(III) solution added at room temperature. Less than fifteen minutes was required for the reaction mixture to regain temperature equilibrium, a time short compared to the exchange half-times (five to twelve hundred hours). Aliquots were removed at known time intervals, the reactants separated, and specific activity measurements made. Two aliquots were removed immediately after the solutions were mixed for measurement of the apparent zero-time exchange (see Separation-Induced Exchange and Coprecipitation Effects under Results), and six aliquots were removed at time intervals chosen so that 20–60% exchange had occurred in the solution. Concentrations were calculated on the volumes of the solutions at 25°. (Corrections for volume changes would be less than 1%.)

Four procedures for the separation of thallium(I) from thallium(III) were studied.

(1) **Hydroxide Separation.**—Thallium(III) hydroxide was precipitated with 15 f. ammonium hydroxide. Thallium(I) chromate was precipitated from the supernatant, washed, and mounted for the specific activity determination of the thallium(I) fraction. Thallium(III) hydroxide was converted to thallium(I) chromate by solution in acid, reduction with sulfurous acid, and precipitation with sodium chromate from an ammoniacal solution. This latter thallium(I) chromate precipitate was mounted for the specific activity determination of the thallium(III) fraction. Since the hydroxide separation was used only when the concentrations of thallium(I) and thallium(III) were equal, the equilibrium specific activity, S_∞, was taken as the average specific activity of each pair of samples.

(2) **Bromide Separation.**—Thallium(I) bromide was precipitated with 2 f. sodium bromide and mounted for the specific activity determination of the thallium(I) fraction. Thallium(III) remaining in the supernatant was converted to thallium(I) bromide by precipitation of thallium(III) hydroxide, solution in acid, reduction with sulfurous acid and precipitation with sodium bromide. The latter thallium(I) bromide was mounted for the specific activity determination of the thallium(III) fraction. The equilibrium specific activity was taken as the average specific activity of each pair of samples.

(3) **Chromate Separation.**—Thallium(I) chromate was precipitated and thallium(III) complexed with cyanide by addition of an aliquot of the reaction mixture to a solution 0.5 f. in sodium chromate, 1.0 f. in sodium cyanide, and 7.0 f. in ammonium hydroxide.[6] Since thallium(I) chromate can be filtered more readily if allowed to remain in contact with its supernatant for some time, it was allowed to stand fifteen minutes, then filtered and mounted for the specific activity determination of the thallium(I) fraction. The equilibrium specific activity, S_∞, was taken as the average specific activity of all the thallium in the reaction mixture. The average specific activity measurements were made on duplicate thallium(I) chromate samples prepared by the above procedure after thallium(III) had been reduced with sulfurous acid. The sizes of the aliquots were chosen so that in any run all thallium(I) chromate samples had the same weight. The equivalence of the average and equilibrium specific activities was checked in several runs by measurement of the specific activity of the thallium(I) fraction at a time when radioactive atoms were randomly distributed. An indirect check on the amount of thallium(III) coprecipitated with thallium(I) chromate was made by preparation of fourteen thallium(I) chromate samples by the same procedure. Seven were precipitated in the presence of thallium(III) ([Tl(I)] = [Tl(III)] = 10 mf.) and seven in the absence of thallium(III). The average weight of the samples precipitated in the presence of thallium(III) was 12.5 ± 0.1 mg. compared to 12.4 ± 0.1 mg. for those precipitated in the absence of thallium(III). Therefore little if any coprecipitation occurred.

(4) **Hexachloroplatinate Separation.**—Thallium(I) hexachloroplatinate was precipitated with hexachloroplatinic acid and mounted for the specific activity determination of the thallium(I) fraction. The equilibrium specific activity was taken as the average specific activity of all the thallium in the reaction mixture.

Errors.—The principal sources of error were the statistical fluctuations in the counting rate (± *ca.* 1%), uncertainty in the weight of the counted samples (± *ca.* 1%), and uncertainty in the concentrations of the solutions (± *ca.* 1%). The error in specific activities due to nonuniform distribution of the samples has been discussed and was considered negligible. We believe the probable error in the rates is not over 3%. The internal consistency of the data indicate the precision may be somewhat higher than 3%.

Results

Separation-Induced Exchange and Coprecipitation Effects.—The exponential exchange law[7,8] expressed in its logarithmic form for the thallium(I)–thallium(III) exchange is

$$Rt = -\frac{[\mathrm{Tl(I)}][\mathrm{Tl(III)}]}{[\mathrm{Tl(I)}] + [\mathrm{Tl(III)}]} \ln (1 - F) \qquad (1)$$

The exchange rate, R, is the rate at which thallium(I) becomes thallium(III) and at which thallium(III) becomes thallium(I). R is a constant when thallium(I) and thallium(III) are uniformly dispersed in the same phase and all conditions, except the distribution of the radioactive atoms, are constant. Square bracketed quantities indicate concentrations in gram atoms per liter, and t is the time the exchange of radioactive atoms is followed (time after addition of tagged thallium(III) to the rest of the reaction mixture). The fraction exchange, F, is a measure of the extent of the exchange of radioactive atoms and approaches an equilibrium value of 1.0. Since thallium(I) was initially inactive, F may be expressed as

$$F = \frac{S_{(\mathrm{I})}}{S_\infty} = \frac{S_{(\mathrm{III})} - S_{(\mathrm{III})0}}{S_\infty - S_{(\mathrm{III})0}} \qquad (2)$$

where the specific activity, S, is defined as the ratio of radioactive to total thallium atoms in the indicated oxidation state or chemical fraction, subscripts (I) and (III) referring to the oxidation states of thallium, and subscripts 0 and ∞ referring to the time the specific activity was measured. As can be seen from equation 1, $(1 - F)$ should decrease exponentially with time so that if 50% exchange occurred in time t, 75% exchange would occur in time $2t$, etc., and a semi-logarithmic

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(6) Harbottle and Dodson[2] used a similar solution containing ethanol with good results.

(7) H. A. C. McKay, *Nature*, **142**, 997 (1938).

(8) R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

plot of $(1 - F)$ against time should be a straight line passing through 1.0 at zero time.

