A Spectrophotometric and Radiochemical Investigation of the Interaction between the Oxidation States of Tin in Aqueous Solution

Thesis by

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Abstract

The spectrophotometry and radioactive exchange of Sn^{II} and Sn^{IV} in hydrochloric acid have been investigated. It is found that mixtures of Sn^{II} and Sn^{IV} in hydrochloric acid exhibit anomalous absorption of ultra-violet light and that with the extent of this anomalous absorption is proportional to the product of the Sn^{II} and Sn^{IV} concentrations, implying absorption by a dimeric complex of Sn^{II} and Sn^{IV}.

It is found that Sn^{II} and Sn^{IV} exchange radioactivity moderately slowly (half-exchange time about 7 min.) in 9N hydrochloric acid. The extent of exchange upon immediate separation after mixing is about 17%, which is either a function of the separation method or an indication that only certain chloride complexes of tin exchange.

It is found that Cu^{I} and Cu^{II} exhibit interaction absorption in 6N HCl.

Table of Contents

I

Introduction

Many observers have noted and reported that solids and solutions containing different oxidation states of an element exhibit intensity of color beyond the contribution of the separate states themselves (1,2,3,4). This coloration is generally believed to be due to the "transfer" of an electron (S) between the oxidation states involved, although the phenomenon is by no means completely understood. In the case of solids, X-ray analysis has revealed that in some of the cases exhibiting anomalous coloration the different oxidation states are at non-equivalent positions in the lattice. Very little is known about solutions exhibiting this phenomenon.

It is clear that a complete understanding of this interaction color would have far-reaching implications upon the theory of oxidation processes in general, and upon the nature of the electronic energy levels in solutions.

Further interest lies in a consideration of the exchange of radioactivity between oxidation states of an element in the light of this interaction phenomenon. If the interaction involves the coming together of the two oxidation states to such proximity that electrons lie in levels common to both states, so that a compound, or complex, is formed, it seems reasonable that such a system would exhibit radioactive exchange.

The present report is a spectrophotometric investigation of the Sn^{II} - Sn^{IV} interaction in aqueous hydrochloric acid, first reported by Whitney (4), with attention to the dependency on concentration of the interacting ions and hydrochloric acid, and of the exchange of radioactivity between Sn^{II} and Sn^{IV} in 9N hydrochloric acid.

II

Spectrophotometry

A. Experimental

The spectrophotometer used was a Beckmann Model DU, with 10 mm light path quartz or Corex cells. On occasion, quartz spacers were used to reduce the light path to 1 mm. Measurements were made against blanks of solutions identical with the unknown except that the blank contained no tin. To protect the spectrophotometer, cells containing hydrochloric acid were sealed with a mixture of beeswax and rosin.

Stock $SnCl_4$ solutions were prepared by dissolving Merck's reagent grade $Sn\ Cl_4 \cdot 5H_2O$ in Baker's reagent grade concentrated hydrochloric acid, and diluting to the desired concentration of $Sn\ Cl_4$ and HCl. $SnCl_4$ concentration was determined by reduction with Sb (Braun, powdered)(5)) and subsequent oxidation with standard iodine solution. The HCl concentration was determined by titration with standard NaOH solution. It was determined by introducing weighed amounts of $SnCl_4 \cdot 5H_2O$ into standard HCl solutions and titrating with NaOH that under these conditions, $Sn(OH)_4$, or at least a non-chloride containing hydrated stannic oxide, was precipitated. The method is not very precise, especially in solutions concentrated in Sn^{IV}, because of the difficulty in end-point determination, but is found to give results reproducible within 2 per cent.

Stock $SnCl_2$ solutions were prepared by dissolving Baker's reagent grade $SnCl_2 \cdot 2H_2O$ in concentrated reagent grade hydrochloric acid, boiling with reagent grade powdered Sn, dilution, and analysis. $Sn^{II}$was analysed directly by oxidation with iodine; Sn^{IV} and HCl by the method given above. At no time was it possible to obtain solutions free of Sn^{IV} by analysis, although the content of this oxidation state was found to be as low as 0.7% of all Sn present. In general, solutions of Sn^{II} contained not more than 5% Sn^{IV}. All handling of Sn^{II} solutions was carried out under an atmosphere of carbon dioxide.

Spectrophotometric measurements were made in 3 hydrochloric acid concentrations: 9.5N, 6N, 3N. In each case, the procedure was first to measure the absorption spectrum of solutions of various concentrations of $SnCl_4$, then of solutions of $SnCl_2$, then of mixtures of the two, varying the proportion of Sn^{IV} to Sn^{II} in the mixtures.

The extent of the anomalous coloration was determined by subtracting from the optical density (D) of the mixture solution at any wavelength the D of Sn^{II} and Sn^{IV} at the same wavelength.

In general, Sn^{IV} solutions were found to follow Beer's Law within the limits of analytical error, so that it was necessary to measure the D of only a few Sn^{IV} concentrations to obtain D at any concentration. Sn^{II} solutions, however, showed marked deviation from Beer's Law, so that many measurements were necessary.

The logical extension of the investigation to alkaline solutions of Sn^{II} and Sn^{IV} was prevented by the turbidity of these solutions, particularly that of Sn^{II}. As a result, Sb was substituted for Sn and measurements made on Sb^{III} and Sb^{V} and mixtures in 7.65N KOH. Within the time available, it was found that spectrophotometrically clear concentrated solutions could not be obtained.

Extraneously to the main purpose of the investigation, measurements were made of the absorption spectra of Cu^{I} and Cu^{II}, and a mixture of these ions, all in 6N HCl, to determine whether interaction absorption existed in this case.

Precision

Analytical.

Measurements of the concentration of Sn^{II} were precise to 0.5%, those on Sn^{IV} to 0.6% and those on HCl to 2.6%.

Spectrophotometric.

All measurements were made on steep D-λ slopes, so that care was exercised to maintain slit widths at minimum values. Nevertheless, calculations of the uncertainty in D_λ based upon the observed value of the slope of the D-λ curve and the band width of the spectrophotometer result in 7-20% on the steep portions of the curve, the percentage uncertainty increasing with lower values of D. The observed values of D represent, of course, not the D at a wavelength λ_0, but rather the integral between limits ~~get~~ SET by the uncertainty in λ (determined by λ and slit width) of a function $D_\lambda d\lambda$. It is clear that if the change of slope of the D-λ curve over the interval of the uncertainty in λ is so slight that the curve may be taken as a straight line, the contributions to the integral of the intervals λ_1 to λ_0 and λ_0 to λ_2, will cancel, giving a value in D_λ precise to the error in reading of the D and λ scales on the spectrophotometer. This rectilinearity may be checked by measuring D at various λ's with several slit width settings for each point. When this is done, it is found that D is independent of slit width above a wavelength characteristic of the substance under investigation; for $SnCl_4$ in 9N HCl this wavelength was below 320 mμ; for $SnCl_2$ in 9N HCl below 350 mμ. Through an oversight, that of the interaction was not measured, however, by analogy with the $SnCl_2$ and $SnCl_4$ curves, 360 mμ may be estimated as a reasonable value. On this basis, spectrophotometric precision is that of reading the instrument and setting the controls, and is certainly less than 1% for any value of D greater than .100. In practice, the independence of D on slit width was not relied upon since slit widths were held as constant as practical with the instrument, giving precision of about 1%.

B.	Data	16 Figures
Figure I Curve	Spectra of Sn^{IV}, Sn^{II}, and mixtures thereof in 9.5N HCl	
I		.231F $SnCl_4$ in 9.5N HCl
II		.309F $SnCl_2$ in 9.5N HCl
III		.399F $SnCl_2$ + .381F $SnCl_4$ in 9.5N HCl
Figure II	Sn^{IV} Spectrum at Several HCl Concentrations	
I		.231F $SnCl_4$ in 9N HCl
II		.203F $SnCl_4$ in 6N HCl
III		.225F $SnCl_4$ in 3N HCl
Figure III	Sn^{IV} Absorption at Several Wavelengths	
I		.5F $SnCl_4$, λ = 310 mμ
II		.3F $SnCl_4$, 310
III		.7F $SnCl_4$, 320
IV		.5F $SnCl_4$, 320
Figure IV	$SnCl_4$ in 9.5N HCl	
I		λ = 315 mμ
II		320
III		325
Figure V	$SnCl_4$ in 6N HCl	
I		λ = 305 mμ
II		310 mμ
III		315 mμ
IV		320 mμ
V		325 mμ

Figure VI	$SnCl_4$ in 3N HCl
I	$\lambda =$ 300 mμ
II	305 mμ
III	310 mμ
IV	315 mμ
Figure VII	$SnCl_2$ Spectra at Several HCl Concentrations
I	.399F $SnCl_2$ in 9.5N HCl
II	.382F $SnCl_2$ in 6N HCl
III	.372 $SnCl_2$ in 3N HCl
Figure VIII	$SnCl_2$ in 9.5N HCl
I	$\lambda =$ 330 mμ
II	335
III	340
IV	345
V	350
VI	355
VII	360
Figure IX	$SnCl_2$ in 6N HCl
I	$\lambda =$ 330 mμ
II	335
III	340
IV	345
V	350
VI	355
VII	360
VIII	365
IX	370
X	375
XI	380

