

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

**Isotopic Exchange in Non-stable Systems<sup>1</sup>**

BY C. P. LUEHR, G. E. CHALLENGER AND B. J. MASTERS

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A general expression has been derived to represent the progress of a simple exchange reaction in a homogeneous system of non-constant volume undergoing simultaneous chemical conversion of either exchanging species into the other. The method has been applied to a number of specific examples and quantitative results have been obtained.

**Introduction**

The course of any simple isotopic exchange reaction, when carried out at chemical equilibrium in a homogeneous system, has been shown<sup>2</sup> to follow the logarithmic rate law expression

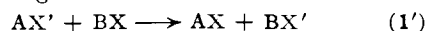
$$R = -\frac{ab}{v(a+b)} \times \frac{\ln(1-F)}{t} \quad (1)$$

in which  $R$  is the rate of the exchange reaction,  $a$  and  $b$  represent the constant amounts of the two exchanging species present in a system of constant volume  $v$ , and  $F$  represents the fraction of complete exchange which has occurred in the time  $t$ . Meyers and Prestwood<sup>3</sup> have discussed the applicability of equation 1 to exchange studies and Norris<sup>4</sup> has tabulated a number of expressions for  $F$  in terms of experimentally determinable quantities.

Previous studies of radiation-induced exchange reactions<sup>5</sup> by two of the present authors have prompted investigation of isotopic exchange kinetics for systems in which chemical equilibrium does not prevail. In the following treatment, consideration has been given to changes in concentration of the two exchanging species arising either through volume changes of the system or through chemical conversion of one exchanging species into the other during the course of the exchange reaction. As in the derivation of equation 1, it has been presumed that all exchangeable atoms in each of the exchanging species are equivalent, and that both species are homogeneously distributed throughout a single phase system.

**Derivation**

Consider a system of variable volume, the volume at time  $t$  being given by the arbitrary function  $v(t)$ . Two molecular species  $CX_p$  and  $DX_q$ , containing  $p$  and  $q$  exchangeable atoms of element X, respectively, are present. For simplicity these species will be represented by AX (corresponding to  $1/p$   $CX_p$  molecule) and by BX (corresponding to  $1/q$   $DX_q$  molecule) throughout the derivation. Atoms of X are exchanged



at a rate (*e.g.*, gram atoms per minute per liter) which is some function of the reactant concentrations

$$R_1 = f[(AX), (BX)] = R_1(t)$$

(1) This work was performed under the auspices of the United States Atomic Energy Commission.

(2) H. A. C. McKay, *Nature*, **142**, 997 (1938); R. B. Duffield and M. Calvin, *THIS JOURNAL*, **68**, 557 (1946).

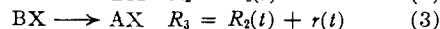
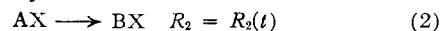
(3) A. C. Wahl and N. A. Bonner, editors, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 7-34.

(4) T. H. Norris, *J. Phys. Chem.*, **54**, 777 (1950).

(5) G. E. Challenger and B. J. Masters, *THIS JOURNAL*, **77**, 1063 (1955).

Since (AX) and (BX) will vary with time in a manner assumed to be known we have indicated that  $R_1$  is also a function of time. The notation  $X'$  used in equation 1' does not necessarily represent a tagged X atom, but is used only to distinguish between the two X atoms. Consequently,  $R_1(t)$  represents the *total* rate of X-atom exchange *via* reaction 1', and does not necessarily refer only to those interactions involving a tagged AX molecule and an untagged BX molecule.

Assume also that chemical conversion reactions occur in the system at the rates



It is indicated that the rate of reaction (3) differs from the rate of reaction (2) by the amount  $r(t)$ , which may be either positive or negative, provided that  $R_3$  does not become negative. Considering the system as a whole, the mole-per-minute rates of the reactions (1'), (2) and (3) are, respectively,  $R_1(t)v(t)$ ,  $R_2(t)v(t)$  and  $R_2(t)v(t) + r(t)v(t)$ .

The mole-per-minute rate of change in the amount of AX present is  $r(t)v(t)$  and the total change in the amount present at time  $t$  is  $\rho(t) = \int_0^t r(t)v(t) dt$  moles. The numbers of moles of AX and BX present at time  $t$  are then

$$\begin{aligned} a' &= (AX)v(t) = a + \rho(t) \\ b' &= (BX)v(t) = b - \rho(t) \end{aligned}$$

where  $a$  and  $b$  are the gram atoms of X initially present as AX and BX, respectively.