If some of the thallium(I) can be separated free of thallium(III) and if no exchange occurs during the separation, then the specific activity of the thallium(I) fraction is equal to the specific activity of the thallium(I) in the reaction mixture just prior to the separation and may be used to calculate the fraction exchange that occurred in solution. However, if the thallium(I) fraction contains some thallium(III) and if exchange occurs during the separation, the specific activity of the thallium(I) fraction will not be equal to the specific activity of the thallium(I) in solution prior to the separation but will be a function of the amounts of thallium(I) and thallium(III) in the separated chemical fraction, their specific activities prior to separation, and the extent of the separation-induced exchange. Similar statements apply to a thallium(III) fraction.

It is shown in the appendix that *when the separation-induced exchange and the incomplete separation effects are reproducible* the following simple relations are true.

$$F = \frac{S - S_0}{S_\infty - S_0} = \frac{F' - F_0'}{1 - F_0'} \qquad (3)$$

S and S_0 are the specific activities of a chemical fraction, enriched in one of the exchange reactants separated at time t and time zero, respectively. F' and F_0' are the fraction exchange observed after separation at times t and zero, respectively. Substitution for F in equation 1 gives

$$\ln (1 - F') = - \frac{[\mathrm{Tl(I)}] + [\mathrm{Tl(III)}]}{[\mathrm{Tl(I)}][\mathrm{Tl(III)}]} Rt + \ln (1 - F_0') \qquad (4)$$

$$\ln (S_\infty - S) = - \frac{[\mathrm{Tl(I)}] + [\mathrm{Tl(III)}]}{[\mathrm{Tl(I)}]\ [\mathrm{Tl(III)}]} Rt + \ln (S_\infty - S_0) \qquad (5)$$

Therefore semi-logarithmic plots of $(1 - F')$ *vs.* t and $(S_\infty - S)$ *vs.* t should be straight lines with intercepts of $(1 - F_0')$ and $(S_\infty - S_0)$, respectively, at $t = 0$. The slopes and half-values of these plots will be the same as those of a semi-logarithmic plot of $(1 - F)$ *vs.* t, and the exchange rate, R, may be calculated from the half-value, $t_{1/2}$ (half-time of the exchange reaction occurring in the solution; $t = t_{1/2}$ when $F = 0.5$), of any of these plots.

$$R = \frac{[\mathrm{Tl(I)}][\mathrm{Tl(III)}]}{[\mathrm{Tl(I)} + [\mathrm{Tl(III)}]} \times \frac{0.693}{t_{1/2}} \qquad (6)$$

Figure 1, curves A, B and C, shows semi-logarithmic plots of $(1 - F')$ *vs.* t for three different separation procedures applied to identical reaction mixtures. Curve D is a plot of $(1 - F)$ *vs.* t, F having been calculated from the F' and F_0' values plotted in curves A, B and C.

The specific activity values used in calculations of the fraction exchange were in units of *counts per min./mg. of sample* and were not the ratio of *radioactive to total thallium atoms* as defined.

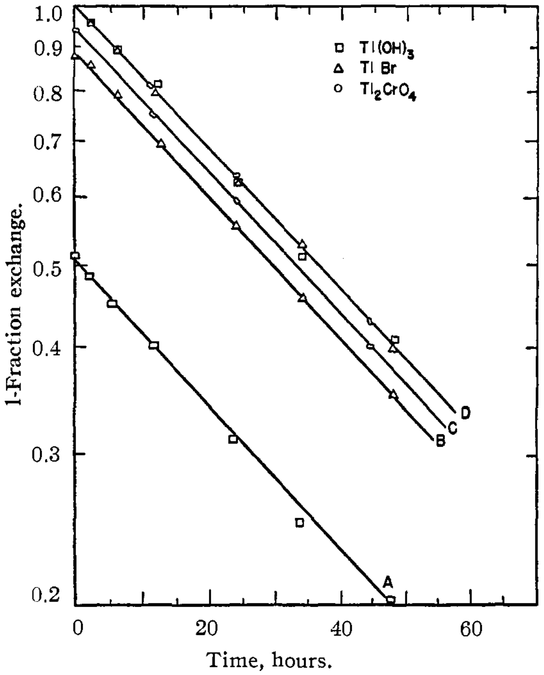

Fig. 1.—Semi-logarithmic plot of (1-fraction exchange) against time, reaction solution: 24.4 mf. $TlClO_4$, 24.4 mf. $Tl(ClO_4)_3$, 1.50 f. $HClO_4$, 24.8°. Curve A: Reactants separated by precipitation of $Tl(OH)_3$; 0.5 ml. 15 f. NH_4OH added to 2.0 ml. aliquots. Curve B: Reactants separated by precipitation of TlBr; 2.0 ml. aliquots added to 0.5 ml. 2.0 f. NaBr. Curve C: Reactants separated by precipitation of Tl_2CrO_4; 2.0 ml. aliquots added to 2.0 ml. 0.5 f. Na_2CrO_4, 1.0 f. NaCN, 7.0 f. NH_4OH. Curve D: Points of curves A, B and C corrected by equation 3.

However, since ratios of specific activities are always used in these calculations, this substitution is justified provided the counting efficiencies and compositions of all the samples from a given run are the same. The agreement of the data with the predicted exponential exchange law is a good indication that the above procedure was justified. Further justification in the case of the chromate separation procedure is given in the experimental section where it is shown that (1) the counting efficiencies of duplicate thallium(I) chromate precipitates are the same and (2) that little if any thallium(III) is coprecipitated with thallium(I) chromate. The latter is evidence that thallium(I) chromate samples have the same composition whether prepared for measurement of the specific activity of the thallium(I) fraction or the average thallium specific activity.

Several separation procedures were studied in order to find one which gave small and reproducible values of F_0'. A brief summary of the results of this study is given in Table I.

As can be seen from the data presented in Table I, only a small and reproducible apparent zero-time exchange occurred during the chromate separation. Therefore this method of separation was used in all the kinetic studies of the homogeneous exchange. Since the thallium(I) chromate precipitate was allowed to stand for fifteen minutes in contact with its supernatant, a check was made to see if the standing increased the apparent zero-time exchange due to the heterogeneous exchange reaction between $Tl_2CrO_4(s)$ and $Tl(CN)_6^{\equiv}$. As seen from the results in Table II, the heterogeneous exchange is very slow.

