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Spectrophotometric and Radiochemical Investigation of the Interaction between Tin(II) and -(IV) in Hydrochloric Acid Solutions[1,2,3]

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This paper is concerned with the non-additive coloration (interaction absorption) that occurs in hydrochloric acid solutions containing tin(II) and tin(IV and with the radioactive exchange properties of this system. The optical density of interaction absorption is proportional to the product of the concentrations of the tin(II) and -(IV). The colored species is a dimeric complex containing one tin(II) and one tin(IV) atom. The absorption spectrum of tin(II), of tin(IV) and of the interaction complex in 3–10 *F* acid are given. In 10 *F* acid, interaction absorption decreases by only 10% when the temperature is changed from 25 to 0°. In 10.0 *F* hydrochloric acid, the rate, *R*, of the thermal homogeneous exchange reaction between tin(II) and -(IV) at 0 and 25° is given by $R = (\mathrm{Sn^{II}})(\mathrm{Sn^{IV}}) \times 4.5 \times 10^7 \times \exp(-10{,}800/RT)$(liter/mole min.). At 25°, the rate constants in 9.0, 10.0 and 11.0 *F* acid are 0.38, 0.55 and 0.73. The second order kinetics for the exchange is consistent with the assumption that the slow step is the electron exchange. The results suggest, but do not prove, that the dimeric optical interaction complex is unsymmetrical and that exchange does not take place every time it forms and decomposes. The mass action solubility product constant, $(\mathrm{Cs^+})^2(\mathrm{SnCl_6^=})$, for $\mathrm{Cs_2SnCl_6}$ in 10 *F* HCl at 25° was measured as 3.6×10^{-8} (mole/liter)^3.

Introduction

In several communications from these laboratories, the intense non-additive light absorption ("interaction absorption") by some aqueous systems containing an element in two different oxidation states has been studied.[5,6,7,8] Diehl and coworkers have also made recent contributions to this subject.[9]

Whitney and Davidson[5] investigated this phenomenon in detail for mixed solutions of antimony-(III) and -(V) in hydrochloric acid and discovered the effect in mixed solutions of tin(II) and -(IV) in the same solvent. The present paper describes a more detailed spectrophotometric study of the mixed tin solutions and an investigation of the rate of the thermal radioactive exchange reaction between the two oxidation states of tin. The article immediately following this one is concerned with the photochemical radioactive exchange reaction of tin(II) and -(IV).

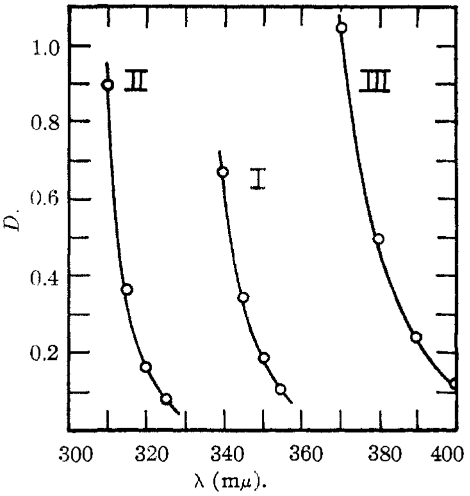

Fig. 1.—Absorption spectra of: I, 0.5 *F* $\mathrm{Sn^{II}}$; II, 0.5 *F* $\mathrm{Sn^{IV}}$; III, 0.5 *F* $\mathrm{Sn^{II}}$, 0.5 *F* $\mathrm{Sn^{IV}}$; all in 9.5 *F* HCl.

Spectrophotometric Studies

Experimental.—Details of our spectrophotometric technique have been described previously.[5,6] Most of the measurements were made at room temperature, 24–28°; a few of them were carried out using a thermostated cell compartment[6] at 25 and 0°.

Tin(IV) solutions were prepared by dissolving reagent grade $\mathrm{SnCl_4 \cdot 5H_2O}$ in reagent grade concentrated hydrochloric acid and suitable dilution. The tin concentration was determined after reduction with powdered antimony to the tin(II) state, by titration with standard iodine solution.

Solutions of reagent grade $\mathrm{SnCl_2 \cdot 2H_2O}$ in hydrochloric acid were boiled with powdered tin to reduce the tin(IV) concentration. They were analyzed by iodine titrations and were handled under an atmosphere of carbon dioxide. The concentrations of tin(IV) in the tin(II) solutions were estimated from the difference in iodine titer before and after treatment with powdered antimony. This estimation was not very accurate, but indicated 1–5% of tin(IV).