Now consider that some of the X atoms present are tagged, and can be represented by  $X^*$ . Then let

$$\begin{aligned} c &= \text{total gram atoms of } X^* \text{ atoms in the system} \\ z &= \text{gram atoms of } X^* \text{ atoms in the system in the species} \\ &\quad \text{BX} \\ c - z &= \text{gram atoms of } X^* \text{ atoms in the system in the} \\ &\quad \text{species AX} \end{aligned}$$

The rate of increase of  $z$  is given by

$$\frac{dz}{dt} = R(t) \frac{c-z}{a+\rho(t)} - \left[ R(t) + \frac{d}{dt} \rho(t) \right] \frac{z}{b-\rho(t)}$$

where

$$R(t) = R_1(t)v(t) + R_2(t)v(t)$$

Note that  $\frac{d}{dt} \rho(t) = r(t)v(t)$ . This is a first-order linear differential equation, the solution of which is

$$z = A \exp \left[ - \int \frac{(a+b)R(t) dt}{(a+\rho(t))(b-\rho(t))} \right] (b-\rho(t)) + \frac{c}{a+b} (b-\rho(t))$$

$A$  being an arbitrary constant. Introduction of the initial conditions yields

$$S_B = (S_{B_0} - S) \exp \left[ - \int_0^t \frac{(a+b)R(t) dt}{(a+\rho(t))(b-\rho(t))} \right] + S$$

$$S_A = (S_{A_0} - S) \exp \left[ - \int_0^t \frac{(a+b)R(t) dt}{(a+\rho(t))(b-\rho(t))} \right] \frac{a(b-\rho(t))}{b(a+\rho(t))} + S$$

The specific tracer ratios  $S_A$ ,  $S_B$  and  $S$  are defined as follows, the subscript 0 indicating initial values:

$$\begin{aligned} S_B &= z/b' & S_A &= (c-z)/a' \\ S_{B_0} &= z_0/b & S_{A_0} &= (c-z_0)/a \\ S &= c/(a+b) \end{aligned}$$

The equations may be put in the form

$$\ln(1 - F_B) = - \int_0^t \frac{(a+b)R(t) dt}{(a+\rho(t))(b-\rho(t))} \quad (4)$$

$$\ln(1 - F_A) = - \int_0^t \frac{(a+b)R(t) dt}{(a+\rho(t))(b-\rho(t))} + \ln \frac{a(b-\rho(t))}{b(a+\rho(t))} \quad (5)$$

Here the "apparent fractions of complete exchange" for BX and AX

$F_B = (S_B - S_{B_0})/(S - S_{B_0})$   $F_A = (S_A - S_{A_0})/(S - S_{A_0})$  are generally unequal.

Alternatively, equations 4 and 5 may be expressed in a more condensed form

$$\ln H = - \int_0^t \frac{(a+b)R(t) dt}{(a+\rho(t))(b-\rho(t))} + \ln \frac{b-\rho(t)}{b}$$

where

$$H = b'(S_B - S)/b(S_{B_0} - S) = a'(S_A - S)/a(S_{A_0} - S)$$

Note that

$$H = b'(1 - F_B)/b = a'(1 - F_A)/a$$

### Discussion

Since many thermal exchange reactions exhibit first-order dependencies upon both AX and BX, the general equations 4 and 5 will be integrated for a number of special cases in which  $R_1(t) = k(\text{AX})(\text{BX})$ , and the results applied to appropriate experimental systems. In addition, several cases of exchange processes following more complicated kinetics, but for which the equations 4 and 5 remain integrable, will be noted.

It is expedient to point out here that all of the expressions developed throughout this paper reduce to equation 1 for stable exchange systems.

**Special Case Ia.**— $R_1(t) = k(\text{AX})(\text{BX})$ ;  $R_2(t) = 0$ ;  $r(t) = \text{arbitrary}$ ;  $v(t) = (v_0 + st)$  liters, where  $s$  is the rate of change of volume in liters per unit time. Then  $(\text{AX}) = (a + \rho(t))/(v_0 + st)$ ,  $(\text{BX}) = (b - \rho(t))/(v_0 + st)$ , and equations 4 and 5 integrate to

$$\begin{aligned} \ln(1 - F_B) &= - \frac{k(a+b)}{s} \ln \frac{(v_0 + st)}{v_0} \quad (6) \\ \ln(1 - F_A) &= - \frac{k(a+b)}{s} \ln \frac{(v_0 + st)}{v_0} + \ln \frac{a(b-\rho(t))}{b(a+\rho(t))} \quad (7) \end{aligned}$$