Figure X	$SnCl_2$ in 3N HCl
I	$\lambda =$ 330 mμ
II	335
III	340
IV	345
V	350

Figure XI	Interaction Absorption in 9.5N HCl
I	$\lambda =$ 360 mμ
II	370 mμ
III	380
IV	390
V	400

The values plotted represent the measured optical density of mixtures of Sn^{II} and Sn^{IV} less the corresponding densities of the ions themselves, as taken from Figures IV and VIII. The following mixtures were used:

(Sn^{II}) (Sn^{IV}) (C_1C_2)	(Sn^{II})	(Sn^{IV})
.047F^2	.137F	.341F
.096	.314	.306
.152	.399	.381
.183	.479	.382

Figure XII	Interaction Absorption in 6N HCl
I	$\lambda =$ 365 mμ
II	370
III	375
IV	380
V	385
VI	390
VII	395
VIII	400

The following mixtures were used:

(Sn^{II}) (Sn^{IV}) (C_1C_2)	(Sn^{II})	(Sn^{IV})
.140F^2	.380	.368
.278	.788	.353
.359	.609	.589
.562	.762	.737
.650	.662	.982

Figure XIII	Interaction Absorption in 3N HCl
I	λ = 335 mμ
II	340
III	345
IV	350
V	355
VI	360

The following mixtures were used:

(Sn^{II}) (Sn^{IV})	(Sn^{II})	(Sn^{IV})
.042F^2	.186F	.225F
.084	.372	.225
.104	.186	.562
.130	.469	.281
.149	.495	.300
.167	.372	.450

Figure XIV	Interaction Absorption at Several Wavelengths		
I	C_1C_2	.15	λ = 360 mμ
II	C_1C_2	.10	360
III	C_1C_2	.05	360
IV	C_1C_2	.20	380
V	C_1C_2	.10	380
VI	C_1C_2	.05	380

Figure XV	Spectra of Sb^{III} and Sb^{II} in Alkaline Solution
I	.022F $KSbO_2$ in 7.65N KOH
II	.170F $KSbO_3$ in 7.65N KOH
Figure XVI	Spectra of Cu^{I}, Cu^{II}, and mixtures thereof in 6N HCl
I	.05F CuCl in 6N HCl
II	.025F $CuCl_2$ in 6N HCl
III	.05F CuCl + .025F $CuCl_2$ in 6N HCl

C. Results and Conclusions

Figure I shows the absorption spectrum of $SnCl_4$, $SnCl_2$, and mixtures of the two in 9N HCl and exhibits the general nature of the effect. Sn^{IV} under these conditions absorbs strongly below about 320mμ, Sn^{II} below about 350, and the mixture below about 360-370 mμ. The absorption spectra of $SnCl_4$ at various HCl concentrations are presented in Figure II. It is seen that the absorption in the near ultra-violet increases with increasing HCl concentration. The same data are presented as a family of curves of D as a function of HCl concentration for different wavelengths in Figure III. The linear variation of D with HCl concentration is striking, and extrapolation suggests that Sn^{IV} loses most of its color in the 300-320 mμ range below 1-2N HCl. The satisfactory manner in which the Sn^{IV} solutions conform to Beer's Law is illustrated in Figures IV, V, and VI.

A plot of the absorption spectra of $SnCl_2$ solutions is exhibited in Figure VII. It is seen that the absorption is stronger in 6N HCl than in 9N or 3N.

The deviations from Beer's Law of the $SnCl_2$ solutions are demonstrated in Figures VIII, IX, and X. As mentioned above, no $SnCl_2$ solution could be obtained free of $SnCl_4$: however, deductions from the D of $SnCl_2$ solutions of a D due to interaction with the amount of $SnCl_4$ believed to be present did not reduce the curves to even near linearity. No explanation of this deviation is available at this time.

The variation of the D of $SnCl_2$ solutions with HCl concentration may be explained in one of two ways: either the more heavily chloride complexed species (the concentration of which certainly increases with increasing HCl concentration) are not as strongly absorbing as the lower, or D of all species decreases at high HCl concentrations, due perhaps to decreased activity of the solvent, or some associated electrostatic phenomenon. This point is worthy of further study, since the interaction D, and hence presumably the interaction complex concentration, increases steadily with HCl concentration.

Whitney and Davidson showed in the cases of Sb^{III}, Sb^{V} interaction that the optical density of interaction absorption is proportionate to the product of the concentrations of Sb^{III} and Sb^{V}. Figures XI, XII, and XIII show that this is true for the Sn^{II}, Sn^{IV} case also. This implies that the absorbing specie is some sort of a dimeric complex formed by a reaction of the type:

$$Sn^{II}Cl_x^{(2-x)} + Sn^{IV}Cl_y^{(4-y)} \rightarrow Sn^{II}Sn^{IV}Cl_{x+y}^{6-x-y}$$

The composition of the complexes involved cannot be determined from the data available. It may be noted from Figure XIV that at any one wave length the amount of interaction absorption increases with increasing HCl concentration. The concentration of interaction complex is presumably very low or the D vs. C_1C_2 curves would show deviation from linearity, since no correction has been made in the concentration of Sn^{II} or Sn^{IV} for the amount of each ion involved in the complex.

No interaction absorption was noted in the case of mixtures of $KSbO_2$ and $KSbO_3$ in 7.65N KOH; however, the concentration of the mixed solutions was so low that the concentration product was only about.001, rather too low to expect observable coloration. The spectra obtained are exhibited in Figure XV. Further work is indicated in the field of alkaline solutions.

It may be seen from Figure XVI that strong interaction takes place in solutions of Cu^{I} and Cu^{II} in 6N HCl. It is interesting that this interaction causes absorption in the transparent region of the Cu^{I} and Cu^{II} ions themselves. Further work is indicated on the concentration and acid dependency of the interaction absorption of this pair of oxidation states.

III

Radiochemistry

A. Experimental

A sample of radioactive tin metal was obtained from the U. S. Atomic Energy Commission as catalog item number 3c (6) containing the following isotopes:

Isotope	Half-life	Estimated Quantity(mc)	Estimated mc/g element	Radiation (MEV) Beta	Gamma
Sb^{125}	2.7y	1.0	Carrier free	0.8,0.3	present
Sn^{113}	100d	1.0	0.16	K, e^-	0.085
Sn^{121}	62h	?	?	2.6	present
Sn^{123}	10d	?	?	0.8	none
Sn^{125}	9m	?	?	2.2	0.74

Since the elapsed time between cessation of irradiation of the sample and its use in experiments was some 120 days, the only isotopes remaining in any significant amount at the time of experiment were Sn^{113} and Sb^{125}. It is noteworthy that in the decay of Sn^{113}, the K-capture leads to the formation of an excited In^{113} nucleus, which reverts to the ground state with the emission of a 390 KEV gamma ray, with a half-life of 105 minutes. The internal conversion electrons from this radiation, rather than the weak radiation from Sn^{113}, were used in counting.

The Sn and Sb in the radioactive sample were separated by the method of Plato and Hartmann (7), and Al absorption curves run on the separate samples. The results for Sb are presented in Figure XVIII, and those for Sn in Figure XVII. The separated Sn was precipitated as the hydroxide with sodium hydroxide and redissolved in HCl to convert it to the chloride.

All exchange experiments were carried out in 9N HCl with the radioactive tin in the stannic state. With the one exception noted below, the procedure was to pipette 5 ml of 0.2F $SnCl_4$ in 9F HCl into each of two previously weighed centrifuge tubes, to one of which was added 5 ml of 9N HCl, and to the other 5 ml of 0.2F $SnCl_2$ in 9NHCl. After a time interval, to each was added 1 ml of a solution of CsCl (28 mg/ml) in 9N HCl, which precipitated Cs_2SnCl_6, leaving the stannous tin in solution. This precipitate was centrifuged, washed with 9N HCl, dried at 100°C for about 16 hours, and weighed. The drying period permitted the Sn^{113} to come to equilibrium with its daughter In^{*113}. After weighing, the precipitate was metathesized with NH_4OH to the basic stannic chloride, centrifuged, washed, slurried onto glass plates, and counted with a bell-jar type Geiger-Müller tube, using a Higginbotham scalar circuit. The specific activity of the precipitate from the Sn^{IV}-Sn^{II} mixture was compared with that of the Sn^{IV}-HCl "blank" to determine the extent of exchange. Experiments were carried out with intervals of 1, 4, 7, and 30 minutes between mixing and precipitation.

To obtain the extent of exchange in a very short interval after mixing, CsCl was added to freshly prepared $SnCl_2$ solution. The resulting precipitate of Cs_2SnCl_6 was centrifuged off, more CsCl added, 5 ml of the resulting solution added to 5 ml of $SnCl_4$ solution, the precipitate centrifuged, and the above procedure carried out.

Precision.

It is to be emphasized that the purpose of this investigation was to obtain a semi-quantitative idea of the Sn^{II}-Sn^{IV} exchange under these conditions, not to obtain high precision results. By the use of "blank" experiments, it was found that the deviation arising in the precipitation, weighing, slurrying and mounting process was about 2%. The other major source of error lay in the fact that the $SnCl_2$ solutions contained up to 5% $SnCl_4$, which would decrease the specific activity of Sn^{IV} even without exchange. To these may be added the usual counting uncertainty of some 4% for the samples counted to give results precise to some 11%.