The heterogeneous exchange between freshly precipitated thallium(III) hydroxide and thallium(I) ion in ammonium hydroxide solution was also measured. The fraction exchange was 22% for a ten-minute contact at room temperature.

Homogeneous Exchange—Procedure.—The general procedure has been described in the experimental section. The ionic strength (concentrations expressed in moles per liter) of all reaction mixtures was adjusted to 3.68 with sodium perchlorate. The reactants were separated by the chromate method. The measured fraction exchanges were corrected by equation 3, and the rates were calculated from the half-times obtained from semi-logarithmic plots of $(1 - F)$ *vs.* t. All points fell on straight lines passing through 1.0 at $t = 0$. A typical plot is shown in Fig. 2.

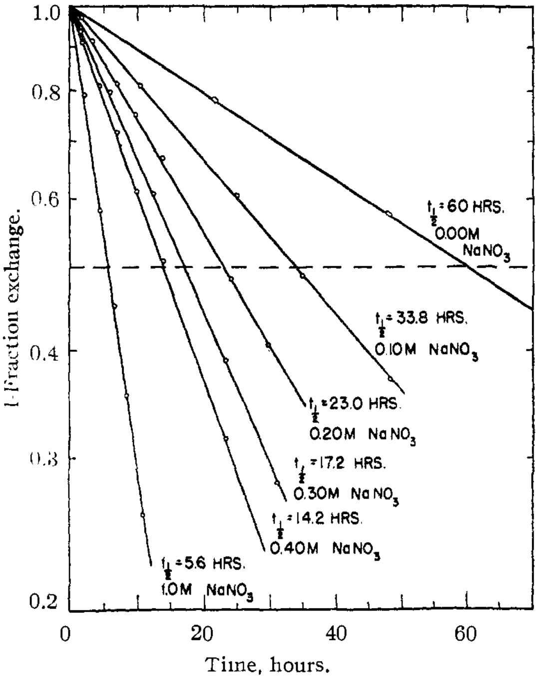

Fig. 2.—Semi-logarithmic plot of (1-fraction exchange) against time at various $NaNO_3$ concentrations (10.0 mf. $TlClO_4$, 10.0 mf. $Tl(ClO_4)_3$, 2.50 f. $HClO_4$, 37.3°, μ adjusted to 3.68 with $NaClO_4$).

Homogeneous Exchange.—[Tl(I)], [Tl(III)] Dependence.—Table III shows the dependence of the exchange half-time on the thallium(I) and thallium(III) concentrations.

TABLE I

APPARENT ZERO-TIME EXCHANGE (F_0')

Reaction mixture [Acid] (f.)	[Tl][a] (mf.)	°C.	Vol., ml.	Separations Ppt.	Vol.[b]	F_0' (%)[c]
0.3 HNO_3	48.8	~25	2.0	$Tl(OH)_3$	0.5*	66.7 ± 0.4
1.0 HNO_3	48.8	~25	2.0	TlBr	0.5*	9.0 ± 1.4
1.5 HNO_3	48.8	25	2.0	$Tl(OH)_3$	0.5	43.5 ± 0.5
				TlBr	0.5	22.5 ± 1.5
1.5 $HClO_4$	48.8	25	2.0	$Tl(OH)_3$	0.5*	51.0 ± 2.0
				TlBr	0.5	12.1 ± 0.3
				Tl_2PtCl_6	10.0*[d]	14.5 ± 0.2
				Tl_2CrO_4	2.0	6.2 ± 0.1
2.5 $HClO_4$	48.8	25	2.0	TlBr	2.0	12.9 ± 0.3
3.5 $HClO_4$	48.8	25	2.0	TlBr	2.0	12.8 ± 0.5
0.8 $HClO_4$[e]	10.0	10	10.0	Tl_2CrO_4	8.0	6.3 ± 0.0
		25	10.0	Tl_2CrO_4	8.0	5.5 ± 0.1
		37	10.0	Tl_2CrO_4	8.0	5.6 ± 0.0
		50	10.0	Tl_2CrO_4	8.0	5.7 ± 0.1
2.5 $HClO_4$[e]	20.0	10	5.0	Tl_2CrO_4	4.0	6.2 ± 0.0
		25	5.0	Tl_2CrO_4	4.0	6.1 ± 0.1
		~25	5.0	Tl_2PtCl_6	1.0	5.3 ± 0.1
		~25	5.0	Tl_2PtCl_6	1.0*	5.4 ± 0.1
		37	5.0	Tl_2CrO_4	4.0	6.0 ± 0.0
		50	5.0	Tl_2CrO_4	4.0	5.6 ± 0.0
2.5 $HClO_4$[e]	15.0[f]	25	5.0	Tl_2CrO_4	4.0	5.2 ± 0.5
	35.0[g]	25	2.0	Tl_2CrO_4	2.0	10.1 ± 0.1
	50.0	25	2.0	Tl_2CrO_4	2.0	6.4 ± 0.0
	30.0	25	5.0	Tl_2CrO_4	4.0	6.5 ± 0.0
	5.0	25	10.0	Tl_2CrO_4	8.0	5.5 ± 0.1

[a] Total thallium concentration; [Tl] = [Tl(I)] + [Tl(III)]. Unless otherwise noted [Tl(I)] = [Tl(III)] = [Tl]/2. [b] Volume of the following precipitating agents

ppt.	reagent
$Tl(OH)_3$	15 f. NH_4OH
TlBr	2 f. NaBr
Tl_2PtCl_6	0.044 f. H_2PtCl_6
Tl_2CrO_4	0.5 f. Na_2CrO_4, 1.0 f. NaCN, 7.0 f. NH_4OH

The reaction mixture was added to the precipitating agent except in runs indicated by an asterisk (*) in which the precipitating agent was added to the reaction mixture. [c] The recorded values are in general the average of two runs; a few are the average of three or four runs. The recorded errors are the average deviation of the individual runs from the average value. [d] 0.0055 f. H_2PtCl_6. [e] μ adjusted to 3.68 with $NaClO_4$. [f] 10.0 mf. Tl(I), 5.0 mf. Tl(III). [g] 10.0 mf. Tl(I), 25.0 mf. Tl(III).

