Radiochemical Investigation of the Kinetics of the Electron Exchange between the Oxidation States of Tin

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Abstract

The kinetics of the electron exchange between Sn^{II} and Sn^{IV} in 10.0 f HCl have been investigated by the use of a radio-active tracer. It is found that the rate of exchange is proportional to the product of the Sn^{II} and Sn^{IV} concentrations. In the HCl concentration range between 9.0 f and 11.0 f, the exchange rate is found to be proportional to the 0.3 power of the HCl activity, giving the empirical rate equation $R = k\,[Sn^{II}]\,[Sn^{IV}]\,(HCl)^{0.3}$.

Radio-active exchange experiments carried out at 0° C. and at 25.2°C. show this exchange to have an activation energy of 10.7 Kcal. per mole. The exchange is found to be homogeneous.

It is found that exposure of the Sn^{II}-Sn^{IV} solutions to illumination from a capillary Hg arc gives a marked photochemical increase in the rate of electron exchange between the two valence states.

Preliminary spectrophotometric investigations of cobalt-glycine systems also have been made.

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Radiochemical Investigation of the Kinetics of the Electron Exchange between the Oxidation States of Tin

A. Introduction

It has previously been reported that Sn^{II} and Sn^{IV} exchange radioactivity moderately slowly in 9 f hydrochloric acid (1). Knowledge of the kinetics of this exchange should lead to a logical explanation of the mechanism by which it takes place, and to a better understanding of oxidation processes. This knowledge may also give a further indication of the nature of the complex which is responsible for the non-additive absorption of ultra-violet light (2) by solutions in which both oxidation states of tin are present.

In view of the existence of non-additive light absorption, it would also be of great interest to determine whether or not there is a photochemical effect on the rate of exchange between Sn^{II} and Sn^{IV}, especially by wave lengths which are not absorbed by either valence state alone, but are absorbed by the mixed solutions. The possibility of such an effect was suggested by Dr. Norman Davidson at the Brookhaven Conference of Dec. 1-3, 1948 (3). The existence of such a photochemical effect would show that in the optically excited state of the complex that is responsible for inter-action absorption electron exchange can take place with a fairly high probability.

The following report indicates the results of investigations of the kinetics of the radioactive exchange in 10.0 f

HCl at 25° C., in which the concentrations of Sn^{IV} and Sn^{II} were varied from 0.006 f to 0.032 f and 0.009 f to 0.077 f, respectively, while the concentration ratios of Sn^{II} to Sn^{IV} varied from 6.65 to 0.27. Results are also given for exchange reactions in 9.0 f HCl and 11.0 f HCl, these reactions having been carried out to determine the effect of variations in the acid concentration on the reaction rate constant in this concentration range. Exchanges were also carried out at 0°C., and the activation energy for the exchange computed. The homogeneity of the reaction was tested by the addition of glass beads to the reaction vessel in specified runs.

The results of an investigation of the photochemical effect of light from a capillary mercury arc upon the rate of radio-active exchange is also included in this report.

B. Experimental

Radio-active tin was obtained from Oak Ridge through Tracer Lab, Inc., Boston, Mass., and was received as C.P. $SnCl_4 \cdot 5\ H_2O$. An aluminum absorption curve was made on the sample as received (Fig. 1), and its specific activity was determined both when the sample was received and 90 days later, as checks on the purity of the activity. The active isotope is Sn^{113}, which has a half-life of 105 days, and decays by K-electron capture to yield meta-stable In^{*113}. Isomeric transition of the excited In^{*113} to the ground state (half-life of 105 min.) produces 0.39 MEV gamma rays, and it is the internal-conversion electrons from this 0.39 MEV radiation that are used in counting.

The activity was introduced in the stannic state in all experiments. Stock Sn^{IV} solutions were prepared by dissolving active $SnCl_4 \cdot 5 H_2O$ in acid of such concentration to make the final solutions 10.0 <u>f</u> in HCl. Except when high concentrations of activity were desired, portions of these solutions were mixed with solutions similarly prepared from Merck reagent grade $SnCl_4 \cdot 5 H_2O$. Sufficient active Sn^{IV} was used to give a counting rate of 1000 to 2000 counts per minute from the initial precipitates.

Stock Sn^{II} solutions were prepared by dissolving weighed amounts of Baker and Adamson reagent grade tin metal in HCl of such concentrations as calculated to keep the final solutions 10.0 <u>f</u> in HCl. These solutions were handled and kept in an atmosphere of carbon dioxide. Since a small amount of oxidation generally takes place in the Sn^{II} solutions even when they are handled under CO_2, the Sn^{II} concentration and the Sn^{IV} concentration were determined by analysis during each exchange experiment, as described below.

Separation of the two oxidation states of tin was accomplished by the method developed by Browne, that is, by precipitating the Sn^{IV} as Cs_2SnCl_6, leaving the Sn^{II} in solution.

The general procedure for an exchange experiment was to bring both the Sn^{II} and Sn^{IV} solutions to constant temperature in a bath thermostated at 25.2 ± 0.1°C., the Sn^{II} solution being in the reaction flask, which was a 125 ml. Erlenmeyer flask fitted with a side arm through which CO_2 could be passed whenever the flask was opened. The Sn^{IV} solution, containing the radio-active tracer, was then pipetted into the reaction vessel. In some experiments, inactive Sn^{IV} was previously mixed with the Sn^{II} solution, so that only part of the Sn^{IV}, containing all of the activity, was pipetted into the mixture. The vessel was shaken during the mixing, and the time of mixing was taken as the time that one-half of the Sn^{IV} solution had been added. The mixing generally required about 15 seconds. 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 per cent. These samples were pipetted into weighed centrifuge cones, and the Sn^{IV} precipitated by adding a solution of 0.150 *f* CsCl in 10 *f* HCl. These steps were, of course, carried out in an atmosphere of CO_2 to prevent oxidation of Sn^{II} by atmospheric oxygen. The time of precipitation of Cs_2SnCl_6 was taken as the time of ending of radio-active exchange.

The centrifuge cones were stoppered and the Cs_2SnCl_6 was centrifuged out, washed with 1 ml. of conc. HCl, dried for about 8 hours at 98°C., and weighed. The weighing served as a check against Sn^{II} oxidation during the reaction and gave a direct analysis of the Sn^{IV} concentration in the reaction mixture. The Cs_2SnCl_6 was then dissolved in 5 ml. of 0.5 *f* oxalic acid solution, and its activity measured ina Radiation Counter Laboratories Mark 1, Model 70 jacketed solution counter.

The rate of exchange was determined by measuring the decrease in activity of the Sn^{IV} with time. The final activity of Sn^{IV} was measured from a sample precipitated after the exchange had run to completion. The initial activity was either measured from Cs_2SnCl_6 precipitated from a portion of the unmixed Sn^{IV} solution equivalent to the amount in each sample taken from the mixture, or calculated from the final activity of Sn^{IV} and the concentrations of Sn^{II} and Sn^{IV} in the mixture, since the initial activity of Sn^{IV} is equal to the final activity times the ratio of the total tin concentration in the mixture to the concentration of Sn^{IV}. In exchanges for which the initial activity of Sn^{IV} was measured, the measured activity varied from the calculated initial activity by 0.6 to 8.6%, with an average difference of 4.% in seven exchanges. Using the different values for the initial activity appreciably changes the amount of apparent "induced" exchange, but does not affect the slope of the lines plotted as described below, and therefore has no effect on the determination of the exchange rate. The total tin concentration in the mixture was determined by oxidizing a measured sample with chlorine gas and determining the tin gravimetrically as Cs_2SnCl_6. The concentration of Sn^{II} in the mixture is then obtained by subtracting the (Sn^{IV}) from the total tin concentration.

The same general procedure was followed for radio-active exchanges at zero degrees, the solutions being immersed in an ice bath. To test for possible surface effects on the walls of the reaction vessel, reactions were carried out in a vessel filled with 6 mm glass beads, increasing the surface area in contact with the solution more than ten fold.

To determine whether the radio-active exchange rate is affected by ordinary daylight or normal laboratory lighting, exchange reactions were carried out with two similar solutions, one of which was exposed to normal laboratory lighting and the other kept in the dark during the exchange. Photochemical effects on the exchange rate were then investigated by exposing the mixed solutions to the radiation of a capillary mercury arc of the type designed by Heidt and Daniels (4). This type of arc was used because of the high light intensity that can be thus attained, and the arc operated at about 450 watts. In this investigation, the general method was the same as that previously used, although the procedure was considerably modified. Ice water was circulated over the mercury arc and through a small bath surrounding the arc, in which the reaction tube was to be placed. The temperature was kept at as near zero degrees as possible, in order to minimize the thermal exchange. One-half ml. portions of radio-active Sn^{IV} solutions were pipetted into 10 ml. pyrex test tubes containing 0.50 ml. of Sn^{II} solution, and the stoppered tube placed beside the mercury arc for various periods of time. Both solutions were in 10.0 f HCl, and were cooled to zero degrees before mixing. The exchange was stopped by precipitation of Cs_2SnCl_6 in the usual manner. Such tubes were mixed and illuminated one at a time, and the tube was so placed against the jacket surrounding the arc that the reaction mixture was directly opposite and parallel with the arc, with its center about 1.5 cm. away.