**Special Case Ib.**—When  $r(t) = 0$ , the last term in equation 7 drops out. The equations then represent the rate of thermal exchange in a system in which solvent is being either added or removed at a constant known rate, with no net chemical changes occurring. This particular case was studied experimentally by measuring the thermal exchange of Tl(I) with Tl\*(III) in 0.8 N H<sub>2</sub>SO<sub>4</sub>, while diluting the solution with 0.8 N H<sub>2</sub>SO<sub>4</sub> at a constant rate. Aliquots were removed at fixed inter-

vals for counting and the bimolecular exchange rate computed by means of equations 6 and 7. The results are presented in Table I.

TABLE I

SPECIAL CASE Ib: Tl(I)-Tl(III) EXCHANGE DURING DILUTION AT 25°

$v_0 = 1$  liter,  $a = b = 1.702 \times 10^{-3}$  moles,  $s = 0.00387$  liters/minute.

$t$ (min.)	$v_0 + st$ , l.	$k$ (liter mole <sup>-1</sup> min. <sup>-1</sup> )
0	1.000	...
30	1.116	1.22
60	1.233	1.22
90	1.349	1.23
120	1.465	1.17
150	1.581	1.20

Although a dilution of approximately 60% occurred during the measurements, the results obtained are in excellent agreement with the bimolecular rate constant of  $k = 1.22$  liter mole<sup>-1</sup> min.<sup>-1</sup> previously obtained from studies<sup>6</sup> of the corresponding stable system.

**Special Case II.**—This is the same as case Ia except that  $v(t) = v = \text{constant}$ .

$$\ln(1 - F_B) = -kt(a+b)/v \quad (8)$$

$$\ln(1 - F_A) = -kt(a+b)/v + \ln \frac{a(b-\rho(t))}{b(a+\rho(t))} \quad (9)$$

In this case BX is being converted to AX while simultaneously undergoing thermal exchange with AX. Note that if the BX fraction (decreasing concentration) is counted, the rate expression is identical in form with equation 1, and  $F_B$  is independent of the amount of BX converted to AX. If the AX fraction is counted, it is necessary only to know how much BX has been converted into AX at the time each sample is taken for counting, the actual kinetics of the conversion process being unimportant.

This case was studied experimentally by titrating the thallic component of a Tl(I)-Tl\*(III) exchange system with a relatively concentrated solution of sodium sulfite, so that the volume change of the solution was negligible. During the course of the experiment the thallic-thallos ratio changed from about 3/1 to 1/3. By counting the Tl(III) fraction and applying equation 8, a value of  $k = 1.19$  liter mole<sup>-1</sup> min.<sup>-1</sup> was found. By counting the Tl(I) fraction and applying equation 9,  $k$  was found to be 1.29 liter mole<sup>-1</sup> min.<sup>-1</sup>. The results obtained by counting the Tl(I) fraction are shown graphically in Fig. 1. It should be noted that this example represents a rather unfavorable situation for measuring an exchange process, since in this case the chemical conversion contribution to the appearance of tagged thallos ions was almost five times the exchange contribution. Nevertheless, the value for the exchange rate constant obtained from this treatment,  $k = 1.29$  liter mole<sup>-1</sup> min.<sup>-1</sup>, agrees quite well with the value determined in the corresponding stable system.<sup>6</sup>

Equations 8 and 9 may also be used to analyze the data of Koskoski, Dodson and Fowler,<sup>7</sup> who studied the exchange of bromide ion with  $\alpha$ -bromo-

(6) B. J. Masters and G. E. Challenger, to be published.

(7) W. Koskoski, R. W. Dodson and R. D. Fowler, THIS JOURNAL, 63, 2149 (1941).

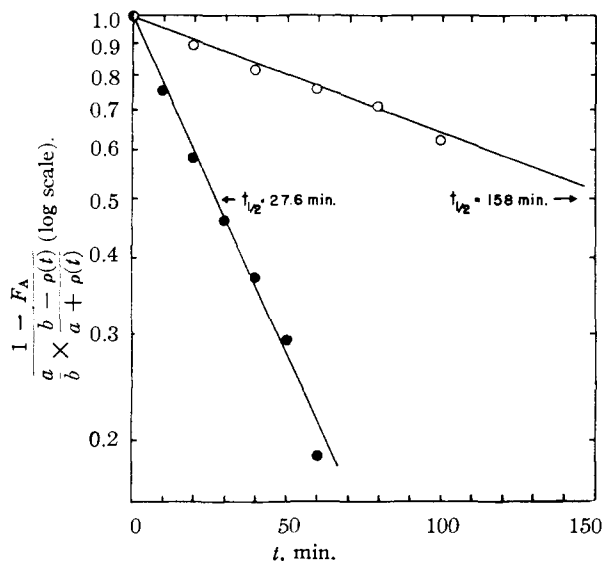
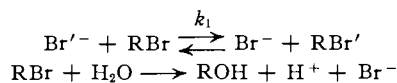