Results.—Figure 1 exhibits the absorption spectrum of a 0.5 *F* tin(IV) solution, a 0.5 *F* tin(II) solution, and of a mixed solution that is 0.5 *F* in each component, all in 9.5 *F* hydrochloric acid. The mixed solution absorbs light of longer wave lengths than that absorbed by either the stannous or the stannic solutions. The optical density of interaction absorption, D_i, is defined by $D_i(\lambda) \equiv D(\lambda, c_{II}, c_{IV}) - D(\lambda, c_{II}) - D(\lambda, c_{IV})$. In this relation, $D(\lambda, c_{II}, c_{IV})$ is the optical density of a solution containing concentrations c_{II} and c_{IV} of the two oxidation states of tin; $D(\lambda, c_{II})$ is the optical density of a solution containing tin(II) at a concentration c_{II} and similarly for $D(\lambda, c_{IV})$. It is understood that all solutions have the same formal concentration of hydrochloric acid.

In conformity with the results of other investigations of interaction absorption in solution[5–8] it is found that in 9.5, 6.0 and 3.0 *F* hydrochloric acid the optical density of interaction absorption

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[1] Presented partly at the 115th Meeting of the American Chemical Society, San Francisco, April, 1949, and partly at the 117th Meeting Detroit, April, 1950.

[2] A more detailed account of these investigations is contained in the M.S. theses by C. I. B. and R. P. C., June, 1948, and 1949, respectively.

[3] For detailed data of Figure 3 order Document 3031 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.05 for photocopies (6 × 8 inches) readable without optical aid.

[4] Responsible co-author.

[5] J. Whitney and N. Davidson, THIS JOURNAL, **69**, 2076 (1947); **71**, 3809 (1949).

[6] H. McConnell and N. Davidson, *ibid.*, **72**, 3168 (1950).

[7] H. McConnell and N. Davidson, *ibid.*, **72**, 5557 (1950).

[8] A preliminary general discussion of this topic is given by J. Whitney *et al.*, "Isotopic Exchange Reactions and Chemical Kinetics," Brookhaven National Laboratory, Upton, N. Y., Dec., 1948, p. 196.

[9] H. Diehl, *et al.*, *Proc. Iowa Acad. Sci.*, **55**, 241, 247 (1948).

is proportional to the product of the concentrations of the tin(II) and -(IV).

$$D_i(\lambda, c_{II}, c_{IV}) = k_i(\lambda)\, c_{II}c_{IV} \qquad (1)$$

Figure 2 displays some of the data that support equation (1).

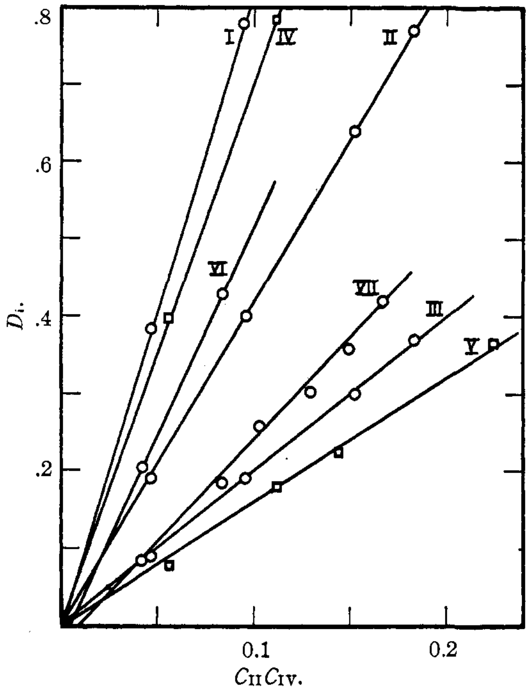

Fig. 2.—Interaction absorption, D_i, as a function of the $c_{II}c_{IV}$ product:

λ(mμ)	360	370	380	365	385	335	345
(HCl)	9.5	9.5	9.5	6	6	3	3

(□, horizontal coördinates are 0.4 $c_{II}c_{IV}$).

In Fig. 3 the values of $k_i(\lambda)$ at room temperature are plotted as a function of wave length for the several hydrochloric acid concentrations studied.[3] The solutions in 10.0 *F* hydrochloric acid were measured at 0° and it was found that the interaction absorption at all wave lengths was decreased by a factor of 10 ± 1% when the temperature was changed from 25 to 0°.

Solutions of tin(IV) in 9.5, 6.0 and 3.0 *F* hydrochloric acid were found to obey Beer's law to ±5% as the tin(IV) concentration was varied from 0.2 to 1.0 *F*. The extinction coefficients of tin(IV) are plotted in Fig. 3.[3]