B. Data	2 Figures, 1 Table
Figure XVII	Aluminum absorption curve of radiation from Sb separated from sample.
Figure XVIII	aluminum absorption curve of Sn separated from sample.

Table I

Mixture	Interval before Precipitation (min.)	Wt. Cs_2SnCl_6 (mg.)	Counts per minute (minus background)*	Counts per minute per mg Cs_2SnCl_6	Per Cent Exchange
A	0	18.6	21	1.13	17
B	1	47.6	80	1.68	9
C	4	51.5	51	.99	33
D	7	47.6	43	.90	47
E	7	49.6	69	1.39	69
F	30	47.4	39	0.82	105
Blank for A, C, D †		50.8	67**	1.32	
Blank for B		50.4	92	1.83	
Blank for E		31.1	73	2.35	
Blank for F		47.7	80	1.68	

* Background count was fairly constant in the vicinity of 15 cts/minute

† "Blank" refers to the Sn^{IV}-HCl mixture run simultaneously.

** $SnCl_4$ solutions changed between E, F, B and A, B, C chronological order of experiments is F, E, B, (ACD). Also, while A, C, D, and their blank were run on matched glass mounting plates, E, F, and B were run on pairs of matched plates so that while each was matched with its blank, they were not matched to each other.

C. Results and Conclusions:

It may be seen from Figure XVIII that breaks occur in the aluminum absorption curve of Sb radiation at thicknesses of 107 and 207 mg/cm^2, corresponding (8) to electron energies of 0.36 and 0.6 MEV, respectively, as compared with reported (9) values of 0.3 and 0.6-0.7 MEV. Also, on Figure XVII, for Sn radiation, on Curve A there may be seen a definite break at a thickness of 125 mg/cm^2, and a rather doubtful break at 11 mg/cm^2, corresponding (3) to .40 and .087 MEV respectively. The reported (10) values of the gamma ray energies in the decay of In^{*113} and Sn^{113} are 0.390 and .085 MEV, respectively. Since the conversion electrons should have energies of 0.363 and .054 MEV, respectively, it is not clear why the observed values should correspond so closely to those reported for the energy of the gamma rays.

Consideration of Curve B, Figure 16, reveals good linearity of the three points corresponding to thicknesses of Al of 45, 62, and 118 mg/cm^2. If Sb^{125} had been present, points corresponding to thicknesses above 107 mg/cm^2 should be displaced to the right of the line defined by the first two points (see Figure XVII). Calculations based on the uncertainty in this point and the corresponding point in the curve for Sb indicate that the Sn^{113} contained Sb^{125} to not more than 2% by activity at absorber thicknesses of about 8 mg, which was that present in exchange experiments.

It is concluded from these experiments that Sn^{II} and Sn^{IV} exchange radioactivity in 9N HCl at a fairly rapid rate, with a "half-exchange" time of about seven minutes.

Of particular interest is the 17% exchange found on immediate precipitation, for which there are three possible explanations: first, experimental error; second, that this figure is associated with the precipitation method of separation, and third, that there exists in the tin solutions chloride complexes which exchange immediately, but are present as 17% of the total tin in solution, in slow equilibrium with the other species present. This latter explanation is worthy of further investigation, as could be done by noting whether the absorption spectrum of tin solutions in HCl changes slowly upon dilution with water.

Further work, also, is needed with solutions of Sn^{IV} and Sn^{II} at lower HCl concentration.

References

1. Hoffman and Hoschile, *Ber*, *48*, 20 (1915).
2. Biltz, Z., *anorg. u. allgem. Chem.*, *127*, 169 (1923)
3. Wells, *Am. Chem. Jour.*, *26*, 268, (1901).
4. Whitney and Davidson, *J. Am. Chem. Soc.*, *69*, 2076 (1947)
5. Kanning, *Quantitative Analysis*, 232 (1938).
6. *Radioisotopes*, Catalog and Price List #2, September 1947, U. S. Atomic Energy Commission, Oak Ridge, Tennessee.
7. Treadwell and Hall, *Analytical Chemistry*, p. 235, Vol. II, 7th Ed.
8. Fowler, W. A., *Nuclear Physics Notes*, Calif. Inst. Tech.
9. *Nuclei Formed in Fission*, J. Am. Chem. Soc. *68*, 2411 (1946).
10. Seaborg, G. T., *Revs. Modern Phys.* , *16*, 1 (1944).