TABLE II

DEPENDANCE OF APPARENT ZERO-TIME EXCHANGE ON TIME INTERVAL BETWEEN PRECIPITATION AND FILTRATION (CHROMATE SEPARATION)

Time, min.	2	10	30	90	210
F_0', %	5.5	5.6	5.8	6.0	6.2

TABLE III

(2.50 f. $HClO_4$, 24.9°, μ adjusted to 3.68 with $NaClO_4$)

$TlClO_4$, mf.	$Tl(ClO_4)_3$, mf.	$t_{1/2}$ hr.	$\frac{1}{[Tl(I)] + [Tl(III)]}$, mole^{-1}·liter
25.0	25.0	72	20.0
10.0	25.0	109	28.6
15.0	15.0	123	33.3
10.0	10.0	189	50.0
10.0	5.0	248	66.7

If the exchange reaction is bimolecular, $R = k[Tl(I)][Tl(III)]$, substitution of $k[Tl(I)][Tl(III)]$ for R in equation 6 gives

$$t_{1/2} = \frac{0.693}{[Tl(I)] + [Tl(III)]} \times \frac{1}{k} \qquad (7)$$

Figure 3, a plot of the data in Table III, shows that the half-time of the exchange is inversely proportional to the total thallium concentration, as predicted from equation 7 for a bimolecular reaction.

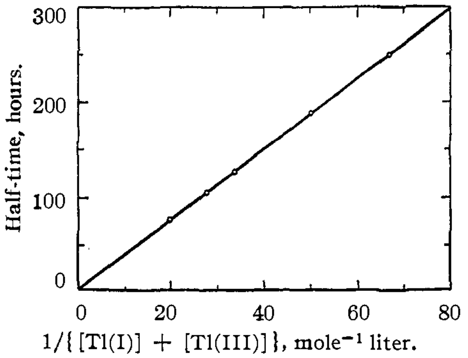

Fig. 3.—Effect of total thallium concentration on the half-time of the exchange (2.50 f. $HClO_4$, 24.9°, μ adjusted to 3.68 with $NaClO_4$).

Homogeneous Exchange—$[H^+]$ Dependence.—Table IV summarizes the data from sixteen runs made at various acid concentrations and at various temperatures. At any one temperature plots of log $R/[Tl(I)]\,[Tl(III)]$ *vs.* log $[H^+]$ resulted in curves whose slopes approached zero at high acid concentration. However, plots of $R/[Tl(I)][Tl(III)]$ against $1/[H^+]$ (see Fig. 4) resulted in straight lines. This suggests that there are two paths for the exchange, one hydrogen ion independent and one hydrogen ion dependent.

$$R = [Tl(I)][Tl(III)]\left\{k + \frac{k'}{[H^+]}\right\} \tag{8}$$

The intercepts of the lines give the values of k at the various temperatures, and the slopes of the lines give the values of k'.

TABLE IV

(μ adjusted to 3.68 with $NaClO_4$)

$HClO_4$, f.	[Tl],[a] mf.	Temp., °C.	$t_{1/2}$ hr.	$R/[Tl(I)]$ $[Tl(III)]$, mole⁻¹· liter·hr.⁻¹
0.80	10.0	9.9	1160	0.0598
1.50	20.0	9.9	720	.0481
2.50	20.0	9.9	840	.0412
3.50	20.0	9.9	930	.0373
0.80	10.0	24.9	288	.241
1.50	20.0	24.9	168	.206
2.50	20.0	24.9	189	.183
3.50	20.0	24.9	198	.175
0.80	10.0	37.3	100	.694
1.50	20.0	37.3	55.5	.625
2.50	20.0	37.3	60.0	.578
3.50	20.0	37.3	63.5	.546
0.80	10.0	50.1	37.3	1.86
1.50	20.0	50.1	19.3	1.80
2.50	20.0	50.1	20.3	1.71
3.50	20.0	50.1	21.0	1.65

[a] Total thallium concentration [Tl] = [Tl(I)] + [Tl(III)]; [Tl(I)] = [Tl(III)]; perchlorate salts used.

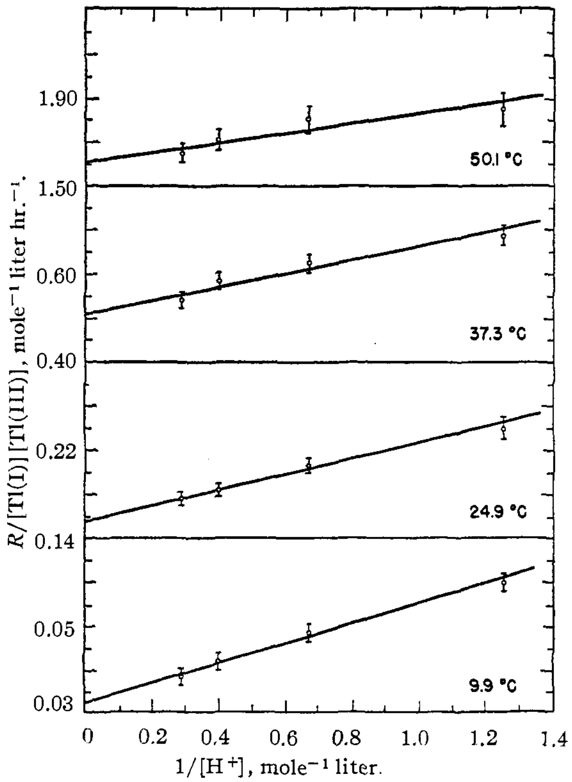

Fig. 4.—Effect of acid concentration on the exchange rate (μ adjusted to 3.68 with $NaClO_4$).

Curves A and B, Fig. 5, are semi-logarithmic plots of k and k' against the reciprocal of the absolute temperature. The experimental activation energies determined from these plots are 17,600 ± 400 cal. for the hydrogen ion independent path and 10,300 ± 1,600 cal. for the hydrogen ion dependent path. The rate constants may be expressed as

$$k = 3.8 \times 10^8\, e^{-17,600/RT} \text{ mole}^{-1}\text{·liter·sec.}^{-1} \tag{9}$$
$$k' = 790\, e^{-10,300/RT} \text{ sec.}^{-1} \tag{10}$$

where R is the gas constant and T is the absolute temperature.