The absorption spectra of tin(II) solutions did not obey Beer's law in that the apparent extinction coefficients increased with tin(II) concentration. This was most probably because of interaction absorption due to the presence of 1–5% of tin(IV) in the solutions studied. Since tin(IV) in hydrochloric acid is less strongly absorbing than tin(II) in the wave length region of interest, the optical density of such solutions may be written as $D = \epsilon c_{II} + k_i c^2_{II}\,(c_{IV}/c_{II})$, assuming that pure tin(II) solutions obey Beer's law. For a roughly constant "contamination ratio," (c_{IV}/c_{II}), this relation corresponds to an apparent extinction coefficient that increases with concentration. The method of chemical analysis employed was not precise enough to allow one to correct for the c_{II}/c_{IV} term. In connection with the subsequent radiochemical studies, a more precise and direct method for the analysis for tin(IV) was developed, *i.e.*, the precipitation of Cs_2SnCl_6. One solution in 10.0 *F* hydrochloric acid, which was found to be 0.0845 and 0.0103 *F* in tin(II) and -(IV), respectively, by this method, was measured in the spectrophotometer. The extinction coefficients of tin(II) calculated from these measurements are plotted in Fig. 3.[3] To correct for the contribution of interaction absorption to the optical density of the solutions, the values of $k_i(\lambda)$ of 74, 105, 148 at λ = 330, 325, 320 mμ for 10 *F* acid were obtained by linear extrapolation of the plot of Fig. 3. The values of ϵ_{II} obtained in this way are consistent with the absorption spectra of the other tin(II) solutions in 6 and 9.5 *F* acid, and indicated that such solutions contained from 1–5% of tin(IV). At short wave lengths (320–340 mμ) the contribution of interaction absorption is relatively less im-

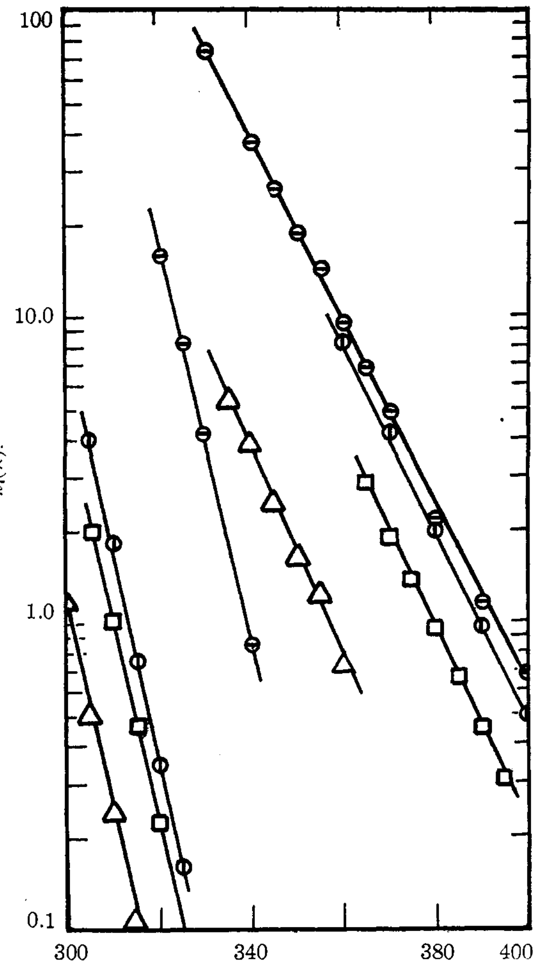

Fig. 3.—The interaction constant, $k_i(\lambda)$, and the extinction coefficients of tin(II) and -(IV) as a function of wave length for several HCl concentrations: ⊖, 10 *F* HCl, 25.5°; ⦶, □, Δ, 9.5, 6, 3 *F* HCl, respectively, 26 ± 2°.

Reading from left to right, there are three curves for the extinction coefficients of tin(IV), one for tin(II), and four for k_i for mixed solutions. The point k_i = 74 at λ = 330 (10 *F* HCl) is extrapolated.

portant for tin(II) solutions contaminated with tin(IV) and in this wave length range, Beer's law was approximately obeyed. It is therefore probable that tin(II) in 10 *F* hydrochloric acid does obey Beer's law and that it has the extinction coefficients given in Fig. 3. The contribution of interaction absorption to the absorption spectra of impure tin(II) solutions is less important for solutions in 3.0 *F* hydrochloric acid and such solutions approximately obeyed Beer's law for tin(II) concentrations of 0.1–0.5 *F*. The extinction coefficient curve for tin(II) in 3.0 *F* acid is the same as that of Fig. 3 for tin(II) in 10 *F* acid but displaced to shorter wave lengths by 5 mμ.

Discussion.—The spectrophotometric results for the mixed tin solutions are in many respects similar to those for the mixed antimony solutions, and there is a corresponding parallelism in the conclusions that can be drawn. The result expressed by equation (1) implies that the species responsible for interaction absorption is a dimeric complex containing one atom of tin(IV) and one atom of tin(II), rather than a monomeric complex of tin(III); that is, the colored complex is formed by an equation of the type

$$\text{SnCl}_4^{=} + \text{SnCl}_6^{=} \rightleftharpoons \text{Sn}_2\text{Cl}_{10}^{-4} \qquad (2)$$

Just as in the antimony case, there is evidence that c_{D}, the concentration of the dimeric interaction complex, is small compared to c_{II} and c_{IV}, in that equation (1) rather than the more complicated equation, $D_{\text{i}} = k_{\text{i}}(c_{\text{II}} - c_{\text{D}})\ (c_{\text{IV}} - c_{\text{D}})$, adequately fits the data. Therefore, the dimeric interaction complex is a strongly absorbing species; one does not know its concentration or extinction coefficients, but only k_{i}, the product of these two quantities.