Spectra of Sn^{II}, Sn^{IV}, and Mixtures thereof in 9.5 N HCl

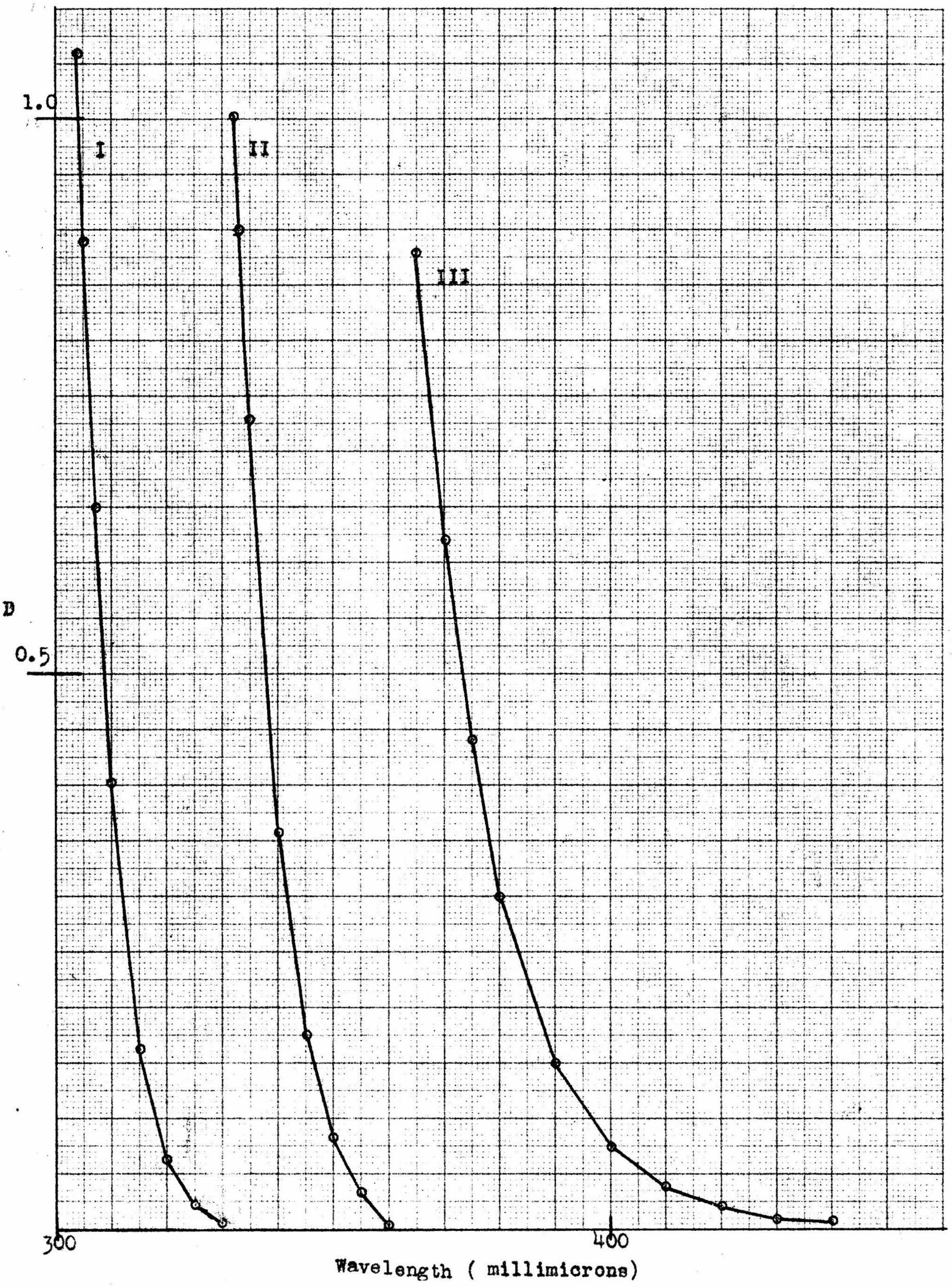


Figure I

Sn^{IV} Spectrum at Several HCl Concentrations

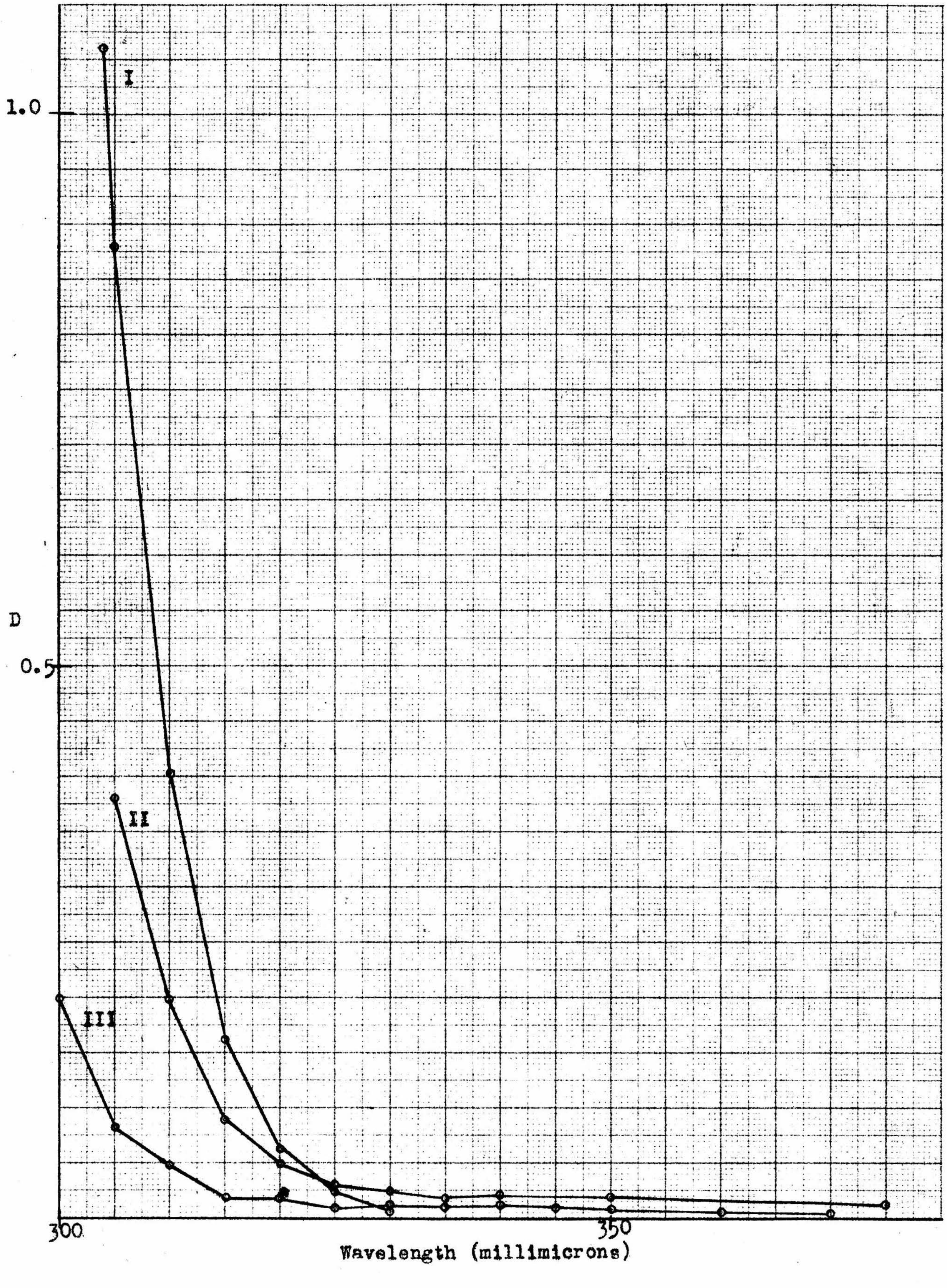


Figure II

Sn^{IV} Absorption at Several Wavelengths