I should like to mention that in current experiments, designed to determine if the photochemical effect on the exchange rate is due to light absorbed by the inter-action complex (2), and to estimate the quantum yield of this photochemical exchange, a Corning Glass #5860 light filter is inserted between the arc and the reaction tube, and the intensity of the radiation passing the filter is estimated by the use of an uranyl oxalate-oxalic acid actinometer. The #5860 filter transmits wave lengths between 320 and 390 millimicrons, and is found to have a maximum transmission of 25% at about 363 millimicrons. Charles I. Browne has shown (1) that Sn^{II} solutions in 9 f HCl do not absorb light of wave lengths greater than 360 millimicrons, and Sn^{IV} does not absorb above 330 millimicrons, but solutions containing both valence states show strong interaction absorption at 365 millimicrons. ~~For this reason, it is desirable to isolate at 365 millimicrons.~~ For this reason, it is desirable to isolate the 3650-63 Angstrom mercury radiation, and study its effect on the exchange rate. The light filter transmits 25% of this radiation and part of the neighboring continuum, which is found to be about 18% as intense as the 3650 A. emission. In estimating the intensity of the transmitted light, the concentrations of Sn^{II}-Sn^{IV} solutions and of the $UO_2C_2O_4$ solution used as an actinometer are adjusted so that the extinction coefficients of the two solutions are nearly identical at the wave lengths transmitted by the filter, as determined by a Beckmann Model DU Spectrophotometer. One ml. of the $UO_2C_2O_4$ solution is pipetted into a tube similar to those used for the Sn^{II}-Sn^{IV} exchange reaction, placed in the same position by the arc, and exposed for similar periods of time. The amount of oxalate decomposed is determined by $KMnO_4$ titration, and, assuming a quantum yield of .50 (5), the amount of light absorbed is thus obtained. Since the Sn^{II}-Sn^{IV} exchange solutions have the same extinction coefficient, they absorb a similar quantity of light, and the quantum yield of the photochemical Sn^{II}-Sn^{IV} exchange can be estimated from the measured exchange rate minus the thermal exchange rate.

The temperature of the illuminated Sn ^{II}-Sn^{IV} solutions is measured by means of a chromel-alumel thermocouple.

Precision

Analytical.

Gravimetric determinations of Sn^{IV} concentrations as Cs_2SnCl_6 proved to be reproducible to 0.3% or less. Use of two different known excess amounts of CsCl solution to precipitate the tin from standard solutions of Sn^{IV} in 10 f HCl, prepared by dissolving weighed quantities of Baker and Adamson reagent grade tin metal in HCl and oxidizing the tin to Sn^{IV} with chlorine, yielded weights of Cs_2SnCl_6 which indicate that the solubility product (Sn^{IV}) $(Cs^+)^2$ is 3.5×10^{-8} moles^3 liter^{-3}. Radiochemical measurement of the % of activity, and thus the % of Sn^{IV}, left in solution after precipitation of marked Sn^{IV} from 10 f HCl confirmed the calculated concentration of Sn^{IV} in the supernatant liquid. The value $K_{sp} = 3.5 \times 10^{-8}$ was consequently used in all analyses of Sn^{IV} to compute the amount of Sn^{IV} left in solution, and the corrections thus added to the analysis varied from 0.0 to 1.3% of the Sn^{IV} precipitated. Measurements of total tin in solution were thus accurate to 0.3%.

Because of the oxidation of small and varying amounts of Sn^{II} to Sn^{IV} during pipetting and centrifugation, individual values for Sn^{IV} concentration varied as much as 5 or 10% in solutions of low Sn^{IV} concentration and relatively high Sn^{II} concentration. Part of this variation may be due to differing amounts of co-precipitation of Sn^{II} with the Cs_2SnCl_6. Titration of samples from Sn^{II}-Sn^{IV} mixtures of concentrations similar to those used in the exchange reactions, using standard iodine solution, and titration of similar samples after precipitation of the Sn^{IV} as Cs_2SnCl_6, showed a reduction in Sn^{II} concentration of as much as 2.5 to 6 %. An amount of Sn^{II} equal to 30 to 70 % of this reduction in titer could be oxidized by iodine from a suspension of the Cs_2SnCl_6, proving that part of this reduction is due to co-precipitation of Sn^{II}. The remainder of the reduction is titer may be due to oxidation of Sn^{II} to Sn^{IV} during manipulation. Co-precipitation of Sn^{II} is a major source of error both in determinations of the Sn^{IV} concentration and in the exchange rate measurements. Calculations in which all the reduction in Sn^{II} titer is considered due to co-precipitation, and the amount of co-precipitation is assumed to be constant under the same precipitation conditions, show that the maximum error introduced by this source in the determination of exchange rate is generally less than 5 %. At least five analyses for Sn^{IV} were obtained during each exchange reaction, and even the lowest values of Sn^{IV} concentration are accurate to about 3 %. Values of Sn^{II} concentration are generally accurate to within 1 %. HCl concentrations are accurate to within 1.5 %.

Radioassay.

All samples were counted to a minimum of 10,000 counts, giving an expected standard deviation of 1 %.

It is interesting to note that the activity of the supernatant liquid, and its rate of decay, measured immediately after precipitation of Cs_2SnCl_6, showed that at least 97 % of the In^{*113} co-precipitated with the Sn. Therefore, it is not necessary to wait a great length of time for the establishment of equilibrium between Sn^{113} and In^{*113}, and no error is introduced by measuring the activity of the precipitates immediately after drying.

The technique of dissolving the radio-active precipitates and measuring their activity in a jacketed solution counter has been found to give good reproducibility, and eliminates many of the counting errors encountered with solid substances. Dissolving similarly prepared radio-active Cs_2SnCl_6 precipitates, and counting each solution to a standard deviation of less than 0.5%, gave values for the different solutions that were well within the expected counting deviation.

Since the exchange rate was determined by measuring the increase in activity of Sn^{IV}, the error, due to the error of radioassay, in the exchange rate constant is least at high Sn^{II} to Sn^{IV} concentration ratios (6). This error was minimized, when other requirements of the experiment permitted, by keeping this ratio high and by taking all samples when the exchange was between 8 and 80 % complete.

C. <u>Data</u> 9 Figures, 1 Table, 1 Log of a Reaction

Log of a typical exchange reaction.

Exchange VI

15 ml. of 0.0494 <u>f</u> marked Sn^{IV} solution added to 60 ml. of Sn^{II} solution, 0.0986 <u>f</u> in Sn. (In this experiment, the total tin concentration in each solution was determined gravimetrically as Cs_2SnCl_6 before the solutions were mixed.)

Total tin conc. in mixture $\frac{15 \times .0494}{75} + \frac{60 \times .0986}{75} = .0888$ <u>f</u>

Removed 10 ml. aliquots, precipitated Sn^{IV} with 3.0 ml. of 0.150 f CsCl solution.

Initial activity: 2.0 ml. (15/7.5) of .0494 f Sn^{IV} solution plus 8 ml. 10 f HCl, precipitated with 3.0 ml. CsCl solution.

Activity from this precipitate (X_0) = 1654 counts per min.

Sample	Reaction time	Wt. of ppt.	Activity per. .0686 gm	(1-D)	-log (1-D)
1	3.2 min	.0692 gm.	1414 c/min	.832	.080
2	6.8 min	.0697 gm.	1244 c/min	.712	.147
3	12.3 min	.0684 gm.	990 c/min	.532	.274
4	19.7 min	.0679 gm.	770 c/min	.376	.424
5	27.0 min	.0682 gm.	612 c/min	.265	.576
6	12 hours	.0674 gm.	236 c/min	0	

Wt. Cs_2SnCl_6 left in solution ($K_{sp} = 3.5 \times 10^{-8}$) = .0007 gm.

(Sn^{IV}) in mixture (a) $= \dfrac{.0686 + .0007}{.597 \times 10} = .0116$ f

(Sn^{II}) in mixture (b) $= .0888 - .0116 = .0772$ f

Plotting -log (1-D) vs. reaction time gives a line of slope .0215.

Exchange rate constant $R = 2.303 \text{ slope} \times \dfrac{ab}{a + b} = 4.99 \times 10^{-4}$ moles liter^{-1} min^{-1}.

Reaction rate constant $k = \dfrac{R}{ab} = \dfrac{2.303 \text{ slope}}{a + b} = 0.557$

Fig. 1 Aluminum absorption curve of Sn^{113}-In^{*113} radiations.