The linear character of the plots (Fig. 3) of log k_{i} (for the interaction dimer) and log ϵ (for the chloro-complexes of tin(II) or -(IV)) *vs.* λ is characteristic of the long wave length tails of the intense ultraviolet "electron transfer" absorption bands[10] of many inorganic substances. This is therefore consistent with the view that the absorption spectrum of the interaction dimer is of the "electron transfer" type. The maximum that presumably exists for k_{i} at shorter wave lengths is not observed because of the more steeply rising light absorptions by the separate chloro-complexes of tin(II) and tin(IV).

If the observed effect of temperature on D_{i} be attributed to a change in the equilibrium constant for (2) (rather than to a change in the extinction coefficients of the interaction dimer), it corresponds to a calculated value of ΔH for (2) of only 600 calories. The significance of this low energy of interaction has already been discussed.[5,8]

The decrease in the extinction coefficients of tin(IV) with decreasing acid concentration may be attributed to hydrolysis of the hexachlorostannate ion, to an ion of the type $\text{SnCl}_{6-n-m}(\text{OH})_m(\text{OH}_2)_n^{n-2}$. The extinction coefficients of tin(II) decrease by a factor of two as the acid concentration is changed from 10 to 3 *F*, suggesting some hydrolysis of the chloro-complexes of tin(II). These hydrolyses are associated with a decreasing degree of interaction absorption; this is also the case for the interaction absorption between the two oxidation states of copper,[6] iron[7] and antimony.[5]

For the sake of brevity, plots of the extinction coefficients of tin(IV) and of k_{i} as a function of the formal concentration of hydrochloric acid at a fixed wave length are not presented. The extinction coefficients of tin(IV) are found to be, within experimental error, linear functions of the HCl concentration. The curves for λ = 305, 310, 315 mμ all intersect the $\epsilon = 0$ axis at $c_{\text{HCl}} = 2.1 \pm 0.15$, suggesting that the hydrolysis of the chloro-complexes of tin(IV) is complete below this acidity. Curves of k_{i} *vs.* c_{HCl} are roughly linear, and intersect the $k_{\text{i}} = 0$ axis at c_{HCl} = 2, 3, 4 for λ = 360, 370, 380, respectively.

The Thermal Radioactive Exchange Reaction

Experimental.—In addition to describing the methods used (by R.P.C.) to study quantitatively the kinetics of the tin(II), tin(IV) exchange reaction, we shall, because of their intrinsic interest, communicate some features of the methods used (by C.I.B.) in the preliminary studies that established the order of magnitude of the exchange rate.

The isotope used was the 105 day $^{113}_{50}\text{Sn}$, which decays by K-electron capture to an excited state of $^{113}_{49}\text{In}$. This reverts to the ground state with a half-life of 105 min. by emission of a 0.39 m.e.v. gamma ray[11]; it is the internal-conversion electrons from the indium gamma radiation that are mainly counted.

For the preliminary measurements, the source of radioactive tin was a sample of neutron activated tin metal from the Oak Ridge pile.[12] Besides ^{113}Sn activity, this contained the 2.7 year beta active ^{125}Sb isotope. After solution of the metal in acid, antimony and tin were separated by the method of Plato and Hartman.[13] This involves distillation of the antimony from a solution in mixed sulfuric and phosphoric acids by the addition of hydrochloric acid. Tin is subsequently distilled by addition of hydrobromic acid. The antimony can be obtained in a carrier-free condition. The separated tin was precipitated as the hydroxide and redissolved in hydrochloric acid to give a solution of active tin(IV) for the exchange experiments.

For the subsequent precise studies, activated tin from Oak Ridge was processed by Tracerlab, Inc., Boston, Mass., and purchased by us as C.P. $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$, with a specific activity of *ca.* 0.1 millicurie per gram. An aluminum absorption curve, taken with a bell jar mica window counter, is displayed in Fig. 4. The observed break in this curve at 101 mg./sq. cm. corresponds to an electron energy of 0.36 m.e.v.,[14] in exact agreement with that expected for a K-conversion electron from 0.39 m.e.v. gamma rays in indium. An approximately weighed sample of the active $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ was dissolved in hydrochloric acid to give the stock solution for the exchange experiments.

Tin(IV) solutions were prepared as described in the section on spectrophotometry. Tin(II) solutions were prepared by dissolving tin metal in hydrochloric acid of known titer and were kept under an atmosphere of carbon dioxide. Nevertheless, some oxidation of tin(II) to tin(IV) occurred, and the concentrations of both components were determined in each run by the Cs_2SnCl_6 method described below.