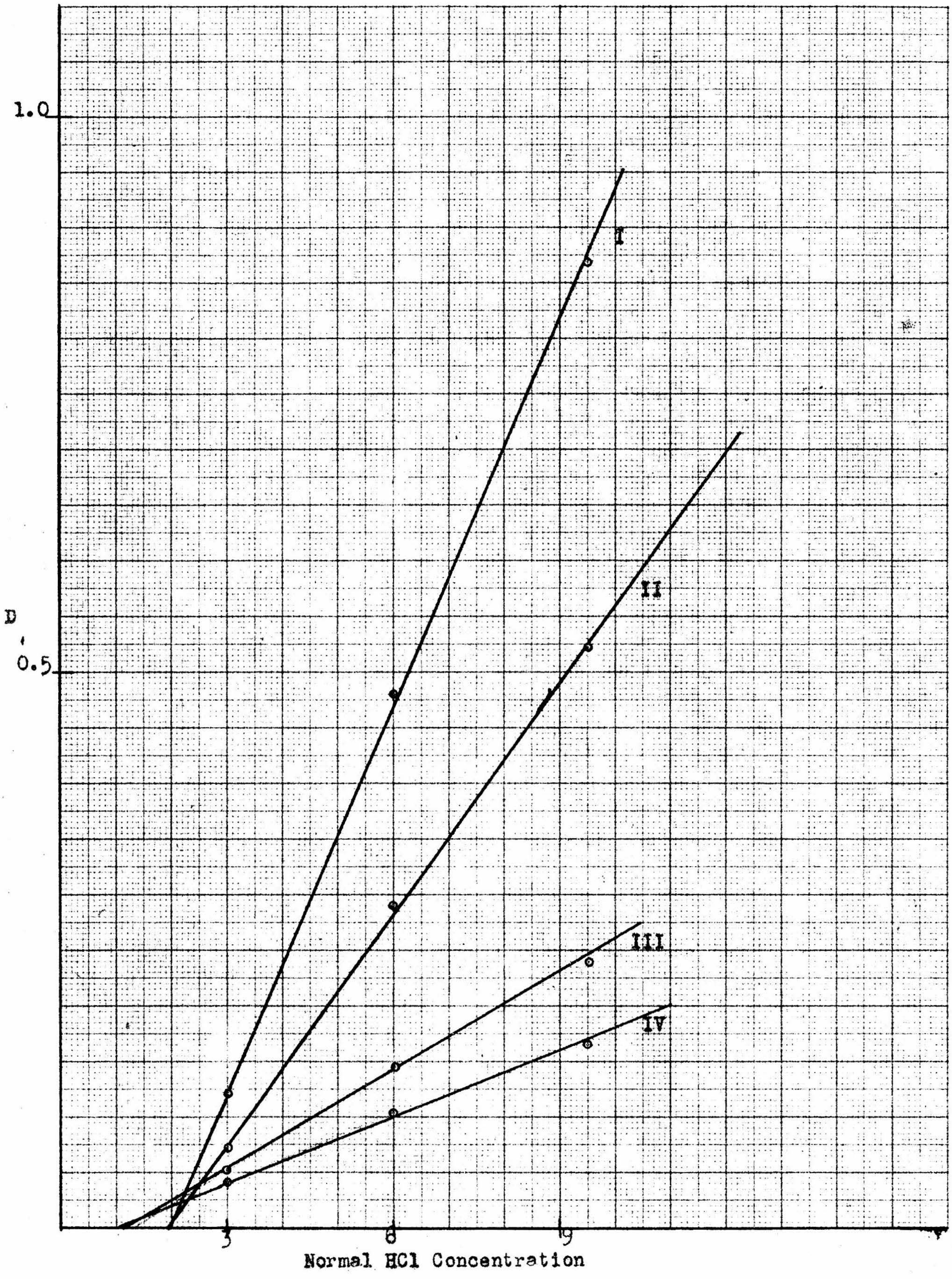


Figure III

Sn$^{\overline{IV}}$ in 9.5N HCl

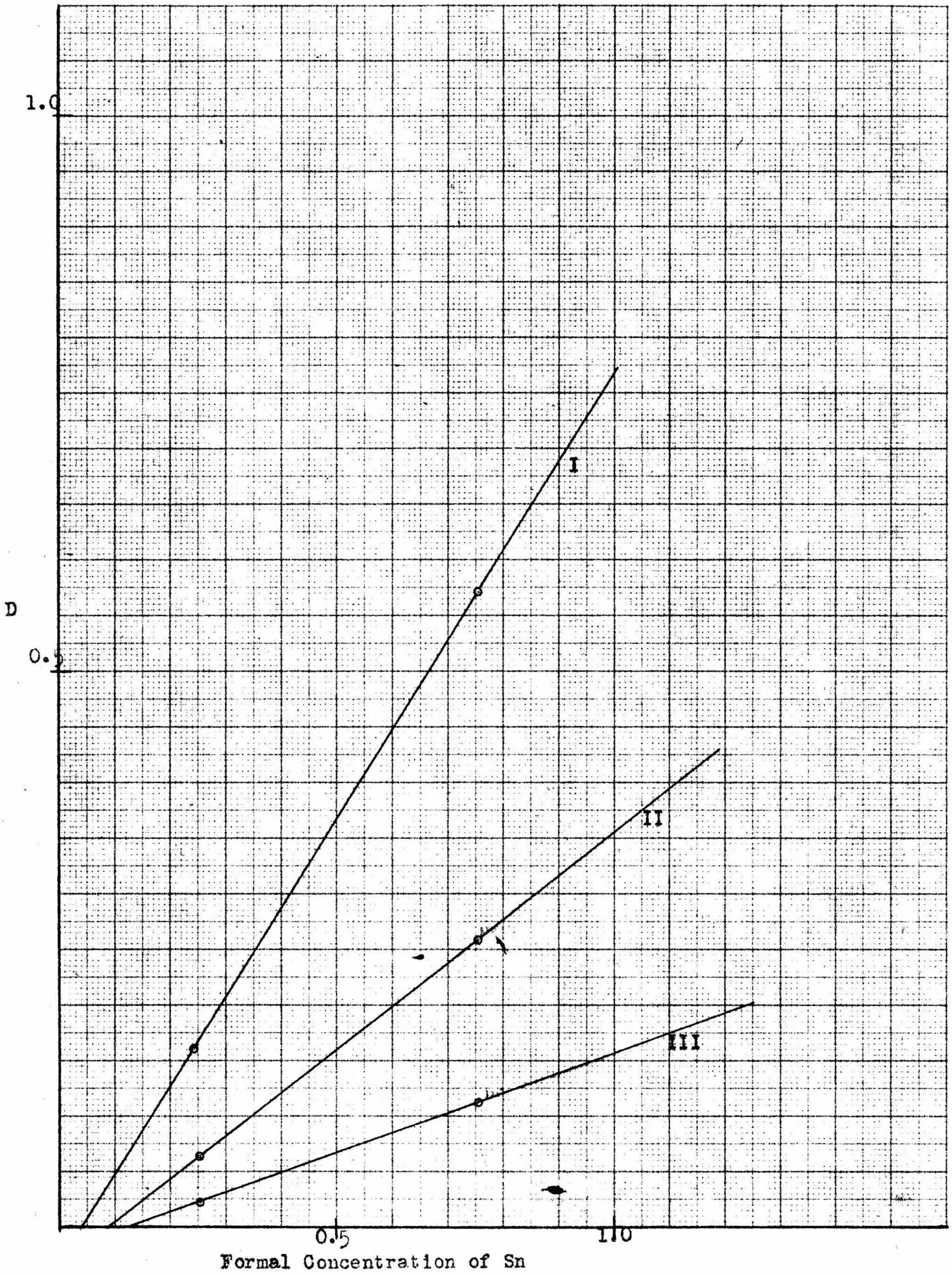


Figure IV

Sn^{IV} in 6N HCl

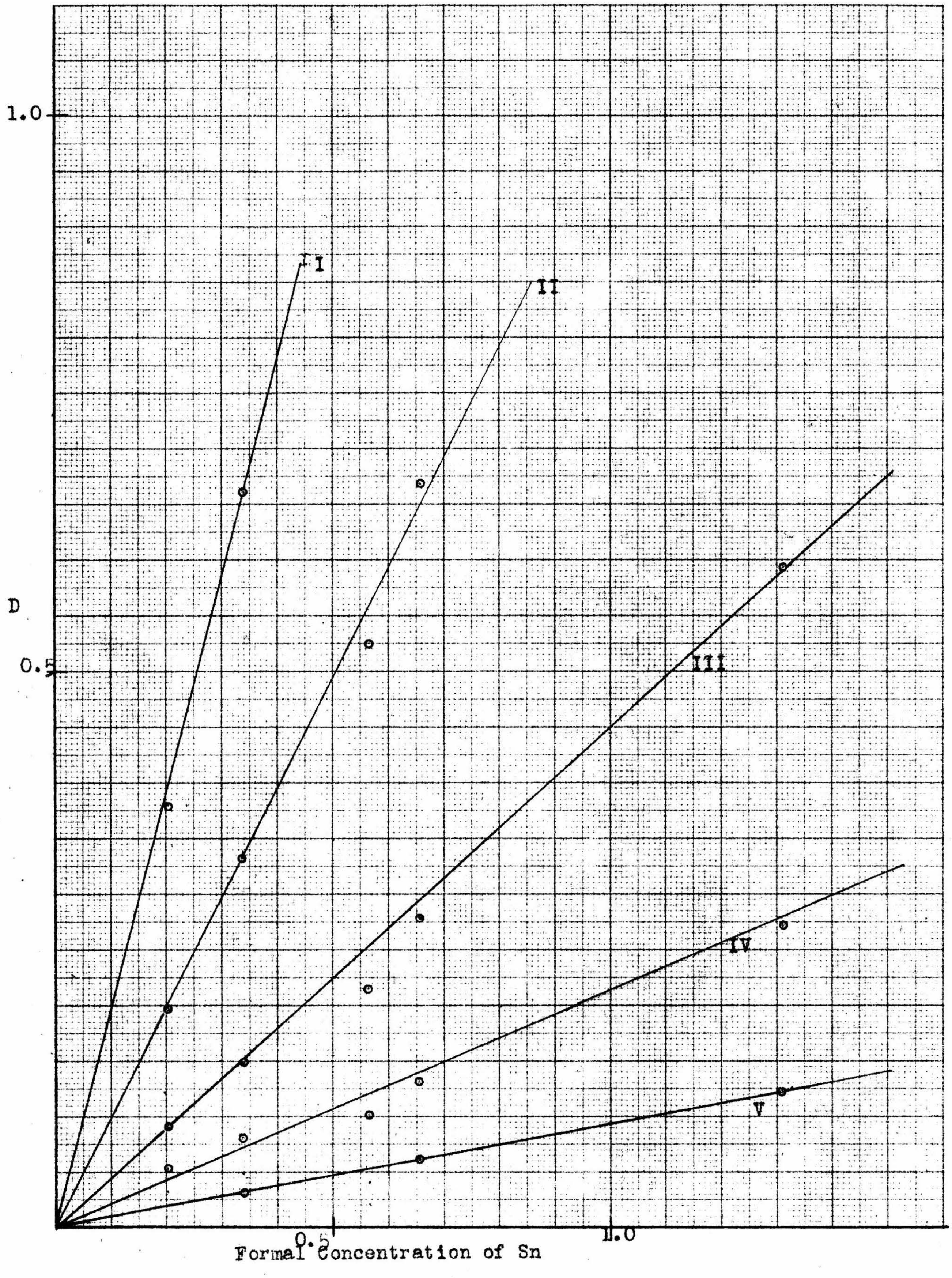
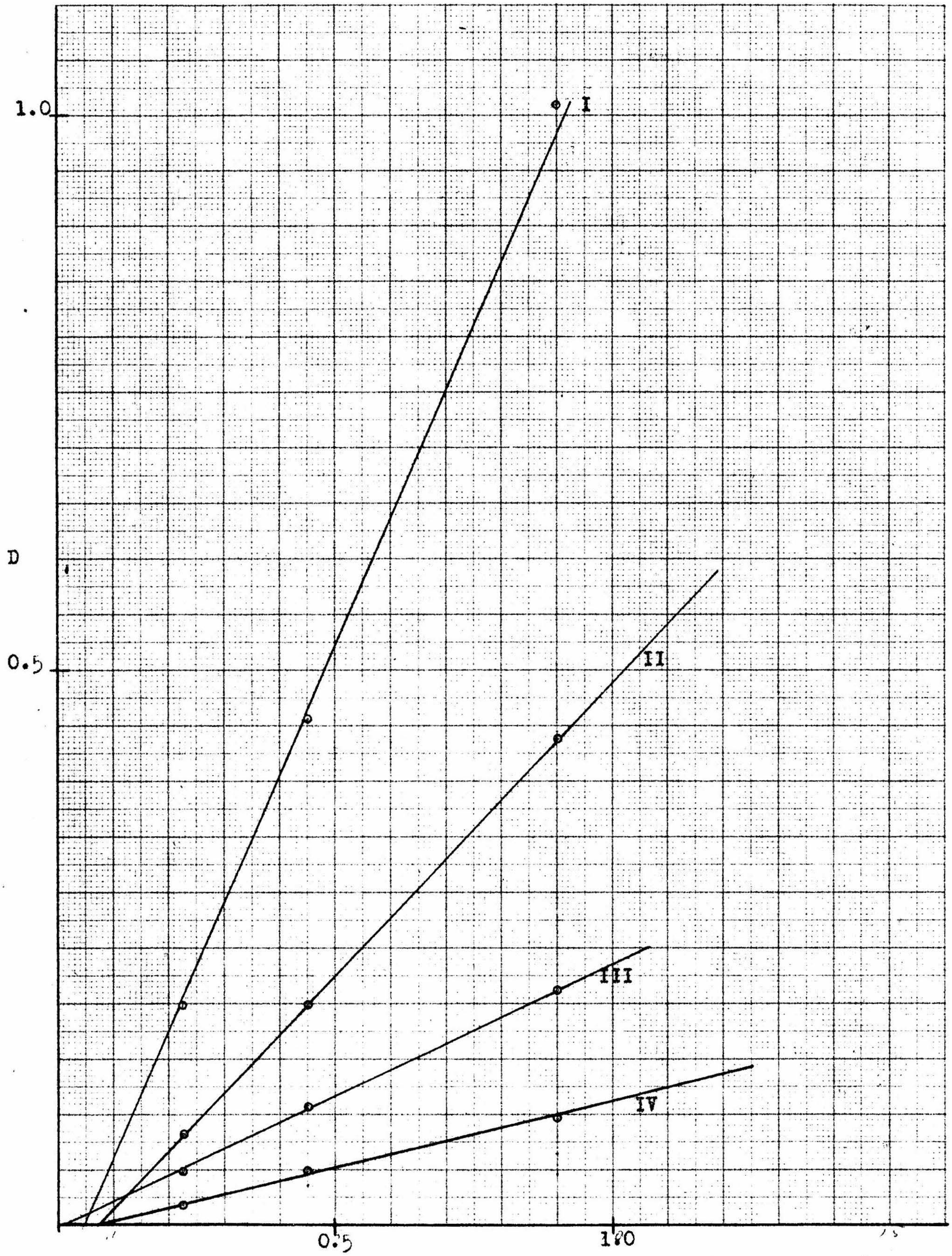