Fig. 2 Rate of exchange in 10.0 f HCl at 25°C.;
$(Sn^{IV}) = .0311$ f ; $(Sn^{II}) = .0085$ f

Fig. 3 Rate of exchange in 10.0 f HCl at 25°C.;
$(Sn^{IV}) = .0116$ f ; $(Sn^{II}) = .0772$ f

Fig. 4 Rate of exchange in presence of glass beads; 10.0 *f* HCL ; 25° ;
(Sn^{IV}) = .0072 *f* ; (Sn^{II}) = .0389 *f*

Fig. 5 Exchange rate in daylight (A) and in dark (B); 10.0 f; HCL;
(Sn^{IV}) = .0065 *f* ; (Sn^{II}) = .0382 *f*

Fig. 6 Exchange rate at 0°C. 10.0 *f* HCl ;
(Sn^{IV}) = .0108 *f* ; (Sn^{II}) = .0569 *f*

Fig. 7 Exchange rate in 9.0 *f* HCl ; 25°C. ;
(Sn^{IV}) = .0063 *f* ; (Sn^{II}) = .0286 *f*

Fig. 8 Exchange rate in 11.0 *f* HCl ; 25°C. ;
(Sn^{IV}) = .0061 *f* ; (Sn^{II}) = .0288 *f*

Fig. 9 Thermal plus photochemical exchange rate ; ca. 5°C. ;
(Sn^{IV}) = .0556 *f* ; (Sn^{II}) = .0900 *f*

Table 1

Exchange Designation	"a" (Sn^{IV})	"b" (Sn^{II})	R/ab
(Varying a:b ratio)			
II	.0102	.0093	.58
III	.0103	.0292	.48
IV	.0323	.0270	.54
V	.0311	.0085	.57
VI	.0116	.0772	.56
(Subdued light)			
X (light)	$.0064_5$	.0382	.53
XI (dark)	$.0064_5$	.0382	.53
(Glass beads in vessel)			
XII	.0055	.0294	.49
XVI	.00718	.0389	.56

TABLE 1 (Continued)

Exchange Designation	"a" (Sn^{IV})	"b" (Sn^{II})	R/ab
(Zero degrees C.)			
XIII	.0108	.0569	.104
(Effect of HCl conc.)			
XIV (9 f)	$.0063_3$	.0286	$.37_7$
XV (11 f)	$.0060_8$	.0288	$.72_8$
(Photochemical plus thermal)			
XVII	.0556	.0900	2.20

D. Results and Conclusions

The aluminum absorption curve of the Sn^{113}- In^{*113} radiations (Fig. 1) shows a sharp break at a thickness of 101 mg/cm^2, corresponding to an electron energy of 0.364 MEV (7). This is in agreement with the energy of internal conversion electrons from 0.390 MEV (8) gamma radiation produced by the isomeric transition of In^{*113}, which would have an energy of 0.362 MEV. No definite break in the curve is observed to correspond to the 0.085 MEV radiation of Sn^{113}. There was no indication of the presence of foreign activities in the sample.

The exponential exchange law (9,10) for the Sn^{IV}-Sn^{II} exchange, expressed in its logarithmic form, is

$$-\ln(1-D) = R\,\frac{(a+b)}{ab}\,t \quad ,$$

in which D is the degree of exchange, or fractional exchange, at time t; R is the rate of exchange, a function of a, b, and temperature, and is constant for a given set of conditions; a and b are the concentrations of Sn^{IV} and Sn^{II}, respectively, in gram atoms per liter ; and t is the reaction time. Since the Sn^{IV} initially contained all the activity, the degree of non-exchange, (1-D), may be obtained from the specific activities (X) of Sn^{IV} at reaction times zero (X_0), infinity (X_∞), and t (X_t), since

$$(1-D) = \frac{X_t - X_\infty}{X_0 - X_\infty} .$$

The rate of exchange, R, may be obtained from plots of $-\ln(1-D)$ vs. t, since the slope of the line produced is equal to $R\,(a+b)/ab$. The slope is determined from the graphs, a and b are determined by analysis, and R calculated in gram atoms per liter per minute.

It is seen from Exchanges II, III, IV, V, and VI, Table 1, that exchange rates after varying both a and b give values of R/ab which are nearly constant. It is therefore concluded that the rate of reaction is proportional to the first power of both the Sn^{IV} concentration and the Sn^{II} concentration; i.e., the reaction in 10 f HCl is second order, and R = k ab. The average experimental value of the reaction rate constant k in 10.0 f HCl is 0.55 liter $mole^{-1}$ min^{-1}. Variations in this value are believed to be largely due to small variations in HCl concentration, these concentrations being accurate to only about 1.5 %.

The rate of exchange is found to be independent of the surface area in contact with the solutions (XII and XVI, Table 1). Extrapolation to time t = 0 of the graphs for exchanges in which glass beads were present showed, however, an abnormally large amount of "induced" exchange. Similar extrapolation of other exchanges showed widely varying and entirely non-reproducible amounts of "induced" exchange, varying from 0.0%

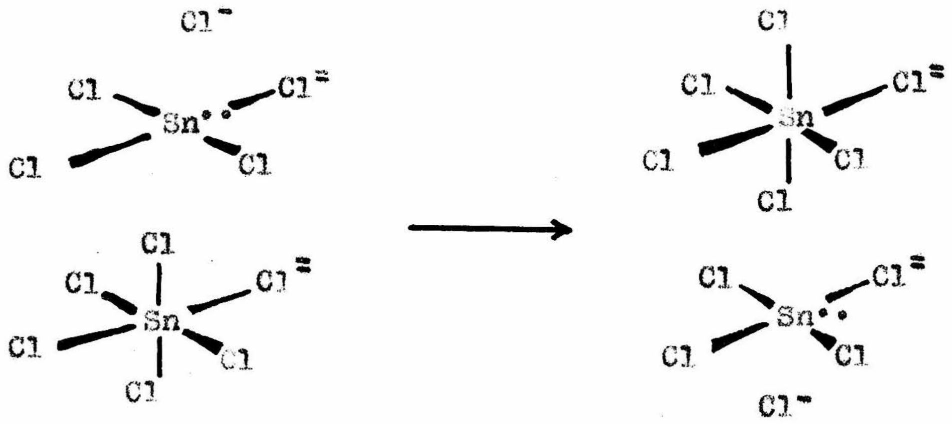
in some exchanges to as high as 23 % (Fig. 5). The two reactions in which glass beads were present showed "induced" exchanges of 38 % and 27 %. Since no "induced" exchange is observed in several instances, and the value does not vary for the different precipitates of a single run, this exchange is not believed to be a result of the precipitation method. As mentioned earlier in this report, the amount of apparent "induced" exchange is dependent upon the method of determining the initial activity of Sn^{IV}, but the large amount of apparent rapid partial exchange that is sometimes observed cannot all be accounted for on this basis. The same curve would be obtained if a certain amount of exchange were to take place at the time of mixing the solutions, perhaps brought about by surface effects on the vessel walls. In some reactions in which "induced" exchange was observed, however, the initial solution contained both Sn^{II} and Sn^{IV} before addition of the marked Sn^{IV}, and rapid exchange on the vessel walls at the time of mixing seems quite unlikely. The slope of the plotted lines, and therefore the measurement of the rate of exchange, is not affected by the "induced" exchange, however, and no error is thus introduced in the rate measurements.

At 0°C., R/ab was found to be 0.104, giving an activation energy of 10.7 Kcal. per mole for the exchange reaction. The complete Arrhenius equation is then

$k = 3.8 \times 10^7 e^{-10,700/RT}$, when k is expressed in liter mol^{-1} min^{-1}.

It is found from exchanges in 9, 10, and 11 <u>f</u> HCl (Table 1, Figs. 7, 8), that, in this concentration range, the reaction rate constant, R/ab, is proportional to the 0.3 power of the HCl activity. This value is obtained from the ratios of the partial vapor pressures of HCl at the three concentrations, given by the I.C.T., on the assumption that the activities of HCl are unaffected by the small amounts of tin present. The empirical rate equation for the electron exchange reaction is, then, $R = k\ a\ b\ (HCl)^{0.3}$. It will be noted that the exchange rate varies as approximately the third power of the HCl concentration.

Although the exchange rate does not vary with the first power of the HCl activity, I should like to mention a possible mechanism by which a symmetrical complex of $Sn^{II} * Sn^{IV}$ may be formed, from which either nucleus may emerge as Sn^{II}. Because of the formation of such substances as Cs_2SnCl_6, it may be assumed that the Sn^{IV} exists in solution mostly as $SnCl_6^{=}$ ions, with six octahedral bonds formed by the Sn^{IV} (11). Sn^{IV} has no electrons remaining in the "O" shell, and could use hybridized $5s5p^35d^2$ orbitals (11) in forming these bonds. If we now assume that the Sn^{II} exists mostly as $SnCl_4^{=}$, and, in an excited state of this ion, the two "O" electrons effectively occupy a 5p orbital rather than the more stable 5s orbital, the $5s5p^25d$ orbitals could possibly be hybridized to give a square planar configuration to the four Sn--Cl bonds. Collision of the octahedral $SnCl_6^{=}$ and planar $SnCl_4^{=}$ could form, together with a single Cl^- ion from the HCl solution, a symmetrical arrangement in which electron exchange may occur.



Such a mechanism would be in agreement with the rate equation $R = K\,ab\,(HCl)$.

A photochemical increase in the exchange rate may be due to the absorption of photons by the Sn^{II} to form the planar $SnCl_4^{=}$ ion, which we have already assumed to be an excited state. The photon absorption also might occur at the time of the collision, or after collision, yielding, in the complex, the excited state necessary for the transfer of electrons. If a photochemical effect on the exchange rate is observed for wave lengths that are absorbed by Sn^{IV}-Sn^{II} mixtures, but not by Sn^{II} alone, the latter possibility would be indicated. If a photochemical effect is observed only with wave lengths that are absorbed by Sn^{II}, a mechanism such as that first suggested would seem logical.

Although the rate of exchange is not appreciably affected by exposure or non-exposure to daylight (Fig. 5) a marked photochemical effect on the rate of exchange has been observed by illumination with a mercury arc (Table 1, Fig. 9).

Current experiments indicate that light absorbed by the inter-action complex and not absorbed by Sn^{II} or Sn^{IV} alone does increase the rate of electron exchange. These results are of a preliminary nature, however, and final conclusions concerning the existence of this effect and the quantum yield it produces have not yet been drawn.