Fig. 1.—O, Tl(I)–Tl(III) exchange in 0.8 *N* H<sub>2</sub>SO<sub>4</sub>, 25°, during reduction with sulfur dioxide:  $a/v = 0.851 \times 10^{-3}$  *M*,  $b/v = 2.553 \times 10^{-3}$  *M*,  $\rho(t = 100 \text{ min.})/v = 1.291 \times 10^{-3}$  *M*. ●, Br<sup>−</sup>–CH<sub>3</sub>CHBrCOOH exchange during hydrolysis:  $a/v = 37.6 \times 10^{-3}$  *M*,  $b/v = 31.8 \times 10^{-3}$  *M*,  $\rho(t = 60 \text{ min.})/v = 7.7 \times 10^{-3}$  *M* (Koskoski, Dodson and Fowler<sup>7</sup>).

propionic acid in aqueous solution. Hydrolysis of the organic bromide during the course of the exchange reaction resulted in a non-stable exchange system.



These investigators derived the expression

$$k_1 = - \frac{1}{(a+b)t} \ln \left\{ 1 - r \frac{(a+b)}{(\text{RBr})} \right\}$$

where  $a$  = initial concentration of RBr,  $b$  = initial concentration of Br<sup>−</sup>, and  $r = (\text{RBr}^*)/[(\text{RBr}^*) + (\text{Br}^*)]$ . It may be shown that  $r(a+b)/(\text{RBr}) = F_B$ , so that the above expression readily may be converted to our equation 8. It may also be shown that  $\frac{a+b}{a} \left\{ 1 - \frac{b(1-r)}{(\text{Br}^-)} \right\} = F_A$  of equation 9, and  $b(\text{RBr})/a(\text{Br}^-) = a(b - \rho(t))/b(a + \rho(t))$  of equation 9. Consequently, using the data of Table II in the paper of Koskoski, *et al.*, values of

$$\log \frac{1 - F_A}{\frac{a(b - \rho(t))}{b(a + \rho(t))}}$$

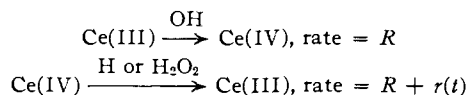
may be calculated and plotted against  $t$  as in Fig. 1. From the slope of this plot,  $k_1$  is calculated to be  $6.0 \times 10^{-3}$  liter mole<sup>−1</sup> sec.<sup>−1</sup>, in good agreement with the value  $6.3 \times 10^{-3}$  liter mole<sup>−1</sup> sec.<sup>−1</sup> reported by Koskoski, *et al.*

**Special Case III.**— $R_1(t) = k(\text{AX})(\text{BX})$ ;  $R_2(t) = R$  (constant);  $r(t) = r$  (constant);  $v(t) = v = \text{constant}$ .

$$\ln(1 - F_B) = -kt(a+b)/v + \frac{R}{r} \ln \frac{a(b - rv)}{b(a + rv)} \quad (10)$$

$$\ln(1 - F_A) = -kt(a+b)/v + \left(\frac{R}{r} + 1\right) \ln \frac{a(b - rv)}{b(a + rv)} \quad (11)$$

An illustration of this situation is provided by the radiation-induced Ce\*(III)–Ce(IV) exchange.<sup>5</sup> In this system, a thermal exchange corresponding to reaction (1') occurs at the rate  $R_1(t)$ , governed by the bimolecular rate constant  $k$ . In addition, water decomposition products are presumed to interact with both exchanging species in a manner analogous to reactions (2) and (3)



From independent measurements,  $r(t)$ , the net rate of ceric ion reduction, was found to be constant for constant irradiation rates. The bimolecular rate constant  $k$  was known from previous independent studies,<sup>5</sup> hence equations 10 or 11 could be directly applied to the irradiated exchange data and solved for  $R$ . These results are presented in Table II.