Figure V

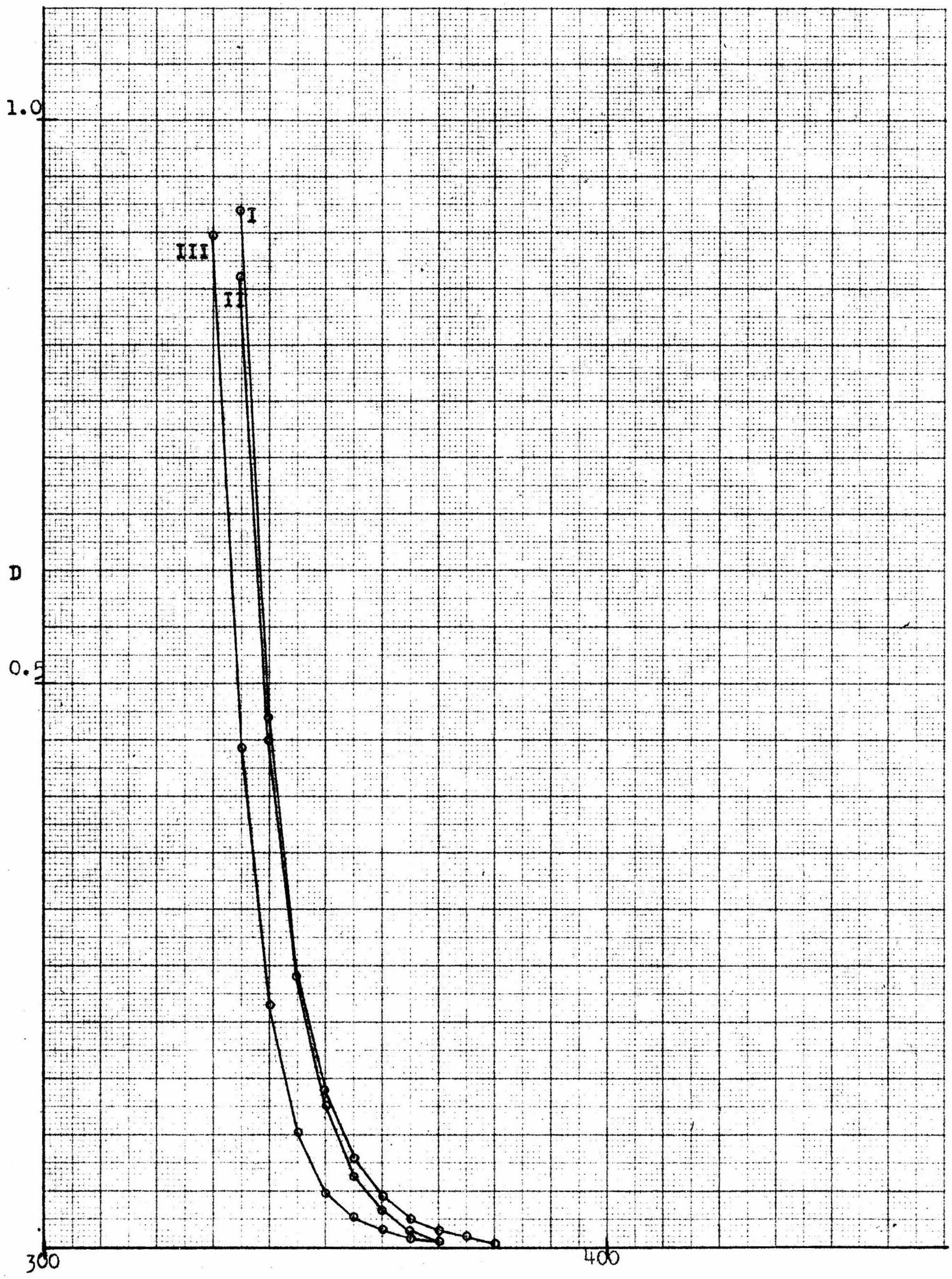
$Sn^{\overline{IV}}$ in 3 N HCl



Formal Concentration of Sn

Figure VI

Sn^{II} Spectra at Several HCl Concentrations



Wavelength (millimicrons)

Figure VII

Sn^{II} in 9.5 N HCl

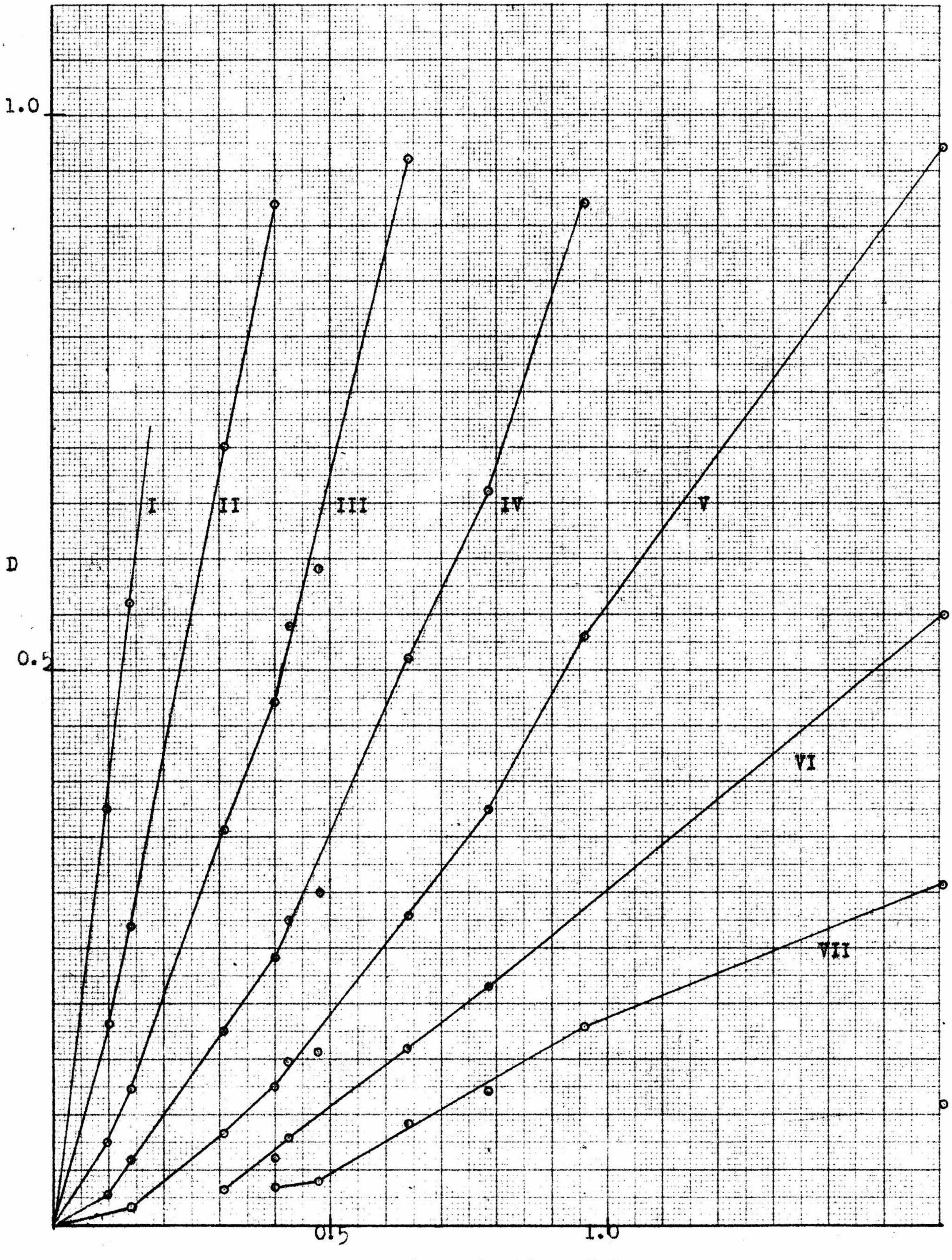
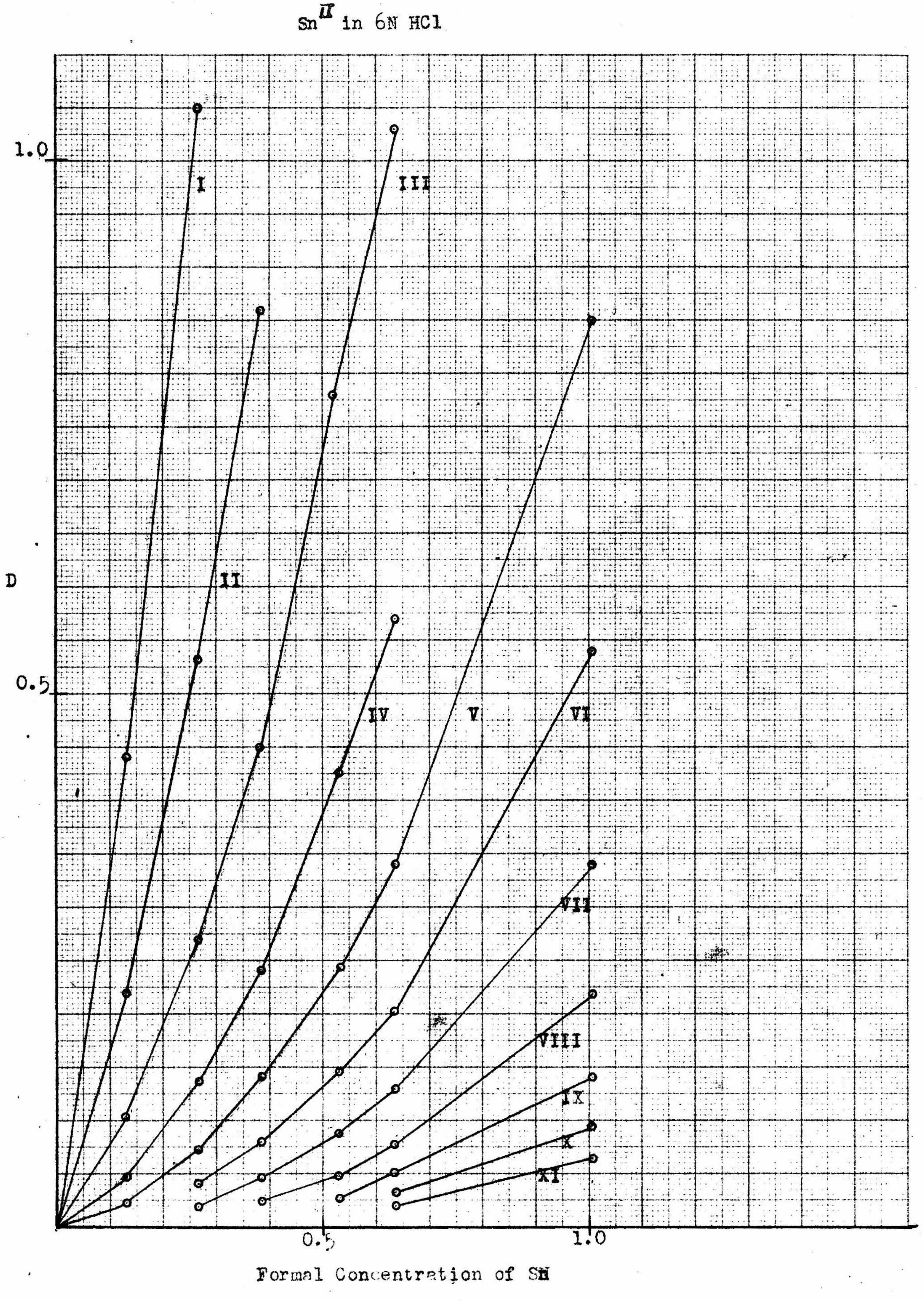