II

Spectrophotometric Investigations of Cobalt-Glycine Systems

A. Introduction

Numerous investigators have studied or mentioned the formation of complexes of certain metallic ions with amino-acids and dipeptides (12,13,14,15,16). Since these metallic ions are present in many proteolytic enzymes, and knowledge of the mechanism by which these enzymes function is of such great importance in understanding physiological reactions, more careful physico-chemical investigations to determine the exact nature of the metal-amino-acid complexes are highly desirable.

The following is a report of spectrophotometric investigations of cobalt-glycine complexes formed in the presence and in the absence of oxygen, with determinations of the effect of changes in pH. A determination of the stability constant of the complex formed in solution containing excess cobalt ions, made by the method of Bjerrum, is also reported. These investigations are of a preliminary nature only, and were undertaken when a delay in receiving a shipment of radioactive tin interrupted the investigations that are described in the main part of this report.

B. Experimental

The spectrophotometric measurements were made with a Beckmann Model DU Spectrophotometer and Corex cells of ten millimeter light path. The blank cells contained distilled water or solutions of composition similar to that of the solution being investigated, but lacking the absorbing solute.

Readings of optical density were made generally at wave length intervals of ten millimicrons. In the investigations of effect of exposure to oxygen, no effort was made to control the ionic strength of the solutions. In all other investigations, the ionic strength was kept at $\mu = 1$ with sodium perchlorate, and the solutions were mixed and kept in an atmosphere of argon gas to minimize oxidation. pH measurements were made with a Beckmann Model G glass-electrode pH meter.

Cobaltous solutions were prepared by dissolving weighed quantities of Merck reagent grade $Co(NO_3)_2 \cdot 6\ H_2O$ in water, and diluting to the desired concentration. Glycine solutions were prepared in a similar manner, using Merck N.F. amino-acetic acid, which was shown to be free of chlorides. Since these observations were meant to be of a preliminary nature, more accurate analyses of the solutions used were not made. In determining the $(CoG)^+$ stability constant, a solution initially containing 0.10 f Co^{++} and 0.05 f glycine was titrated under argon with 0.05 f NaOH, the pH being recorded from the glass-electrode pH meter after each addition of 0.5 cc. of base.

C. <u>Data</u> (Two figures)

Figure 10. Effect of exposure to oxygen on the spectrum of cobalt-glycine at pH 9.6.

I. 0.116 <u>f</u> glycine ; 0.058 <u>f</u> KOH.

II. 0.010 <u>f</u> Co^{++}.

III. 0.010 <u>f</u> Co^{++};0.116 <u>f</u> glycine ; 0.058 <u>f</u> KOH . Unoxidized.

IV. Solution III exposed to air four hours.

V. Solution III exposed to oxygen gas (slowly bubbling) for twenty-four hours.

Figure 11. Effect of pH on cobalt-glycine solutions.

I. 0.010 f Co^{++}.

II. 0.010 f Co^{++}; 0.10 f glycine; 0.19 f HCl (pH = 2.28)

III. 0.010 f Co^{++}; 0.125 f glycine. (pH = 4.68

IV. 0.010 f Co^{++}; 0.10 f glycine; 0.02 f NaOH (pH = 7.27)

V. 0.010 f Co^{++}; 0.10 f glycine; 0.04 f NaOH (pH = 9.23)

VI. 0.010 f Co^{++}; 0.10 f glycine; 0.10 f NaOH (pH = 11.0)

($NaClO_4$) in all solutions to maintain ionic strength of one.)

D. Results and Conclusions

One of the purposes of the investigations in the absence of oxygen was to determine whether the cobaltous ion itself complexes with glycine, or if the complexes which were previously observed actually involve oxidation of the cobalt to the cobaltic state. It is seen from Figure 1 that, at pH 9.6, the cobaltous ion forms a complex with glycine which has an absorption maximum at 500 mμ. Slow oxidation takes place in the presence of oxygen, causing the optical density to increase at all visible wave lengths. The optical density increases most rapidly in the wave length region between 340 and 420 mμ, another maximum developing at 370 mμ. This increased absorption may be due not only to the formation of cobaltic complexes, but also to the formation of decomposition products of glycine, for addition of $BaCl_2$ solution to the oxidized mixture showed appreciable quantities of carbonate to be present. It is probable that cobalt ions catalyze the oxidative decomposition of glycine, just as they have been observed to catalyze the oxidation of poly-hydroxy compounds such as mannitol (17). A very slight decrease in pH was observed in the solution as oxidation progressed.

In strongly acid solution the spectra of cobalt-glycine mixtures were found to be identical with that of cobalt alone at the same concentration. Only a slight variation from this line was observed for a mixture of aqueous cobaltous solution and glycine solution to which neither acid nor base had been added, but some complex-formation is indicated in this case by the decrease in pH below that of either component when the two solutions are mixed. Decrease in pH upon complex formation is brought about by reactions such as $Co^{++} + G^{\pm} \rightleftharpoons CoG^{+} + H^{+}$ and $Co^{++} + 2\ G^{\pm} \rightleftharpoons CoG_2 + 2\ H^{+}$. More strongly absorbing cobalt-glycine complexes are formed only in neutral or alkaline solutions. The spectrum of cobalt-glycine mixture at pH 11.0 (Fig. 2) is nearly identical with that of partially oxidized solutions at a lower pH (Fig. 1), even though the solutions were mixed under argon and the determination of the spectrum began immediately thereafter. Oxidation takes place much more rapidly in strongly alkaline solution.

Exposure to oxygen does not affect the spectra of strongly acid mixtures.

The determination of the stability constant of the cobalt-glycine complex formed in solution containing excess cobalt was the beginning of an effort to establish the exact composition of the complex or complexes that are formed under different conditions. The pH of the solution was plotted against the volume of NaOH solution added, giving a line of nearly uniform slope from pH 5.0 to pH 7.2, above which cobaltous hydroxide began to precipitate, and below which the increase in pH was much more rapid. An amount of NaOH equivalent to about 9%

of the glycine present was required to bring the pH up to 5.0. Analysis of this data on the assumption that in excess cobalt only the complex with one glycine molecule per cobalt atom is formed, that is, $Co^{++} + G^{\pm} \rightleftharpoons Co^{++}G^{-} + H^{+}$, leads to a constant value of 4.83 for pK_1, where $K_1 = \frac{(H^+)}{(G^{\pm})} \frac{(Co^{++}G)}{(Co^{++})}$, over the pH range from 5 to 7. This value is accurate only within about 5 %, since the concentrations of the solutions used were not known to much greater accuracy than this. Attempts to interpret the data on the basis of two glycine molecules combining with each Co^{++} did not give constant values for pK_2 ($pK_2 = 2\ pH - 2 \log \frac{(CoG_2)^{1/2}}{(Co^{++})^{\frac{1}{2}}\ (G^{\pm})}$). The constant value of pK_1 indicates that $Co^{++}G^{-}$ is the only complex formed under these conditions.

Further work along these lines would yield desirable information. Such work may over-lap that proposed by Mellor and Maley (18).

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Aluminum Absorption Curve of Sn^{113} and In^{*113} Radiations