Homogeneous Exchange—$[NO_3^-]$ Dependence.—Five runs were made at 37.3° in which the sodium nitrate concentration was varied from 0.100 to 1.00 f. and the other conditions were held constant. The experimental exchange curves obtained along with the curve for the ex-

TABLE V

(10 mf. $TlClO_4$, 10 mf. $Tl(ClO_4)_3$, 2.50 f. $HClO_4$, 37.3°, μ adjusted to 3.68 with $NaClO_4$)

$NaNO_3$, f.	$t_{1/2}$, hr.	$R/[Tl(I)][Tl(III)]$, mole⁻¹·liter·hr.⁻¹
0.000	60.0	0.578
.100	33.8	1.03
.200	23.0	1.51
.300	17.2	2.02
.400	14.2	2.49
1.00	5.6	6.2

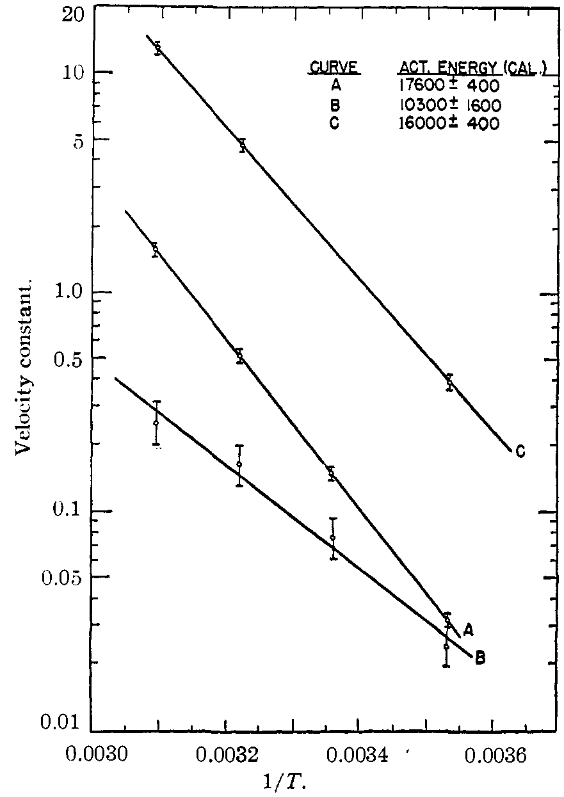

Fig. 5.—Temperature dependence of the three exchange paths. Curve A: $[H^+]$ independent path (k vs. $1/T$). Curve B: $[H^+]$ dependent path (k' vs. $1/T$). Curve C: $[NO_3^-]$ dependent path (k'' vs. $1/T$).

change in the absence of sodium nitrate are shown in Fig. 2. Table V is a summary of these data, and Fig. 6 is a plot of the rate against the sodium nitrate concentration.

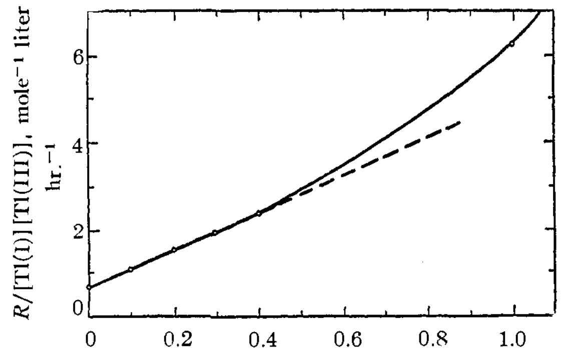

Fig. 6.—Effect of sodium nitrate concentration on the exchange rate (10.0 mf. $TlClO_4$, 10.0 mf. $Tl(ClO_4)_3$, 2.50 f. $HClO_4$, 37.3°, μ adjusted to 3.68 with $NaClO_4$).

Below 0.4 f. sodium nitrate the exchange rate is a linear function of the sodium nitrate concentration which suggests still a third path for the exchange in the presence of nitrate.

$$R = [Tl(I)][Tl(III)]\{k + (k'/[H^+]) + k''[NO_3^-]\} \quad (11)$$

The temperature dependence of k'' was investigated by measurement of the exchange rates at 9.9 and 50.1° (10 mf. $TlClO_4$, 10 mf. $Tl(ClO_4)_3$, 2.50 f. $HClO_4$, 0.400 f. $NaNO_3$, μ adjusted to 3.68 with $NaClO_4$). The half-time at 9.9° was 179 hours and at 50.1°, 5.03 hours. From the previously determined values of k and k', values of k'' were calculated at the various temperatures. A plot of k'' vs. $1/T$ is shown in Fig. 5, curve C. The experimental activation energy of the nitrate dependent path is 16,000 ± 400 cal. The rate constant may be represented as

$$k'' = 2.5 \times 10^8\, e^{-16{,}000/RT} \text{ mole}^{-2}\text{·liter}^2\text{·sec.}^{-1} \quad (12)$$

A summary of the experimentally determined rate constants is given in Table VI.

TABLE VI

SUMMARY OF EXPERIMENTAL RATE CONSTANTS

(10.0–25.0 mf. $TlClO_4$, 5.0–25.0 mf. $Tl(ClO_4)_3$, 0.80–3.50. f. $HClO_4$, 0.00–0.40 f. $NaNO_3$, μ adjusted to 3.68 with $NaClO_4$)

Temp., °C.	k, mole^{-1}·liter·hr.$^{-1}$	k', hr.$^{-1}$	k'', mole^{-2}·liter^2·hr.$^{-1}$
9.9 ± 0.1	0.032 ± 0.002	0.023 ± 0.004	0.38 ± 0.02
24.9 ± .1	.154 ± .008	.07 ± .01	(1.60)[a]
37.3 ± .1	.510 ± .025	.15 ± .03	4.7 ± 0.2
50.1 ± .1	1.61 ± .08	.24 ± .05	13.0 ± .5

[a] Calculated from equation 12.