Figure VIII



Sn^{II} in 6N HCl
1.0
0.5
D
I
II
III
IV
V
VI
VII
VIII
IX
X
XI
0.5
1.0
Formal Concentration of SH

Figure IX

Sn^{II} in 3N HCl

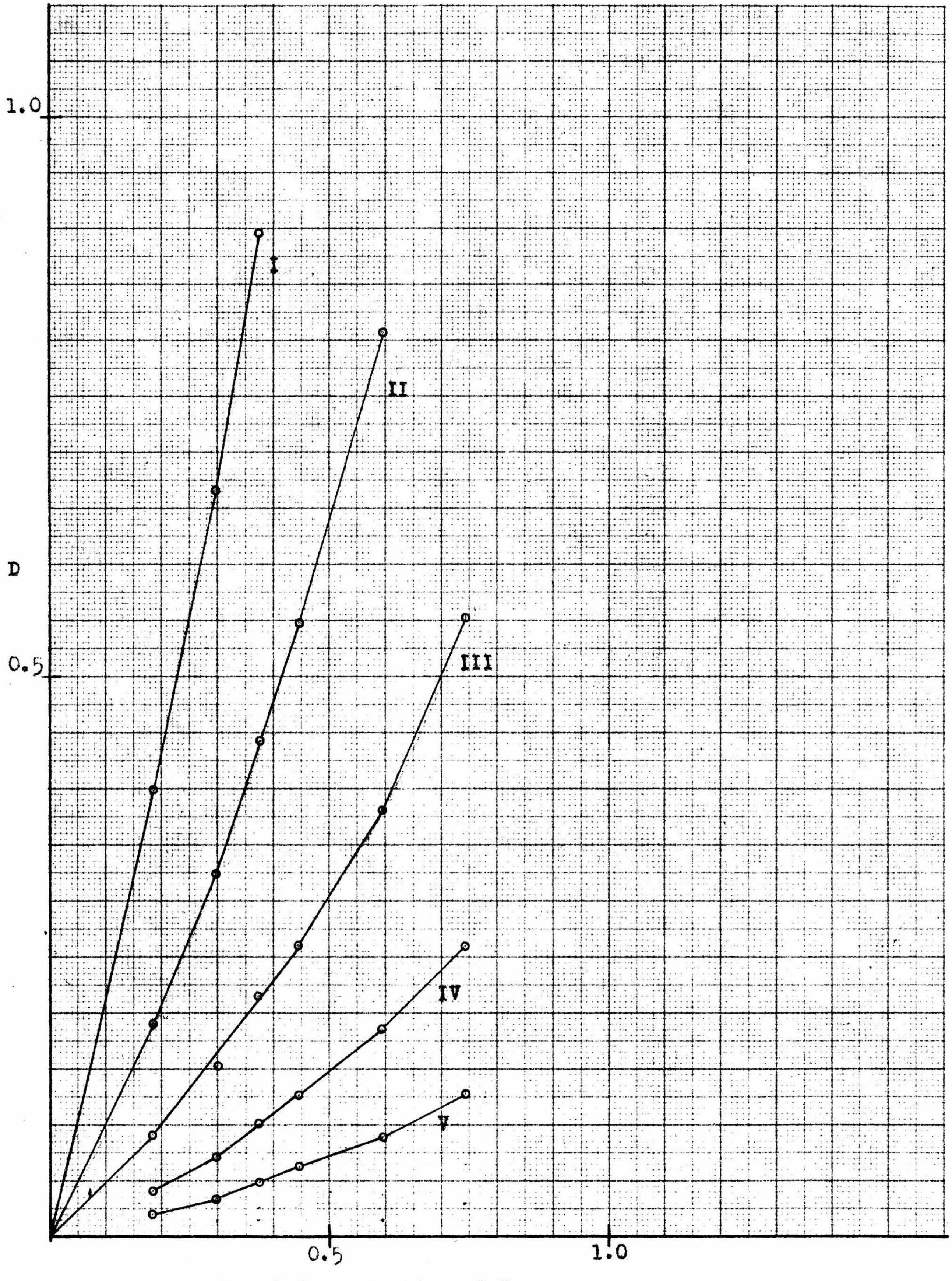


Figure X

Interaction Absorption in 9.5 N HCl

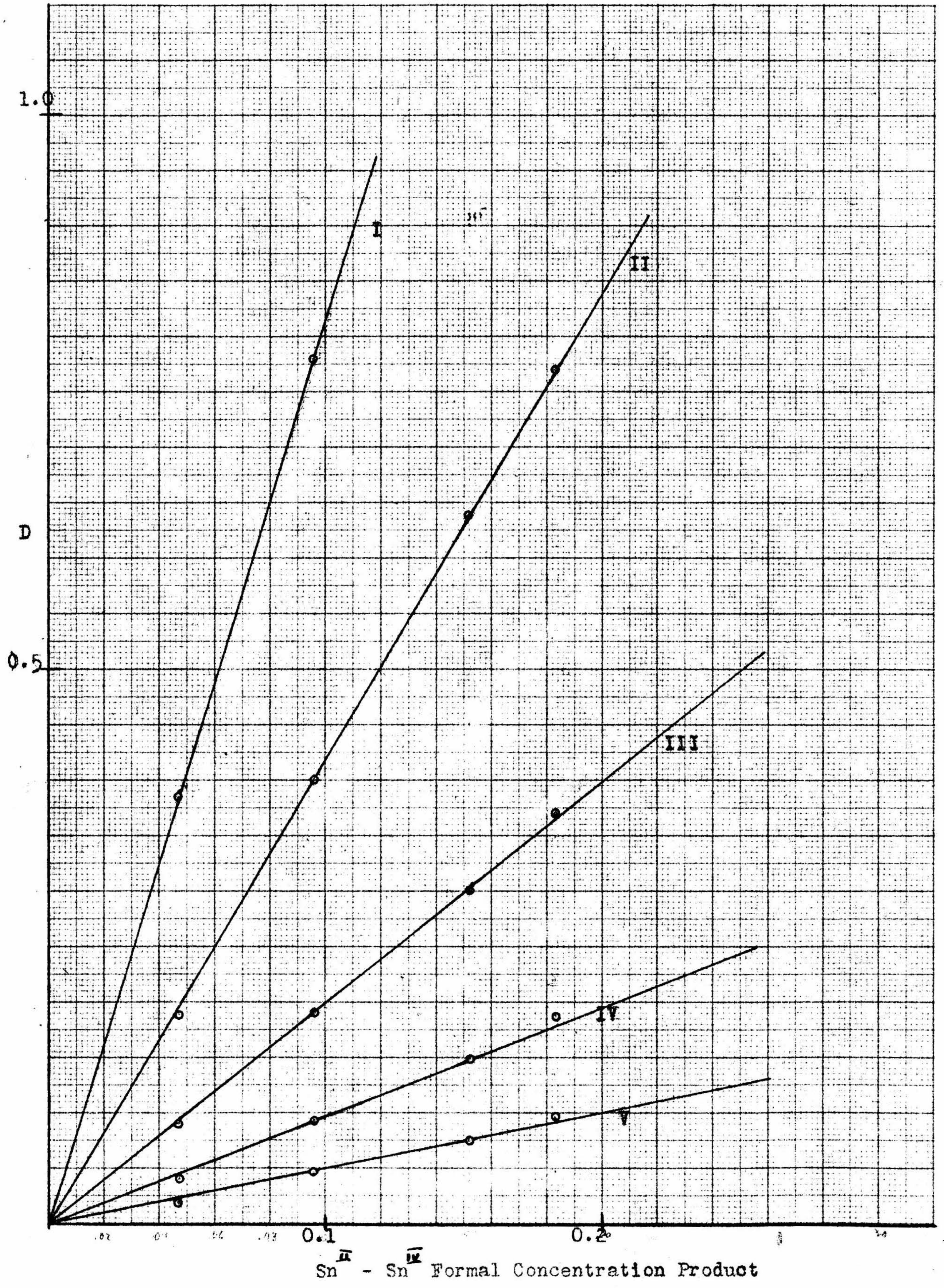