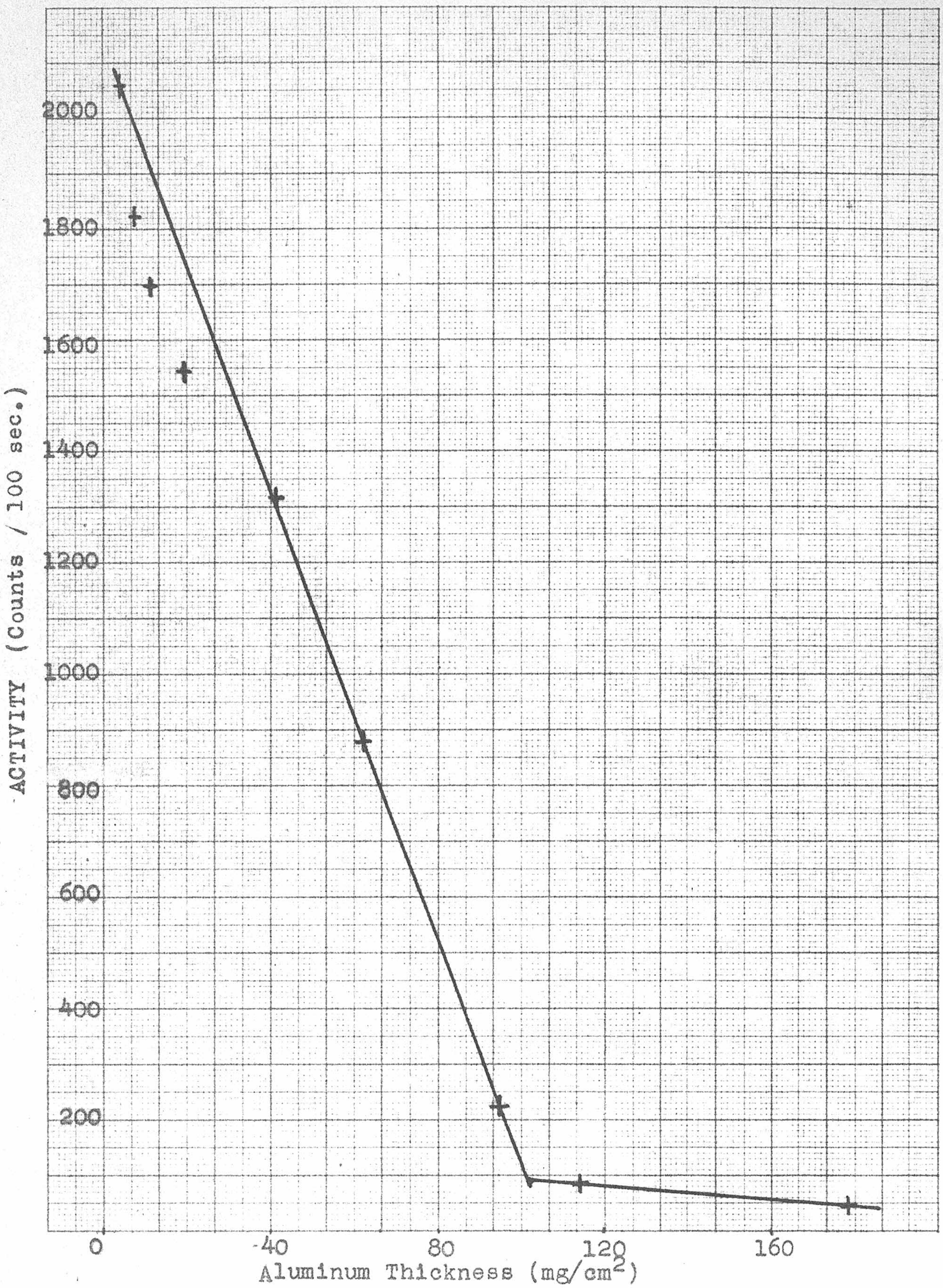
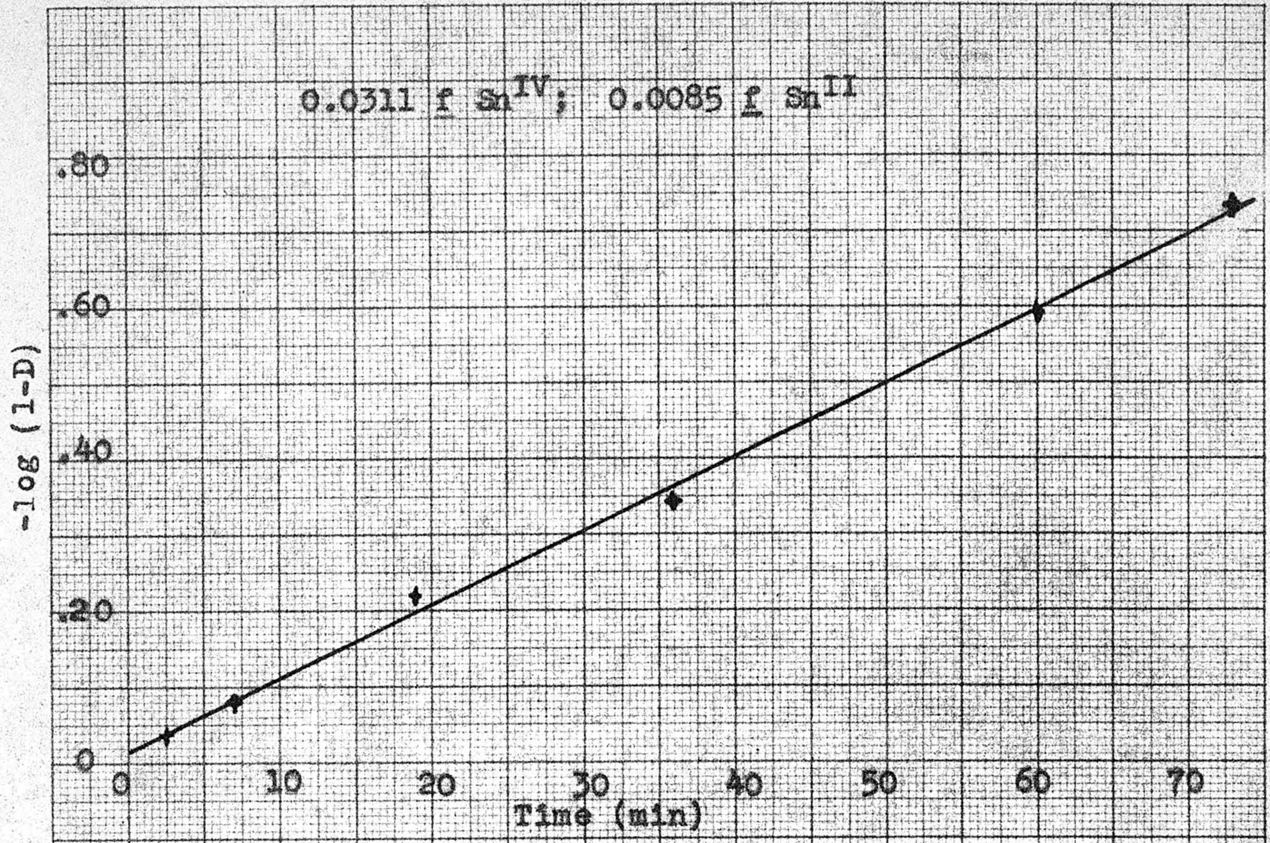
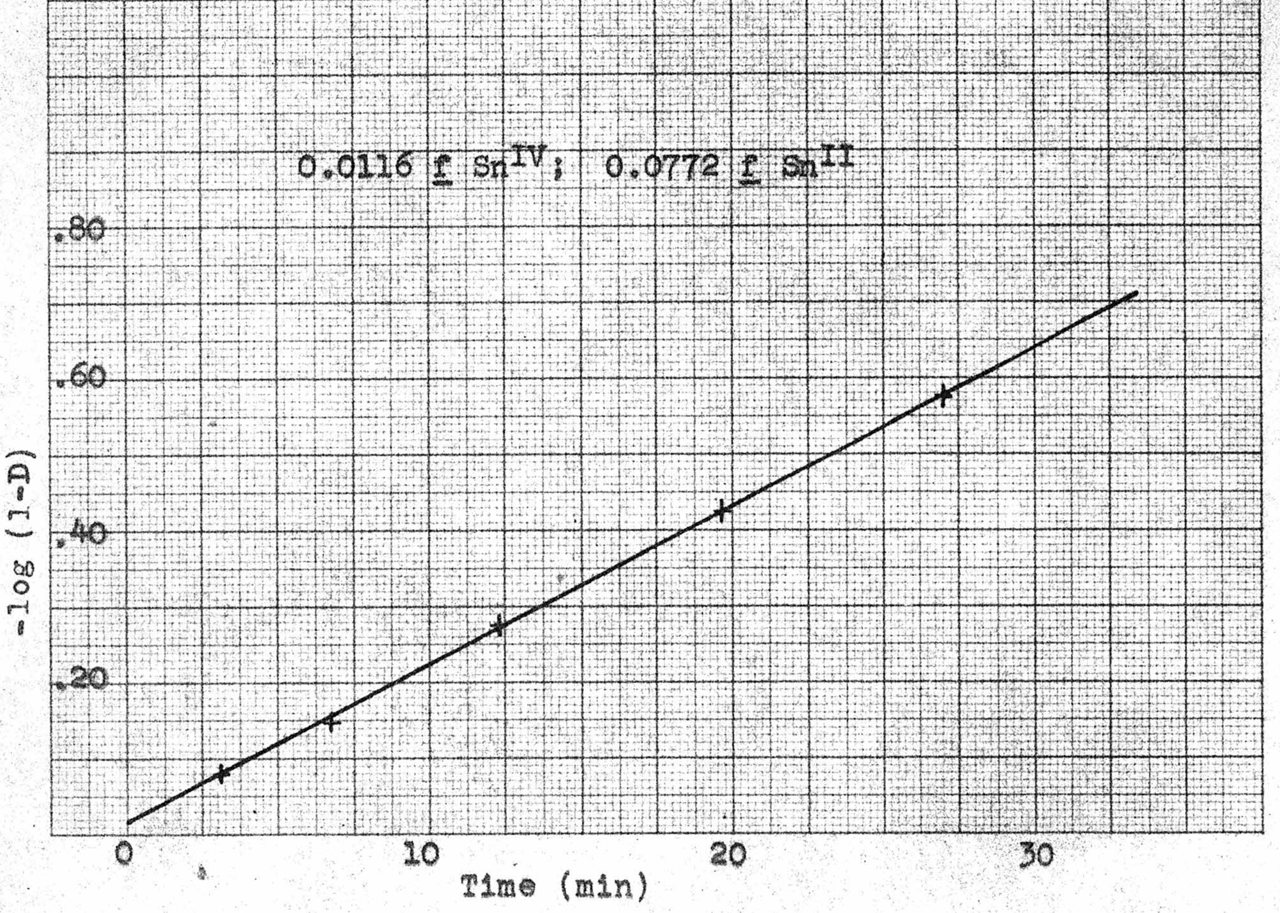