Heterogeneous Catalysis.—The exchange reaction at 37.3° (solution 10.0 mf. $TlClO_4$, 10.0 mf. $Tl(ClO_4)_3$, 2.50 f. $HClO_4$, μ adjusted to 3.68 with $NaClO_4$) was run in the presence of a three inch length of 0.01 inch platinized platinum wire. A similar experiment was run in the presence of five grams of pulverized silica gel. The solutions in both experiments were stirred during the runs. The half-time of the exchange in the presence of the platinum black was 1.6 hours and in the presence of silica gel 61.5 hours. These values may be compared with the half-time of 60.0 hours obtained under the same conditions in the absence of solid catalysts. The small increase in half-time in the presence of silica gel is probably not real and may be due to inaccuracies in the calculated specific activities caused by contamination of the thallium(I) chromate with silica. As the run progressed the silica became increasingly difficult to separate from the solution, and the thallium(I) chromate samples became increasingly heavy. The large decrease in the half-time of the exchange in the presence of platinum black is real and indicates the exchange may occur more rapidly in the presence of a conductor.

Discussion

Separation-Induced Exchange and Coprecipitation Effects.—It is of interest to know what proportion of the apparent zero-time exchange is due to separation-induced exchange and what proportion to incomplete separation. The large, *ca.* 50%, apparent zero-time exchange caused by precipitation of thallium(III) hydroxide is difficult to explain purely on the basis of incomplete separation. For such an explanation it would be necessary to postulate *ca.* 25% cross contamination of the thallium(I) and thallium(III) fractions. Such a figure appears at least an order of magnitude too large in view of the very low solubility of thallium(III) hydroxide in ammonium hydroxide and the clear and colorless appearance of the supernatant and wash resulting from centrifugation of the hydroxide. Also the color of thallium(I) chromate prepared for counting directly from the ammoniacal supernatant and wash was very sensitive to small amounts of thallium(III) impurity; we estimate a few per cent. of thallium(III) gave the chromate a distinctly brown color. Therefore we believe that most (> 90%) of the apparent zero-time exchange caused by the hydroxide separation was due to separation-induced exchange.

The coprecipitation of thallium(III) with thallium(I) chromate in the chromate separation was discussed in the experimental section, and it was concluded that little if any coprecipitation occurred. Therefore separation-induced exchange again seems to be the important factor in the apparent zero-time exchange.

In the bromide and hexachloroplatinate separations no attempt was made to resolve the separation-induced exchange and coprecipitation effects.

The rates of heterogeneous exchange between freshly precipitated thallium(III) hydroxide and thallium(I) ion and between freshly precipitated Tl_2CrO_4 and $Tl(CN)_6^{=}$ were not sufficiently large to account for the observed separation-induced exchanges. Therefore it seems likely that most of the separation-induced exchange occurred while the precipitates were forming.

Separation-induced exchange may be an important factor in many isotopic exchange studies. At the present time there seems to be no reason to believe it need be zero or measurable. When chemical methods of separation are used and when the apparent zero-time exchange is 100%, there is no way of telling whether the rapid exchange occurred in solution prior to the separation or whether it occurred during the separation. Therefore unless physical methods of separation were used, reports of instantaneous complete exchange should be interpreted with caution.

Homogeneous Exchange.—Thallium(I) perchlorate and thallium(I) hydroxide are strong, soluble electrolytes, so essentially all thallium(I) in perchloric acid solution must exist as Tl^+. Sherrill and Haas[9] found that the solubility of thallium(III) hydroxide in perchloric acid was proportional to the cube of the hydrogen ion concentration, indicating that most thallium(III) present in perchloric acid solution exists as Tl^{+++}.

The kinetic data, which are well represented by the rate law given in equation 11, indicate that in perchloric acid solution containing sodium nitrate the exchange between thallium(I) and thallium(III) proceeds via three independent paths. The following simple mechanism is consistent with the experimental rate law.

Path (1).—Two electrons are transferred directly from Tl^+ to Tl^{+++}

$$\mathrm{Tl}^{+} + \mathrm{Tl}^{*+++} \underset{k}{\overset{k}{\rightleftarrows}} \mathrm{Tl}^{+++} + \mathrm{Tl}^{*+} \qquad (13)$$

Path (2).—A small fraction[10] of one of the reactants (probably Tl^{+++}) is hydrolyzed, and two electrons are transferred between the hydrolysis product and the other reactant (the OH^- may or may not be transferred when the transition state decomposes)

$$\mathrm{Tl}^{*+++} + \mathrm{H_2O} = \mathrm{Tl^*OH}^{++} + \mathrm{H}^{+}\ K_h\ \text{(rapid, reversible)} \qquad (14)$$

$$\left\{\begin{array}{l}\mathrm{Tl}^{+} + \mathrm{Tl^*OH}^{++} \xrightarrow{k_1} \mathrm{Tl}^{+++} + \mathrm{Tl^*OH}\ \text{(rate determining)} \\ \mathrm{Tl^*OH} + \mathrm{H}^{+} \longrightarrow \mathrm{Tl}^{*+} + \mathrm{H_2O}\ \text{(rapid follow reaction)}\end{array}\right\} \qquad (15a)$$

or

$$\mathrm{Tl}^{+} + \mathrm{Tl^*OH}^{++} \underset{k_1}{\overset{k_1}{\rightleftarrows}} \mathrm{TlOH}^{++} + \mathrm{Tl}^{*+}\ \text{(rate determining)} \qquad (15b)$$

$$k' = K_h k_1 \qquad (16)$$

Path (3).—A small fraction[11] of one of the reactants (probably Tl^{+++}) is complexed with nitrate ion, and two electrons are transferred between the nitrate complex and the other reactant (the NO_3^- may or may not be transferred when the transition state decomposes)

$$\mathrm{Tl}^{*+++} + \mathrm{NO_3}^{-} = \mathrm{Tl^*NO_3}^{++}\quad K\ \text{(rapid, reversible)} \qquad (17)$$

$$\left\{\begin{array}{l}\mathrm{Tl}^{+} + \mathrm{Tl^*NO_3}^{++} \xrightarrow{k_2} \mathrm{Tl}^{+++} + \mathrm{Tl^*NO_3}\ \text{(rate determining)} \\ \mathrm{Tl^*NO_3} \longrightarrow \mathrm{Tl}^{*+} + \mathrm{NO_3}^{-}\ \text{(rapid follow reaction)}\end{array}\right\} \qquad 18)a)$$

or

$$\mathrm{Tl}^{+} + \mathrm{Tl^*NO_3}^{++} \underset{k_2}{\overset{k_2}{\rightleftarrows}} \mathrm{TlNO_3}^{++} + \mathrm{Tl}^{*+}\ \text{(rate determining)} \qquad (18b)$$

$$k'' = Kk_2 \qquad (19)$$

The large increase in the exchange rate caused by the presence of platinum black indicates that

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(9) M. S. Sherrill and A. J. Haas, Jr., THIS JOURNAL, **58**, 953 (1936).