TABLE II

RADIATION INDUCED EXCHANGE OF Ce(III)–Ce(IV) BY 50 KVP. X-RAYS IN 0.8 *N* H<sub>2</sub>SO<sub>4</sub> AT 0°

$k$  = thermal exchange rate constant = 26.8 liter mole<sup>−1</sup> min.<sup>−1</sup>;  $r$  = Ce(IV) reduction rate =  $18.2 \times 10^{-6}$  liter mole<sup>−1</sup> min.<sup>−1</sup>

Time	$\frac{(a + rv)}{a} \times 10^3$ moles × 10 <sup>3</sup>	$\frac{(b - rv)}{b} \times 10^3$ moles × 10 <sup>3</sup>	$(1 - F_B)$	$R$ , mole liter min. <sup>−1</sup>
0	0.906	1.055	1.000	...
2	0.952	1.019	0.840	17.11
4	0.979	0.982	.697	18.33
6	1.015	.946	.584	18.16
8	1.052	.909	.482	18.87
10	1.088	.873	.422	16.49

The constancy of these  $R$  values, calculated by means of equation 10, appears to justify the assumption that  $R_2(t) = R$  remained constant throughout the experiment.

The situation illustrated by this example is one that commonly occurs in radiation chemistry mechanisms, so that equations 10 and 11 should be generally applicable to such studies.

**Further Special Cases.**—Some other situations for which equations 4 and 5 are easily integrated are the following

A.  $v(t) = v$  (constant);  $R_1(t) = k(\text{AX})^m(\text{BX})^n$ ;  $R_2(t) = R$  (constant);  $r(t) = r$  (constant). Both  $m$  and  $n$  must be integers, 0, 1, 2, ...

B. Same as A, with either  $m$  or  $n = 1$ . Then the other exponent may take any value, not necessarily an integer.

C.  $v(t) = (v_0 + st)$  liters;  $R_1(t) = k(\text{AX})^m(\text{BX})^n$ ; either  $R_2(t)$  or  $R_2(t)(v_0 + st) = R$  (constant);  $r(t)(v_0 + st) = r$  (constant). Then  $m$  and  $n$  may take the following values:  $m = 0, n = 0$ ;  $m = 0, n = 1$ ;  $m = 1, n = 0$ ;  $m = 1, n = 1$ ;  $m = 2, n = 0$ ;  $m = 0, n = 2$ .

D.  $R_1(t) = k(\text{AX})^m(\text{BX})^n$ ;  $R_2(t)v(t) = R$  (constant);  $r(t)v(t) = r$  (rate in system independent of volume variations).

Then if  $v(t) \propto (a + rt)^{(m-1)/(m+n-1)}$  the resulting integral is easily evaluated. This suggests the procedure of making the volume vary with time as above (by adding solvent) for the sole purpose of simplifying the mathematical results.

E. Same as C except that  $R_1(t) = k_1(\text{AX})^m$ .

$(BX)^{n_1} + k_2(AX)^{m_2}(BX)^{n_2} + \dots$  where the conditions in case C are satisfied by the number pairs  $m_1, n_1; m_2, n_2$ ; etc.

F. Same as A except that  $R_1(t) = k_1(AX)^{m_1}(BX)^{n_1} + k_2(AX)^{m_2}(BX)^{n_2} + \dots$  where the conditions in case A or B are satisfied by the number pairs  $m_1, n_1; m_2, n_2$ ; etc.

G.  $v(t) = v$  (constant);  $R_1(t) = k(AX)(BX)$ ;  $R_2(t) = k_2(AX)$ ;  $R_3(t) = k_3(BX)$ .

**Acknowledgment.**—We wish to thank Dr. R. D. Fowler of this Laboratory for his interest in this work and for assistance in the present interpretation of Koskoski, Dodson and Fowler's results.<sup>7</sup>

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[CONTRIBUTION FROM THE UNIVERSITY OF NEW MEXICO]

## The Kinetics of the Exchange of Antimony between Antimony Trichloride and Antimony Pentachloride in Carbon Tetrachloride<sup>1</sup>

BY FRANKLIN B. BARKER AND MILTON KAHN

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A measurable exchange has been observed between antimony trichloride and antimony pentachloride in carbon tetrachloride. The exchange reaction was investigated over a temperature range from 50.1 to 81.0°; the concentration of antimony trichloride ranged from 0.0153 to 0.115 *M* and that of antimony pentachloride from 0.0055 to 0.0667 *M*. The rate law for the exchange reaction is  $R = 1 \times 10^6 e^{-19,000/RT} (\text{SbCl}_3) + 4 \times 10^6 e^{-15,000/RT} (\text{SbCl}_3)(\text{SbCl}_5)^2$  where the units of *R* are moles  $\times$  liter<sup>-1</sup>  $\times$  sec.<sup>-1</sup>.