The general procedure for the exchange experiments was to mix inactive tin(II) with labeled tin(IV) solutions and to determine the decrease in the tin(IV) activity with time. Tin(IV) was separated from the exchange mixtures by precipitation as the insoluble Cs_2SnCl_6 after addition of cesium chloride solution.

For the preliminary experiments, the precipitate of Cs_2SnCl_6 was collected by centrifugation, washed, weighed in the centrifuge cone, and metathesized by digestion with

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(10) Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

(11) G. T. Seaborg, *ibid.*, **20**, 585 (1948).

(12) "Radioisotopes, Catalog and Price List No. 2," (U. S. Atomic Energy Commission, Oak Ridge, Tenn., 1947), item No. 3C.

(13) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, 7th Edition, John Wiley and Sons, Inc., New York, N. Y., 1928, p. 235.

(14) L. E. Glendenin, *Nucleonics*, **2**, 13 (1948).

aqueous ammonia to tin(IV) hydrous oxide. This could be transferred as a slurry to a glass plate, dried and counted as a thin sample (3 mg./sq. cm.).

The precise experiments took place in a thermostated water-bath. The active tin(IV) solution was pipetted into the tin(II) solution in the reaction flask, a 125-ml. erlenmeyer flask with a side arm through which CO_2 could be passed whenever the flask was opened. The vessel was shaken during mixing (*ca.* 45 sec.) and the time of starting the reaction taken at the point where half of the tin(IV) solution had been added. Samples were removed from the reaction mixture at roughly equal time intervals, such that generally five samples were obtained in which the expected degree of exchange was between 8 and 80%. The exchange reaction in the sample was ended by addition of a solution of 0.150 *M* CsCl in 10 *F* HCl. All these manipulations took place in an atmosphere of carbon dioxide. The precipitate of Cs_2SnCl_6 was centrifuged, washed with 1 ml. of 10 *F* HCl, dried at 98°, and weighed. Each such weighing gave a direct determination of the concentration of tin(IV) in the reaction mixture. The precipitate was dissolved in 5.0 ml. of 0.5 *F* oxalic acid solution and transferred to a Radiation Counter Laboratories Mark 1, Model 70 jacketed solution counter. This counter has a 1 mm. annulus for the active solution, and a wall thickness of 30 mg./sq. cm. In view of Fig. 4, these are reasonable dimensions for the efficient counting of ^{113}Sn samples.

The Cs_2SnCl_6 samples were not dissolved and counted until 12–20 hours after precipitation; the $^{113}In^*$ activity at this time indicates the amount of ^{113}Sn precipitated originally. (Observation of the activity of a solution immediately after precipitation of Cs_2SnCl_6 and of the decay rate of the solution showed that at least 97% of the $^{113}In^*$ coprecipitated with the Cs_2SnCl_6.)

The activities of three samples prepared from aliquots of the same active solution were the same within the counting error (0.5% standard deviation in this case), indicating satisfactory reproducibility of the radio-assay technique. For the exchange experiments, samples were counted to a minimum of 10,000 counts.

For each run, the specific activity of the tin(IV) was determined after a time sufficiently long so that exchange equilibrium was established. The total tin concentration in a mixture was determined after oxidation of an aliquot with chlorine gas by precipitation of Cs_2SnCl_6. Knowing the tin(IV) concentration, the tin(II) concentration was calculated by difference. These data permit calculation of the initial tin(IV) activity. In some cases, the initial tin(IV) activity was also directly measured on a portion of the tin(IV) solution before mixing.

Results (a) Incidental.—The solubility of Cs_2SnCl_6 was studied as follows. (a) 2.0 ml. of 0.15 *F* CsCl in 10 *F* HCl added to 10.0 ml. of 0.0100 *F* Sn^{IV} in 10 *F* HCl. The precipitate was washed with one ml. of concentrated HCl. In duplicate experiments, the precipitates weighed 57.1 and 57.3 mg. (theor., 59.7). (b) Similarly, with 3.0 ml. of 0.15 *F* CsCl and 10.0 ml. of 0.01 *F* Sn^{IV} solutions, the precipitate weighed 58.8 mg. The solubility products, $(Cs^+)^2$ $(SnCl_6^=)$ calculated from (1) and (2) are 2.8×10^{-8} and 4.2×10^{-8} (mole/liter).[3] That there was actually tin(IV) in the supernatant solutions was verified by neutralization with ammonia and a hydrogen sulfide precipitation. In each case turbidity comparisons with standards indicated the presence of the expected amounts of tin (~0.4 and 0.1 mg.). In another measurement of the solubility of Cs_2SnCl_6, the activity of a supernatant solution after precipitation of Cs_2SnCl_6 was compared with the activity of the precipitate, dissolved to give a solution of the same volume. The activity of the supernatant was 11 c./min.; that of the precipitate from the initially 0.0075 *F* Sn^{IV} solution, 900 c./min. Therefore, after precipitation, $(SnCl_6^=) = 9.4 \times 10^{-5}$; and $(Cs^+) = 0.0196$, $K_{SP} = 3.6 \times 10^{-8}$. This value was used in correcting analyses for the amount of tin(IV) not precipitated.