(10) If a large fraction of one of the reactants (Tl(III)) were hydrolyzed, the concentration of the unhydrolyzed reactant (Tl^{+++}) would decrease with decreasing hydrogen ion concentration and the curves in Fig. 4 would bend downward. The experimental points may indicate some deviation in this direction, but the deviation is within the experimental error.

(11) If a large fraction of one of the reactants (Tl(III)) were complexed by nitrate ion, the concentration of the uncomplexed reactant (Tl^{+++}) would decrease with increasing nitrate ion concentration and the curve in Fig. 6 would bend downward. The high point at 1 f. $NaNO_3$ in Fig. 6 may indicate that paths involving two or more nitrate ions may be becoming important (*e. g.*, reaction between $Tl^*(NO_3)_2^+$ and Tl^+).

in the presence of a conductor the transfer of electrons may be accomplished by still a fourth path, the electrons presumably being transferred through the conductor.

The entropy of activation for reaction 13, calculated from the experimental rate constants by use of the absolute rate theory,[12] in a solution of ionic strength 3.68 is −20 E. U. That predicted[12] for a reaction between +1 and +3 ions at zero ionic strength is about −30 E. U. The predicted entropy of activation will increase as the ionic strength of the solution increases, but no quantitative calculation has been attempted because of the known large deviations from the Debye–Hückel limiting law at high ionic strengths. (The velocity constants and heats and entropies of activation for reactions 15 and 18 cannot be calculated because the unknown equilibrium constants and heats of reactions 14 and 17 are included in the measured quantities.)

The mechanisms of electron transfer reactions and the relative importance of factors which determine the rates of such reactions are not well understood.[13] Although our study of the thallium(I)–thallium(III) exchange does little to clarify this important subject, it does point out certain inadequacies in some of the current theories.

The "equi-valence change" hypothesis proposed by Shaffer[14] and modified by Remick[15] predicts, among other things, that oxidizing and reducing agents which gain or lose the same number of electrons will react rapidly. The slow thallium(I)–thallium(III) exchange reaction is not consistent with this portion of the theory. Perhaps the theory should be modified to require a reasonable free energy decrease if a two electron transfer reaction is to be rapid.

The "coulombic-repulsion" hypothesis of Gorin[16] and Weiss[17] predicts that reactions between ions with charges of like sign will be slow. The slowness of the thallium exchange reaction and the catalytic effect of a conductor in the solution are consistent with this theory. However, the rapid oxidation[18] of tin(II) by thallium(III) in 3 f. perchloric acid appears to be inconsistent with the theory, unless it is assumed that Sn^{++} was in equilibrium with small but appreciable amounts of neutral molecules such as $Sn(OH)_2$ or that an undetected trace of catalytic impurity was present. An obvious difference between the thallium(I)–thallium(III) exchange reaction and the tin(II)–thallium(III) reaction is the over-all free energy change involved. Although there is no general correlation between the rate and the over-all free energy change of a reaction, this factor may be of importance in electron transfer reactions.

Appendix

Correction for Incomplete Separation of Reactants and Separation-Induced Exchange.—Consider an exchange reaction between the molecular species A and B in which atoms of element X, which is common to both species, are exchanged. Define specific activity as the ratio of radioactive X atoms to the total number of X atoms in the same molecular species or chemical fraction. Let

S_A = Specific activity of reactant A at time *t* and prior to the separation
S_{A_0} = Specific activity of reactant A at time zero and prior to the separation
S_B = Specific activity of reactant B at time *t* and prior to the separation
S_{B_0} = Specific activity of reactant B at time zero and prior to the separation
S_∞ = Equilibrium specific activity of A and B
S = Specific activity of the chemical fraction enriched in A and separated from the reaction mixture at time *t*
S_0 = Specific activity of the chemical fraction enriched in A and separated from the reaction mixture at time zero
a = Atoms of element X that were contained in species A prior to the separation and that appear in the chemical fraction enriched in A
b = Atoms of element X that were contained in species B prior to the separation and that appear in the chemical fraction enriched in A
F = Fraction exchange at time *t* prior to the separation

$$= \frac{S_A - S_{A_0}}{S_\infty - S_{A_0}} = \frac{S_B - S_{B_0}}{S_\infty - S_{B_0}}$$

F' = Fraction exchange observed after separation at time *t*

$$= \frac{S - S_{A_0}}{S_\infty - S_{A_0}}$$

F_0' = Fraction exchange observed after separation at time zero

$$= \frac{S_0 - S_{A_0}}{S_\infty - S_{A_0}}$$

Assume that under a given set of exchange and separation conditions *a* and *b* are independent of the time of separation, *i. e.*, that the separation-induced exchange and the degree of separation of the reactants are reproducible.

$$S = \frac{aS_A + bS_B}{a + b} \quad (1)$$

$$S_0 = \frac{aS_{A_0} + bS_{B_0}}{a + b} \quad (2)$$

$$S_\infty - S = \frac{aS_\infty + bS_\infty - aS_A - bS_B}{a + b} = \frac{a(S_\infty - S_A) + b(S_\infty - S_B)}{a + b} \quad (3)$$

$$S_\infty - S_0 = \frac{a(S_\infty - S_{A0}) + b(S_\infty - S_{B0})}{a + b} \quad (4)$$

$$\frac{S_\infty - S}{S_\infty - S_0} = \frac{a(S_\infty - S_A) + b(S_\infty - S_B)}{a(S_\infty - S_{A_0}) + b(S_\infty - S_{B_0})} \quad (5)$$

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[12] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 434.