Figure 1

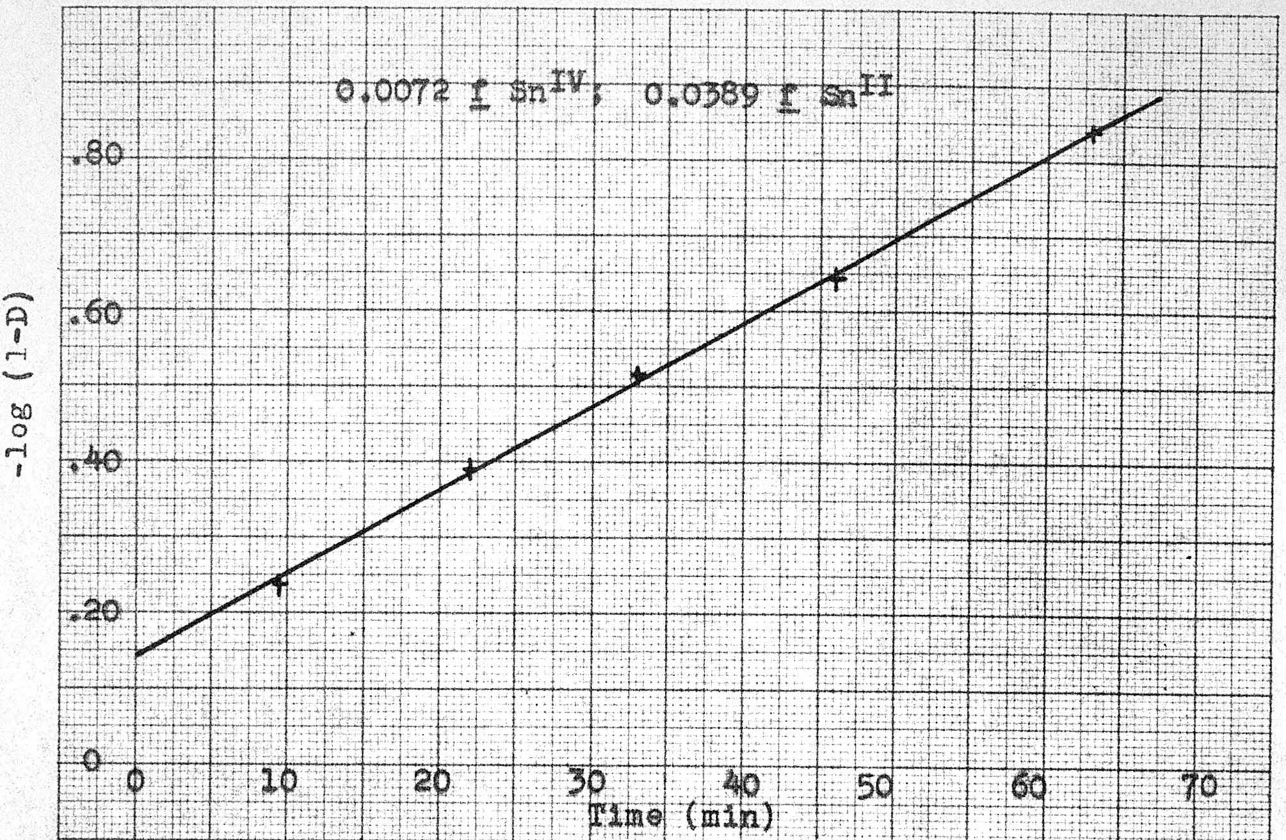
Rate of Exchange in 10.0 f HCl at 25° C.



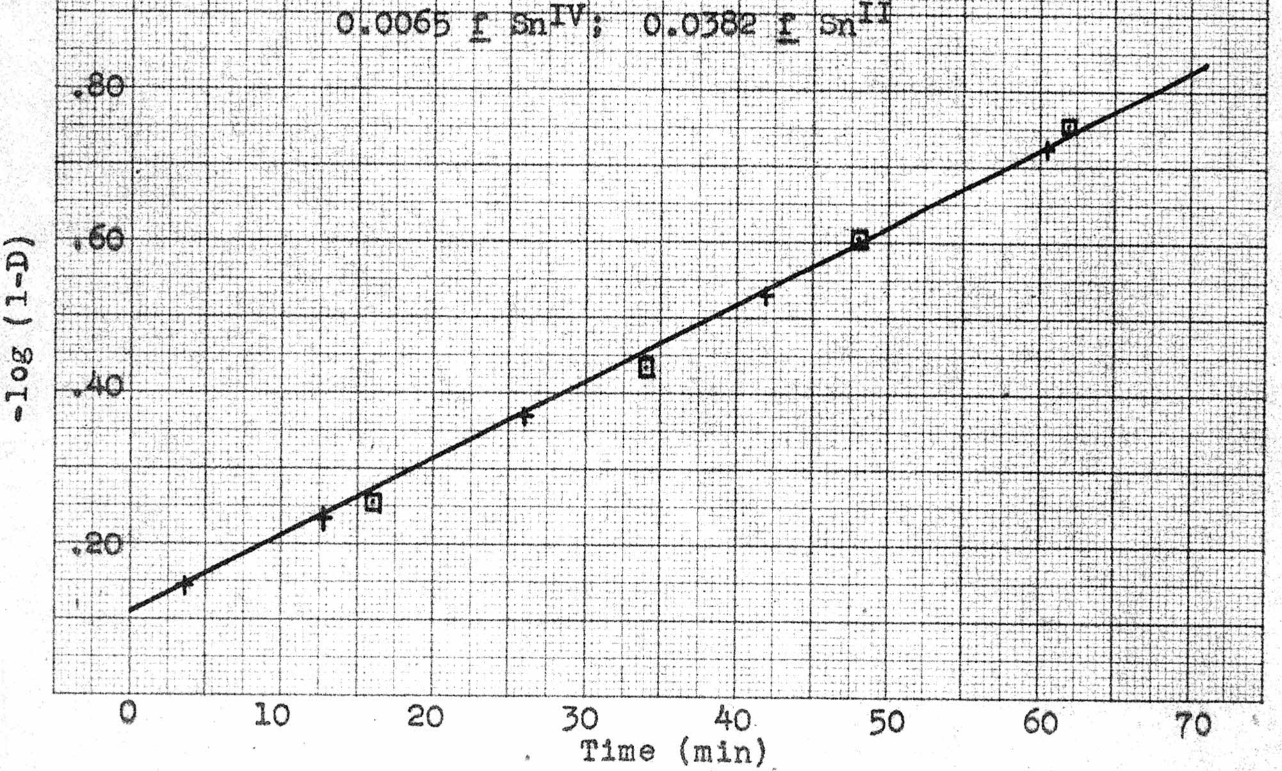


Figures 2 and 3

Exchange Rate in Presence of Glass Beads; 10 f HCl; 25° C.



Exchange Rate in daylight (+) and in Dark (⊡); 10f HCl; 25° C.



Figures 4 and 5

Exchange rate at Zero Degrees; $0.0108\ \underline{f}\ \mathrm{Sn}^{IV}$; $0.0569\ \underline{f}\ \mathrm{Sn}^{II}$