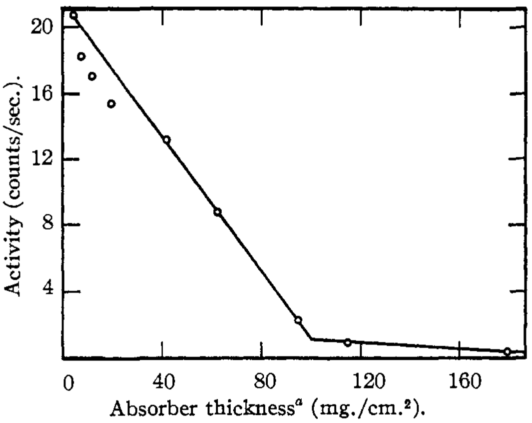

Fig. 4.—Aluminum absorption curve of ^{113}Sn–$^{113}In^*$ radiation. (Data obtained with 3 mg. of active tin precipitated as $SnO_2 \cdot xH_2O$ and slurried onto an area of 5 sq. cm. on an aluminum plate). ^{a} Including window thickness (4 mg./sq. cm.).

Evidence for some coprecipitation of tin(II) by Cs_2SnCl_6 was obtained by measuring the decrease in the iodine titer of a tin(II)–(IV) mixture due to the precipitation of Cs_2SnCl_6. Furthermore the washed precipitate was suspended in hydrochloric acid and titrated with iodine. Table I records the results.

TABLE I

COPRECIPITATION OF Sn^{II} BY Cs_2SnCl_6^{a}

Cs^{+b}	Sn^{IIb}	Sn^{IVb}	Decrease of Sn^{II} on pptn., %	Original Sn^{II} in ppt., %
0.090	0.053	0.027	4.9	
.080	.018	.018	6.0	4.0
.035	.031	.0054	2.5	0.8

^{a} All measurements at room temperature in 10 *F* HCl. ^{b} Calculated concentrations (mole/liter) before precipitation.

The estimate of the amount of coprecipitation in the next to last column of the table is probably high due to a small amount of oxidation of tin(II) during the manipulations. The estimate in the last column would be low if there were incomplete reaction between iodine and tin(II) coprecipitated with Cs_2SnCl_6. While precipitates of Cs_2SnCl_6 from pure tin(IV) solutions were invariably white, precipitates from mixed solutions sometimes contained yellow specks when they were removed from the drying oven. The color disappeared as the samples cooled in air. There is a hint here of the formation of an unstable colored mixed oxidation solid that could be responsible for variable coprecipitation.

Results (b) The Exchange Reaction.—The results of the exchange experiments are analyzed using the well known equation

$$\ln (1 - E) \equiv \ln \frac{x(t) - x(\infty)}{x(0) - x(\infty)} = -R\,(c_{II}, c_{IV}) \frac{c_{II} + c_{IV}}{c_{II}c_{IV}}\, t \qquad (3)$$

The quantity $x(t)$ is the activity of the tin(IV) separated from unit volume of the exchanging mixture at time t, and R is the rate of exchange of tin atoms between the two oxidation states in the particular solution. E is the degree of exchange.

Table II presents the results of a typical run. To 60 ml. of tin(II) solution, 0.0986 F in total Sn (as determined with Cs_2SnCl_6), was added 15 ml. of 0.0494 F radioactive tin(IV) solution. The weight of Cs_2SnCl_6 not precipitated from each aliquot in these experiments is calculated as 0.7 mg. The calculated c_{IV} is 0.0116 F, implying that $c_{II} = 0.0772$ F (and that the tin(II) solution contained 2.2% of tin (IV)). The initial activity, $x(0)$, was observed by precipitation of Cs_2SnCl_6 from a mixture of 2.0 ml. of the active tin(IV). solution plus 8 ml. of 10 F HCl as 1654 c./min. Therefore, the calculated value of $x(\infty)$ (= 1654 × 0.0116/0.0888) is 216. The observed value, 236 c./min., has been used in the calculations. A plot of ln $(1 - E)$ *vs.* t gives an excellent straight line with a slope corresponding to a rate of exchange, R, of 5.0×10^{-4} mole/liter min.; the intercept of the line gives $E = 0.04$ at $t = 0$.

TABLE II

RESULTS OF A TYPICAL EXCHANGE EXPERIMENT

t, (min.)	Wt. of Cs_2SnCl_6 precipitated[a] (g.)	Activity per 0.0686 g. Cs_2SnCl_6 $x(t)$ (c./min.)	$1 - E$[b]
3.2	0.0692	1414	0.832
6.8	.0697	1244	.712
12.3	.0684	990	.532
19.7	.0679	770	.376
27.0	.0682	612	.265
720	.0674	236	0
Av.	0.0686		

[a] 10-ml. aliquots plus 3.0 ml. of 0.150 F CsCl solution. [b] Calculated using $x(\infty) = 236$.