[13] A. E. Remick, *Record Chem. Progress*, **9**, 95 (1948).

[14] P. A. Shaffer, *Cold Spring Harbor Symposia Quant. Biol.*, Vol. **VII**, 50 (1939).

[15] A. R. Remick, THIS JOURNAL, **69**, 94 (1947).

[16] M. H. Gorin, *ibid.*, **58**, 1787 (1936).

[17] J. Weiss, *J. Chem. Soc.*, 309 (1944).

[18] A. C. Wahl, unpublished work.

From the definition of F

$$1 - F = \frac{S_\infty - S_A}{S_\infty - S_{A_0}} = \frac{S_\infty - S_B}{S_\infty - S_{B_0}} \tag{6}$$

$$(S_\infty - S_A) = (1 - F)(S_\infty - S_{A_0}) \tag{7}$$

$$(S_\infty - S_B) = (1 - F)(S_\infty - S_{B_0}) \tag{8}$$

Substitution of equations 7 and 8 in 5 gives

$$\frac{S_\infty - S}{S_\infty - S_0} = \frac{(1 - F)[a(S_\infty - S_{A_0}) + b(S_\infty - S_{B_0})]}{a(S_\infty - S_{A_0}) + b(S_\infty - S_{B_0})} = 1 - F \tag{9}$$

Therefore

$$F = 1 - \frac{S_\infty - S}{S_\infty - S_0} = \frac{S - S_0}{S_\infty - S_0} \tag{10}$$

Alternatively from the definitions of F' and F'_0

$$1 - F' = \frac{S_\infty - S}{S_\infty - S_{A_0}} \tag{11}$$

$$1 - F'_0 = \frac{S_\infty - S_0}{S_\infty - S_{A_0}} \tag{12}$$

$$\frac{1 - F'}{1 - F'_0} = \frac{S_\infty - S}{S_\infty - S_0} = 1 - F \tag{13}$$

$$F = 1 - \frac{1 - F'}{1 - F'_0} = \frac{F' - F'_0}{1 - F'_0} \tag{14}$$

Summary

1. In aqueous perchloric acid solution a slow exchange between Tl(I) and Tl(III) has been observed. The exchange rate in aqueous solutions 0.8 to 3.5 f. $HClO_4$, 0.0 to 0.4 f. $NaNO_3$, 10–25 mf. $TlClO_4$, 5–25 mf. $Tl(ClO_4)_3$, 10 to 50°, and μ adjusted to 3.68 with $NaClO_4$ is well represented by

$$R = [Tl(I)][Tl(III)]\left\{k + \frac{k'}{[H^+]} + k''\,[NO_3{}^+]\right\}$$

where

$$k = 3.8 \times 10^8\, e^{-17,600/RT} \text{ mole}^{-1}\cdot\text{liter}\cdot\text{sec.}^{-1}$$

$$k' = 7.9 \times 10^2\, e^{-10,300/RT} \text{ sec.}^{-1}$$

$$k'' = 2.5 \times 10^8\, e^{-16,000/RT} \text{ mole}^{-2}\cdot\text{liter}^2\cdot\text{sec.}^{-1}$$

2. The presence of platinum black in the exchange solution caused a marked increase in the exchange rate; the presence of finely divided silica gel caused no measurable change in the rate.

3. Four precipitation methods for the separation of Tl(I) and Tl(III) were studied. All caused measurable and reproducible apparent zero-time exchanges due to coprecipitation or separation-induced exchange or both. It was found that separation-induced exchange was the predominant effect for at least two of the methods studied.

4. The following expression is derived which relates F, the fraction exchange that occurs in solution in time t, to F', the observed fraction exchange at time t, and F'_0, the observed fraction exchange at time zero (apparent zero-time exchange).

$$F = (F' - F'_0)/(1 - F'_0)$$

This expression is valid as long as the separation-induced exchange and the degree of separation are reproducible in a given exchange run. The expression has been checked experimentally.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

A Magnetic Study of Sulfur Vapor[1,2]

BY ALLEN B. SCOTT

By comparison with O_2, it has long been assumed that diatomic sulfur molecules are in the $^3\Sigma$ state and are thus paramagnetic. Neel[3] has measured the susceptibility of sulfur vapor at several temperatures, and, basing his calculation of the concentration of S_2 upon the vapor density measurements of Preuner and Schupp,[4] showed that this assumption was approximately correct, though his value for $\chi_M T$ was about 40% different from the theoretical value, and varied considerably with temperature. He was unable to conclude whether the disagreement was due to error in his magnetic data, error in the vapor equilibrium data, or was really an indication that S_2 was not truly in the triplet state.

An attempt has been made in this Laboratory to reinvestigate the susceptibility of sulfur vapor as a step in elucidating the complex equilibrium among the aggregates in sulfur vapor. If it can be established that S_2 has the theoretical moment of the triplet state, the measurement of susceptibility will then suffice to determine the concentration of S_2 in the presence of higher aggregates. In this paper are reported the results of a determination of the susceptibility of sulfur vapor at several temperatures between 550 and 850° which indicate that S_2 has the correct moment for the triplet state.

Experimental

The method was essentially that used in the measurement of the susceptibility of thermally dissociated iodine vapor.[5] A method for detecting the amount of displacement of the balance beam, consisting of a micro-

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[1] The work described in this paper was supported by a grant-in-aid from the Cottrell Fund of the Research Corporation, whose assistance is gratefuly acknowledged. Published with the approval of the Oregon State College Monographs Committee as Research Paper No. 136, Department of Chemistry, School of Science.

[2] Presented before the Division of Physical and Inorganic Chemistry at the San Francisco Meeting of the American Chemical Society, March 28, 1949.

[3] Neel, *Compt. rend.*, **194**, 2035 (1932).

[4] Preuner and Schupp, *Z. physik. Chem.*, **68**, 129 (1909).

[5] Scott and Cromwell, THIS JOURNAL, **70**, 3981 (1948).