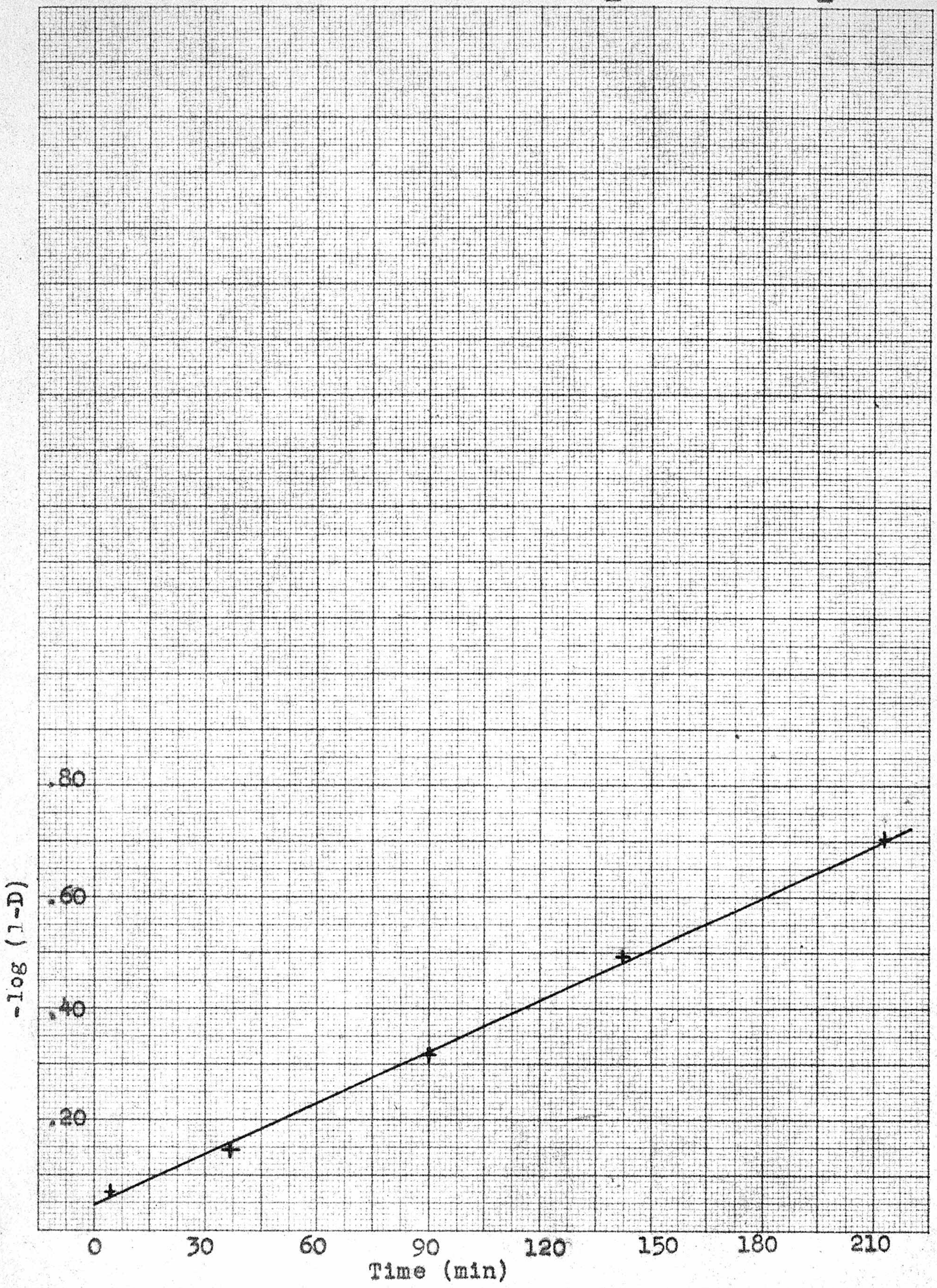
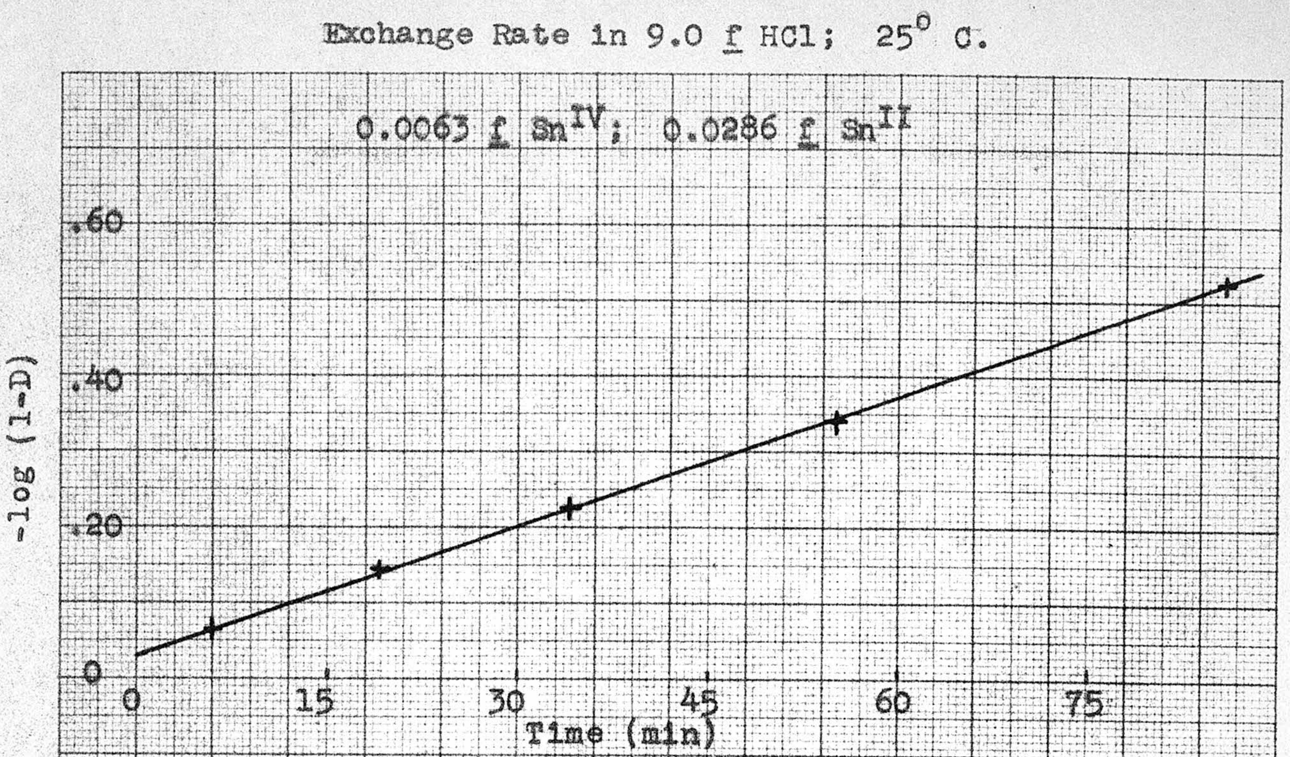
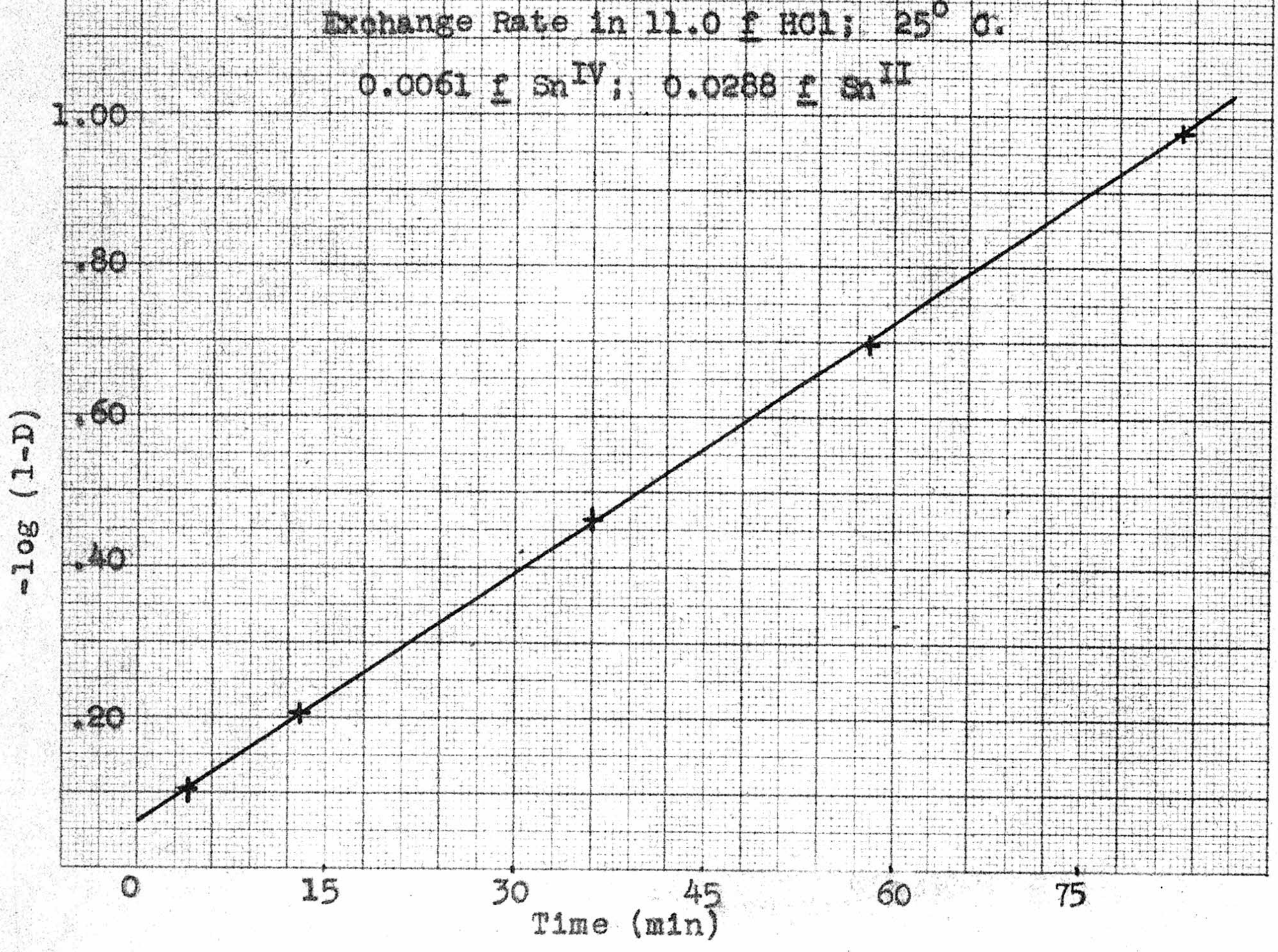


Figure 6





Figures 7 and 8

Thermal plus Photochemical Exchange Rate; ca 5° C.