In considering the experimental errors, it is easy to show by expansion of (3) that the discrepancy of 9% between the calculated and measured values of $x(\infty)$ produces an uncertainty in R of *ca.* 1%, that is, of the order of the uncertainty in $x(\infty)$ divided by $x(0)$. Uncertainties in $x(0)$ affect only the intercept of the plot of ln $(1 - E)$ *vs.* t and not the slope.

Coprecipitation of some tin(II) by the Cs_2SnCl_6 precipitate affects the calculation of c_{II} and c_{IV} as well as that of the x's; the analysis of possible errors is therefore rather involved. For the last case of Table I where $c_{IV} = 0.005$ and $c_{II} = 0.03$, the indicated amount of coprecipitation is between 0.8 and 2.5% of the total tin(II) concentration. For several runs with similar c_{II} and c_{IV} values, the effect of assuming 2.5% coprecipitation as (a) $SnCl_2$ and (b) Cs_2SnCl_4 was computed. The intercepts of the curves of $-\ln(1 - E)$ *vs.* t varied somewhat for the different cases (from 0.1 to 0.25) but the slopes were affected by less than 1%.

The principal errors in the experiments are believed to be *ca.* 1% counting error and *ca.* 1% error in the various chemical analyses.

The results of the experiments are presented in Table III. Values of the apparent amount of exchange at zero time are not given because this quantity is so sensitive to the experimental errors. In general, for the experiments in the table, the apparent exchange at zero time was between −5 and +15%; it was 30–40% for the two experiments in vessels packed with glass beads.

TABLE III

RATE OF EXCHANGE BETWEEN TIN(II) AND -(IV)

c_{IV}	c_{II} (mole/liter)	(HCl)	T, °C.	$R/c_{II}c_{IV}$ (liter/mole min.)
0.0102	0.0093	10.0	25.2	0.58
.0103	.0292	10.0	25.2	.48
.0323	.0270	10.0	25.2	.54
.0311	.0085	10.0	25.2	.57
.0116	.0772	10.0	25.2	.56
.00645	.0382	10.0	25.2	.53
.00645	.0382	10.0	25.2	.53[a]
.0055	.0294	10.0	25.2	.49[b]
.00718	.0389	10.0	25.2	.56[b]
.0108	.0569	10.0	0	.104
.00633	.0286	9.0	25.2	.377
.00608	.0288	11.0	25.2	.728

[a] Room light rigorously excluded. [b] Reaction vessel packed with glass beads.

The data in the table show that the exchange reaction is homogeneous and second order, *i. e.*, $R = k_E c_{II}c_{IV}$. Assuming a constant energy of activation, the results in 10 F acid are expressed by the equation, $k_E = 4.5 \times 10^7 \exp(-10{,}800/RT)$ (liter/mole min.). At 25°, the rate constants in 9, 10, 11 F HCl are 0.38, 0.55 and 0.73.

Discussion

The second order kinetics (at a constant hydrochloric acid concentration) for the exchange reaction makes it plausible that the slow step in the exchange is an oxidation–reduction reaction involving one tin(II) and one tin(IV) atom. The alternative suggested previously[8] that there was a slow exchange of tin atoms between, say, two tin(II) complexes, one of which (a) is present at a low concentration, and (b) exchanges readily with tin(IV) complexes is eliminated by the rate law. Thus in the tin case as in the antimony(III), (V) case in hydrochloric acid,[15] the rate of exchange is slow enough to be measured although optical interaction absorption occurs in these two systems. The exchange between the chloro-complexes of iron(II) and -(III) in hydrochloric acid is "rapid"[16] and there is optical interaction in this system. There is no optical interaction[17] between $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$, but the exchange is rapid.[18] Thus there is no correlation between "fast" and "slow" exchange and the optical interaction effect.

The following statement will, for brevity, be called proposition (A): Radioactive exchange (for the mixed tin or antimony solutions) takes place with a probability of 0.5 every time a strongly absorbing interaction dimer forms and decomposes according to (2).

The slowness of the exchange reaction suggests that A is false and that the tin atoms in the interaction dimer are not equivalent. However, this is

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(15) N. Bonner, THIS JOURNAL, **71**, 3909 (1949).

(16) G. T. Seaborg, *Chem. Revs.*, **27**, 199 (1940).

(17) J. Ibers and N. Davidson, THIS JOURNAL, **73**, 476 (1951).