### Introduction

This paper deals with the kinetics of the exchange of antimony atoms between antimony trichloride and antimony pentachloride in carbon tetrachloride. The exchange reaction was found to proceed through two paths; one path is first order with respect to antimony pentachloride; the other path is first order with respect to antimony trichloride and second order with respect to antimony pentachloride.

### Experimental

**Radioactivity.**—The 60-day  $\text{Sb}^{124}$ , which was used as tracer in all experiments, was produced by neutron-irradiation of reagent grade antimony trichloride. After allowing at least five weeks for the decay of the 2.8-day  $\text{Sb}^{122}$ , the irradiated antimony trichloride was distilled twice in a helium atmosphere at a pressure of 50 mm. of mercury.

The radiochemical purity of the tracer was checked by observing the decay of an active solution of antimony. The antimony decayed with a half-life of 60.3 days over a period of four half-lives in satisfactory agreement with the previously reported value.<sup>2</sup> Also, the specific activity of an aliquot of an active antimony trichloride solution was the same as that of an aliquot purified from arsenic, tin, indium, copper, bismuth, cadmium, lead, mercury, iron and chromium carriers.

**Chemicals.**—Baker C.P. carbon tetrachloride was further purified according to the method of Fieser,<sup>3</sup> treated with chlorine and chlorine dioxide as described by Dickinson and Jeffreys,<sup>4</sup> and finally distilled from phosphorus pentoxide.

Helium and argon, used interchangeably for inert atmospheres, were washed with "Oxorbent" and sulfuric acid, and passed over "Drierite."

U.S.P. boric acid was further purified by recrystallization from water.

Hydrogen sulfide and sulfur dioxide, obtained from the Ohio Chemical and Surgical Supply Company, were used without further purification.

Matheson chlorine was used without further treatment for the purification of carbon tetrachloride.

The chlorine used in the preparation of antimony pentachloride solutions was prepared by the action of hydrochloric acid on manganese dioxide. The liberated chlorine was first passed through a saturated potassium permanganate solution and subsequently through sulfuric acid.

All other chemicals were of reagent grade and were used without further purification.

**Procedure.**—A stock solution of active antimony trichloride, prepared by dissolving the twice-distilled active antimony trichloride in carbon tetrachloride, was stored under an inert atmosphere. A stock solution of antimony pentachloride was prepared by allowing chlorine to react in carbon tetrachloride with an excess of inactive antimony trichloride. The reaction mixture was contained in a sealed flask under an inert atmosphere and maintained at 50.1° for a period of ten days; under these conditions more than 99% of the chlorine was consumed.

The stock solutions were analyzed for antimony(III) by titration with standard potassium bromate,<sup>5</sup> for antimony(V) by iodometric titration,<sup>6</sup> and for chloride by the Volhard method.<sup>7</sup>

Because all solutions were prepared at room temperature it was necessary to correct the analytically determined concentrations for the volume change of the reaction mixtures at the higher temperatures. These corrections were calculated from the expression for the cubical coefficient of expansion for carbon tetrachloride.<sup>8</sup>

A reaction mixture was prepared from appropriate amounts of the stock solutions and carbon tetrachloride, and 10-ml. portions of this mixture were sealed in ampoules containing an inert atmosphere. The ampoules were wrapped in aluminum foil to exclude light and then placed in a constant temperature ( $\pm 0.1^\circ$ ) water-bath. All operations from the mixing of the solutions to the wrapping of the ampoules were carried out in a dark room illuminated by a photographer's red safe-light.

At suitable time intervals the reaction was quenched by cooling an ampoule under the tap; the reactants were separated and the radioactivity in each fraction determined.

**Separation Procedure.**—Five to 10 ml. of the reaction mixture was added to a solution which contained 22.5 ml. of absolute ethanol, 1.5 ml. of concentrated hydrochloric acid and 1.0 ml. of 48% hydrofluoric acid. Approximately 1 ml. of a 1% solution of "Aerosol OT" in absolute alcohol was added and hydrogen sulfide was passed into the solu-

(1) This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission and submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of New Mexico, June, 1954, by Franklin B. Barker. Presented before the Physical and Inorganic Division of the American Chemical Society in Minneapolis, September, 1955.

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