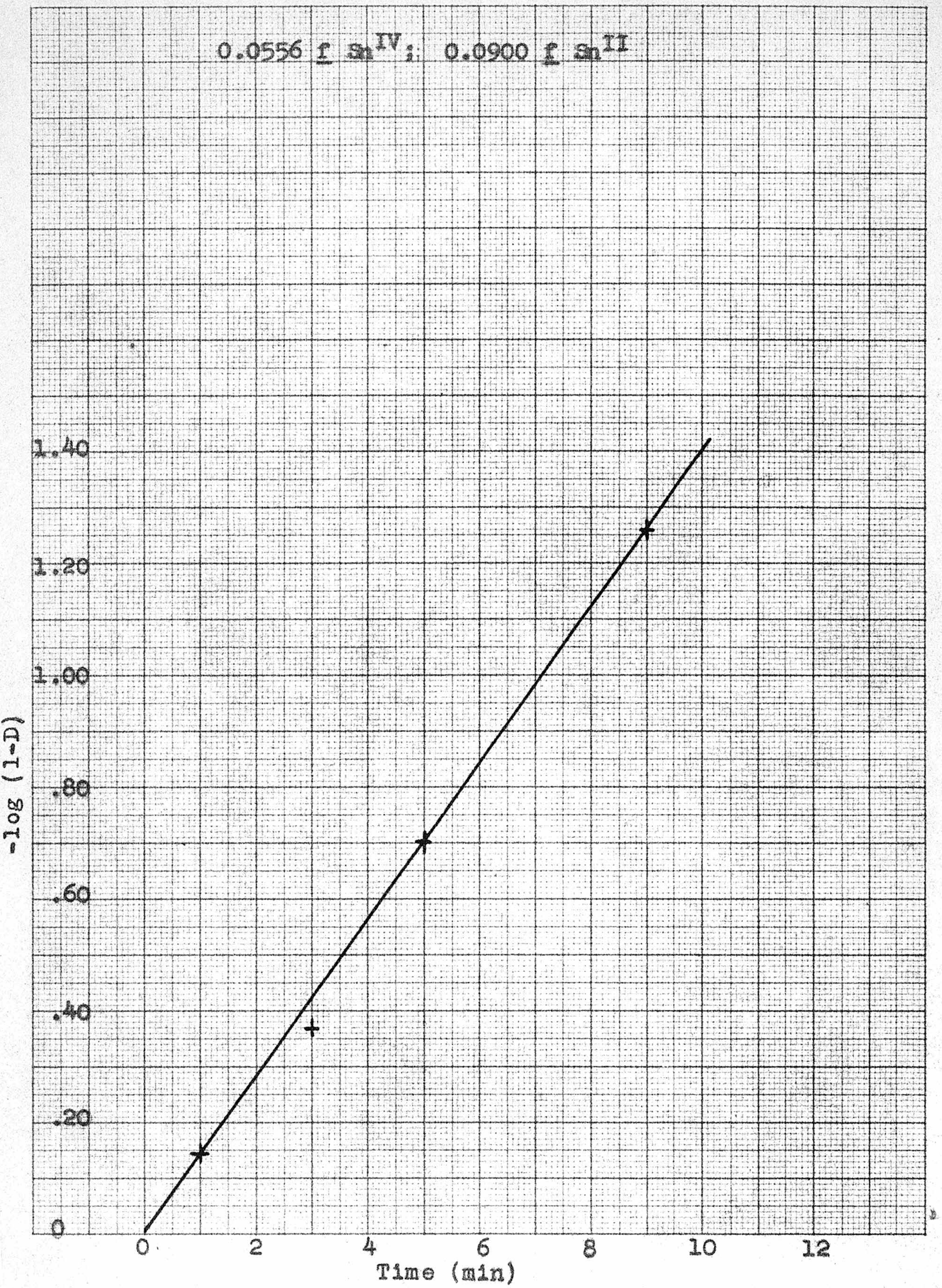
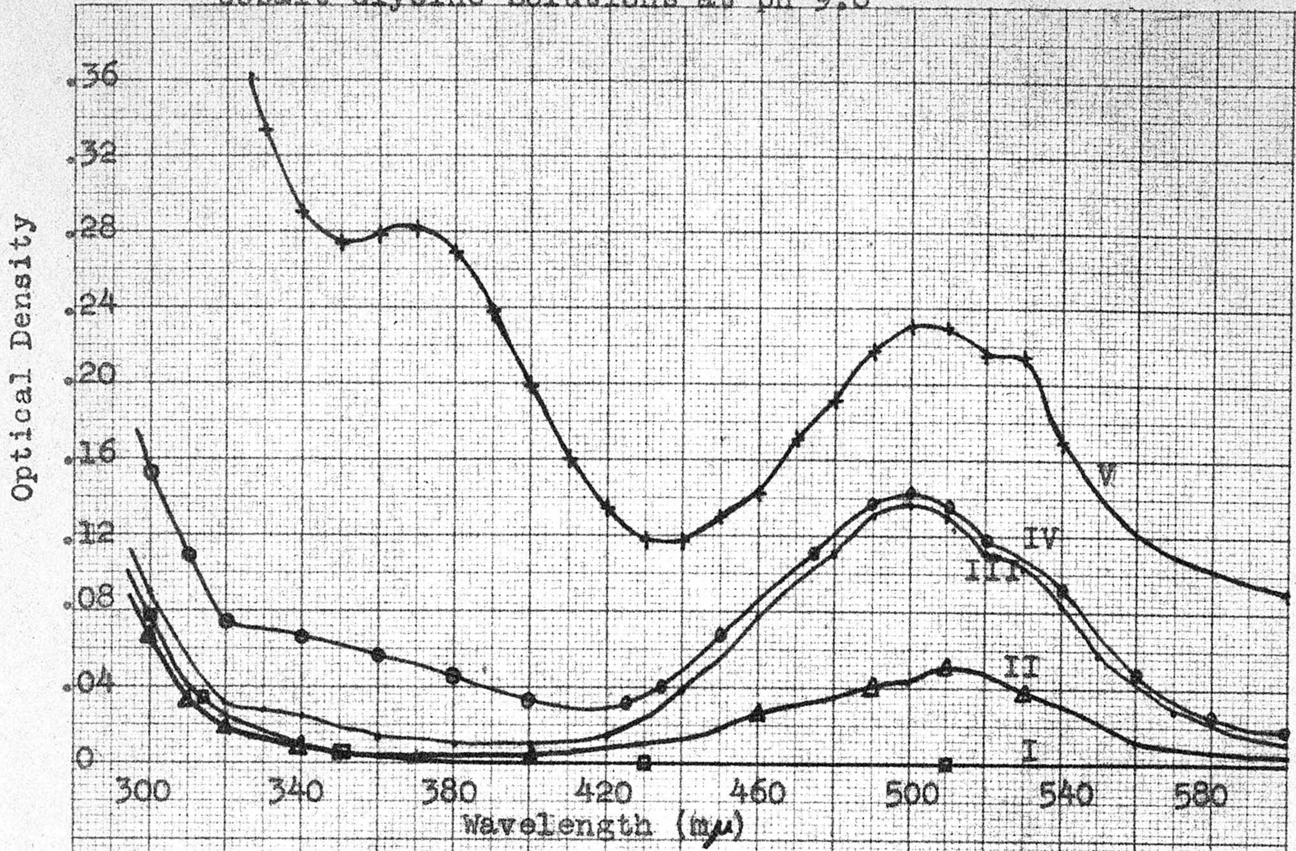
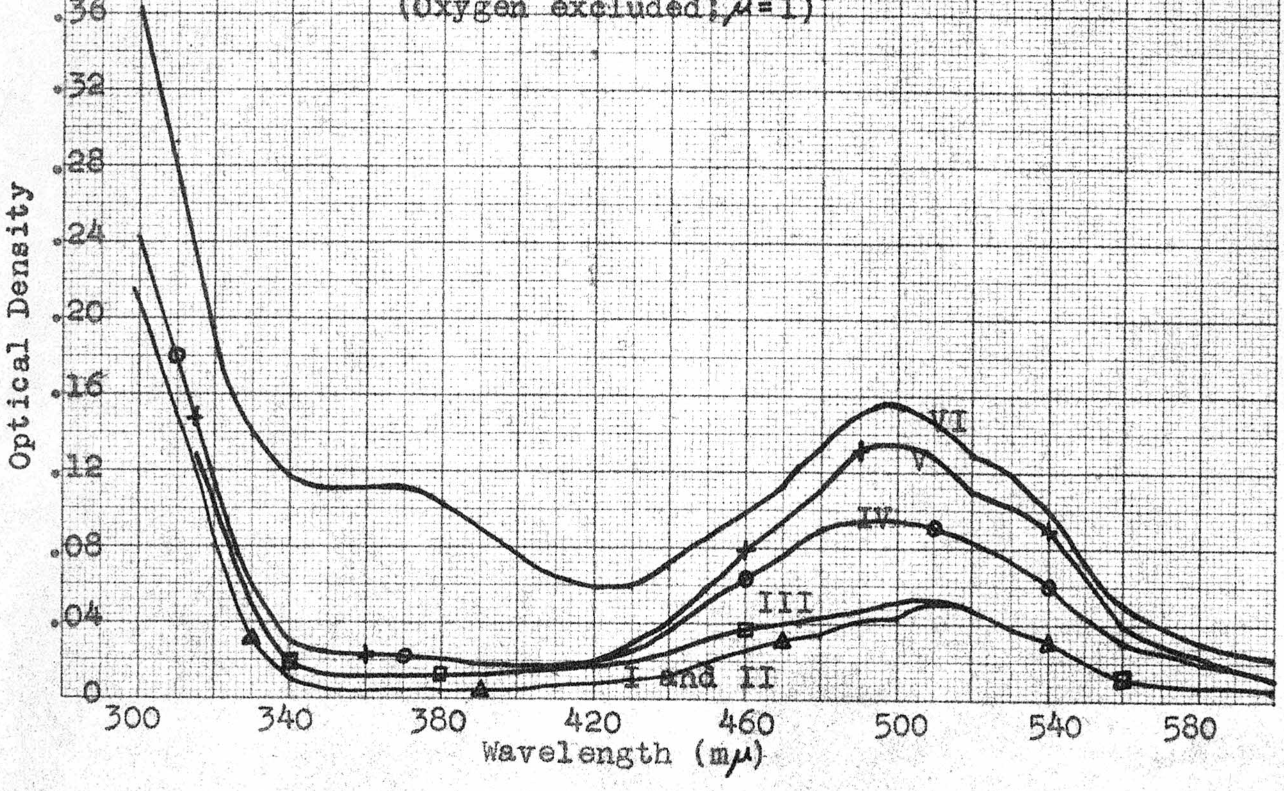


Figure 9

Effect of Exposure to Oxygen on the Absorption Spectrum of Cobalt-Glycine Solutions at pH 9.6



Effect of pH on Spectrum of Cobalt-Glycine Solutions (Oxygen excluded; μ = 1)



Figures 10 and 11