(18) R. C. Thompson, *ibid.*, **70**, 1045 (1948).

a plausible, not a certain, conclusion. We write

$$\mathrm{d}c_\mathrm{D}/\mathrm{d}t = fc_\mathrm{II}c_\mathrm{IV} - bc_\mathrm{D} \qquad (4)$$

where f and b are the rate constants for the forward and reverse reactions of (2). At equilibrium, $c_\mathrm{D}/c_\mathrm{II}c_\mathrm{IV} = f/b$. If A is true, $k_\mathrm{E} = f/2$. The greatest measured value of the interaction constant, k_i, is about 50 at λ = 340 mμ but the maximum of the absorption band has not been reached. The maximum extinction coefficients for the "electron-transfer" spectra of inorganic ions are usually of the order[9] of 10^4. Organic dyes have maximum ϵ's of the order[19] of 10^5 or less. Probably, therefore, for the extinction coefficient, ϵ_D, of the interaction dimer, $\epsilon_\mathrm{D}(340\ \mathrm{m}\mu) < 10^5$, $f/b = k_\mathrm{i}/\epsilon_\mathrm{D} > 5 \times 10^{-4}$. As judged visually, the interaction color develops within a second when antimony(III) and -(V) solutions are mixed and we will assume that this is also true for tin solutions[20] in 10 F HCl. Therefore, $b \geq 60$ min.$^{-1}$. Then $f/2 > 0.015$ (liter/mole min.). This is not inconsistent with the value $f/2 = 0.55$ that follows from proposition (A). The results obtained so far therefore do not disprove A.

However, in view of the limiting nature of the assumptions used in the above argument, it is plausible that A is false, that the strongly absorbing interaction dimer is not symmetrical and that exchange does take place every time this ion forms and decomposes. The photochemical results presented in the next article also support this conclusion. Of course, one does not know whether the actual exchange takes place *via* the formation of the interaction dimer which sometimes gets enough thermal activation for electron exchange to occur before the dimer dissociates or whether the path of the actual exchange is entirely unrelated to (2).

A referee reviewing this contribution has made the interesting suggestion that the effect of increasing hydrochloric acid concentration in increasing the interaction absorption and the exchange rate is due to the formation of complexes like $\mathrm{HSnCl_4^-}$ and $\mathrm{HSnCl_6^-}$. The decreased electrostatic repulsion between these complexes would favor the formation of protonated interaction dimers. Furthermore, the high charge density of the proton attached to a tin(II) or -(IV) complex might also serve to aid transfer of electrons from one tin complex to the other.

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[19] See, for example, S. E. Sheppard, *Rev. Mod. Phys.*, **14**, 303 (1942).

[20] It makes very little difference whether this entire speculative argument is presented for the tin or the antimony case. If, as is probable, the antimony exchange reaction in concentrated hydrochloric acid is second order, then Bonner's result (ref. 14) yields 0.83 (liter/mole min.) for the rate constant; for tin in 11 F HCl, the constant is 0.73.

[CONTRIBUTION NO. 1452 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Photochemical Exchange Reaction between Tin(II) and Tin(IV) in Hydrochloric Acid Solution[1]

BY ROY P. CRAIG AND NORMAN DAVIDSON[2]

By using high light intensities a photochemical radioactive exchange reaction between tin(II) and -(IV) in 10 F hydrochloric acid at 0° has been observed. The photochemical exchange is probably caused by light absorbed by the interaction dimer which is responsible for the non-additive light absorption by the system in the 330–400 mμ wave length range. The quantum yield for the exchange is estimated as 0.2, showing that the interaction dimer is not symmetrical in the optically excited state.

Spectrophotometric studies reported in the previous paper[3] (subsequently referred to as B.C.D.) show that, in hydrochloric acid solutions containing tin(II) and -(IV), there is a strongly colored complex ion, the optical interaction dimer, which contains one tin(II) and one tin(IV) atom, and which is formed according to an equation of the type

$$\mathrm{SnCl_6^{-}} + \mathrm{SnCl_4^{-}} \rightleftarrows \mathrm{Sn_2Cl_{10}^{-4}} \qquad (1)$$

The number of chlorides in the complex is unknown. The slowness of the radioactive exchange reaction between the two oxidation states of tin probably shows that the interaction dimer is unsymmetrical and that electron transfer does not take place (with a probability of 0.5) every time the dimer forms and decomposes according to (1).

In general, the intense non-additive absorption of light by systems containing an element in two different oxidation states may be regarded as being due to *the vibration of electrons between the atoms in the two different oxidation states under the influence of the electric vector of the light wave. This picture immediately suggests the possibility of a photochemical exchange reaction caused by light absorbed by the interaction dimer.* The present paper reports experiments designed to test this possibility for the tin(II)–(IV) system in hydrochloric acid solution.

The feature giving rise to most of the difficulties in the execution of the experiments is the high light intensity required to cause the photochemical reaction to be as fast as the thermal exchange reaction. Figures 1 and 3 of B.C.D. show that, for solutions in 10 F hydrochloric acid, light with wave lengths in

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[1] Presented at the 117th Meeting of the American Chemical Society, Detroit, Michigan, April, 1950.

[2] Responsible co-author.

[3] C. I. Browne, R. P. Craig and N. Davidson, THIS JOURNAL, **73**, 1946 (1951).