Figure XI

Interaction Absorption in 6 N HCl

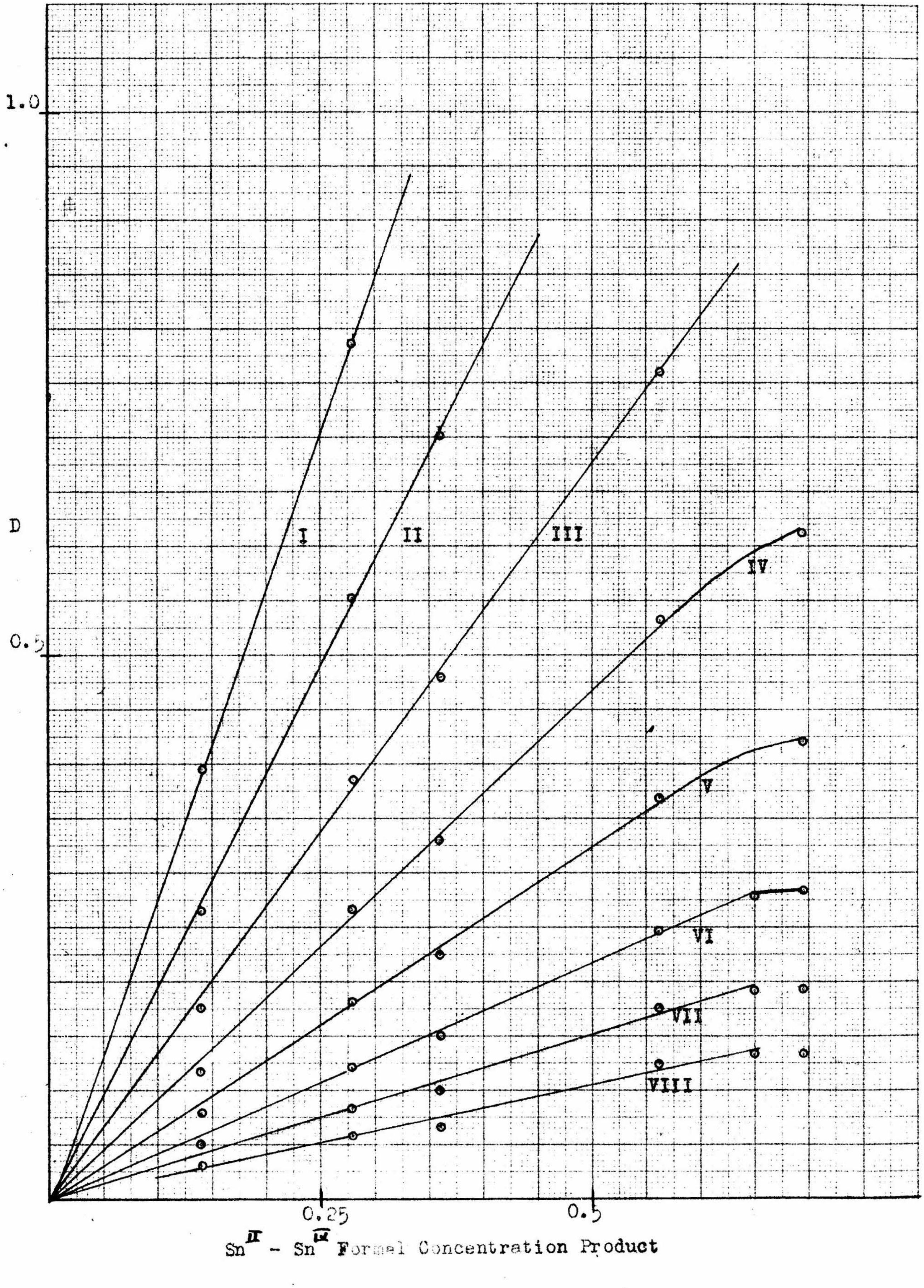


Figure XII

Interaction Absorption in 3 N HCl

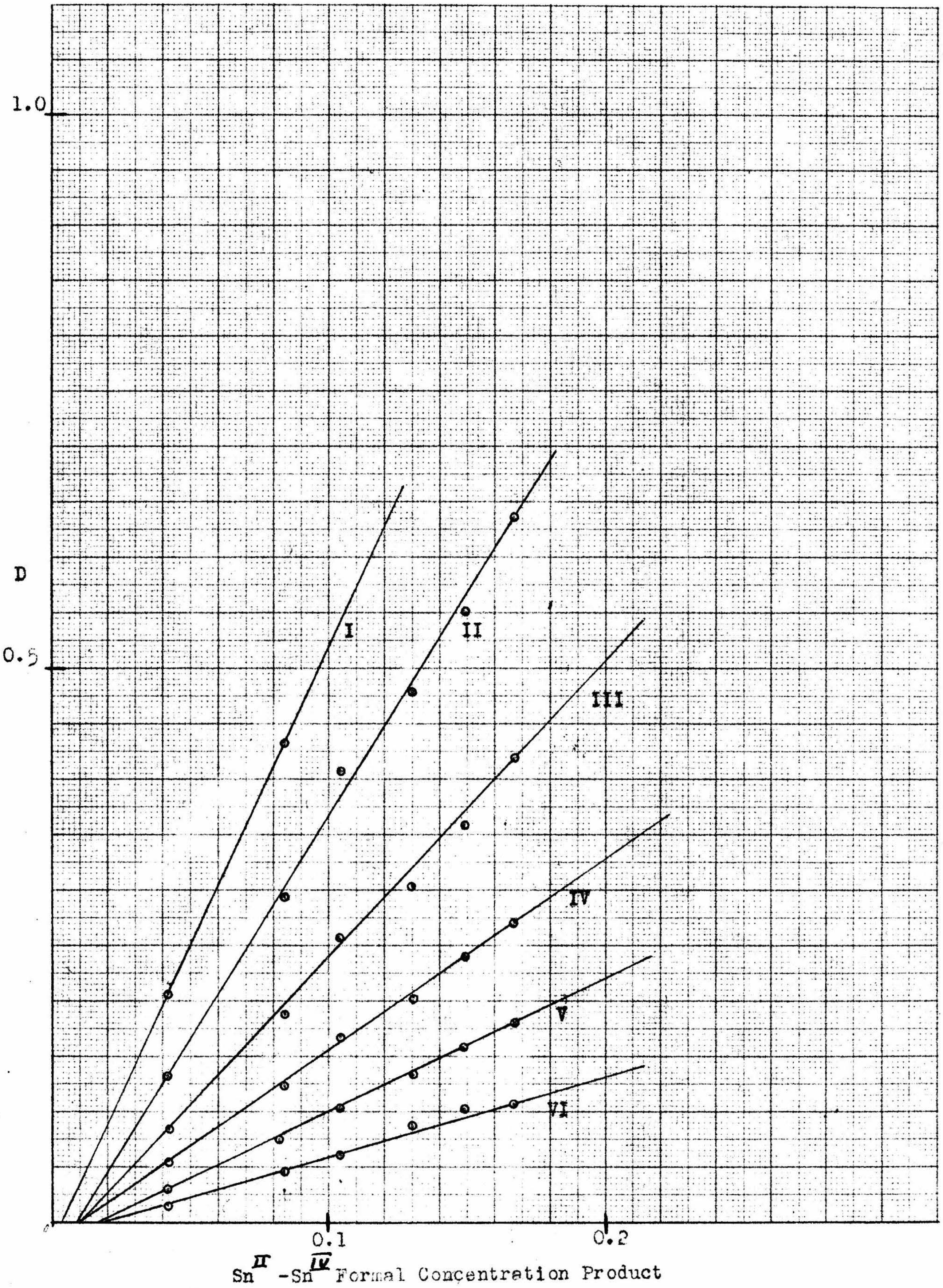


Figure XIII

Interaction Absorption at Several Wavelengths

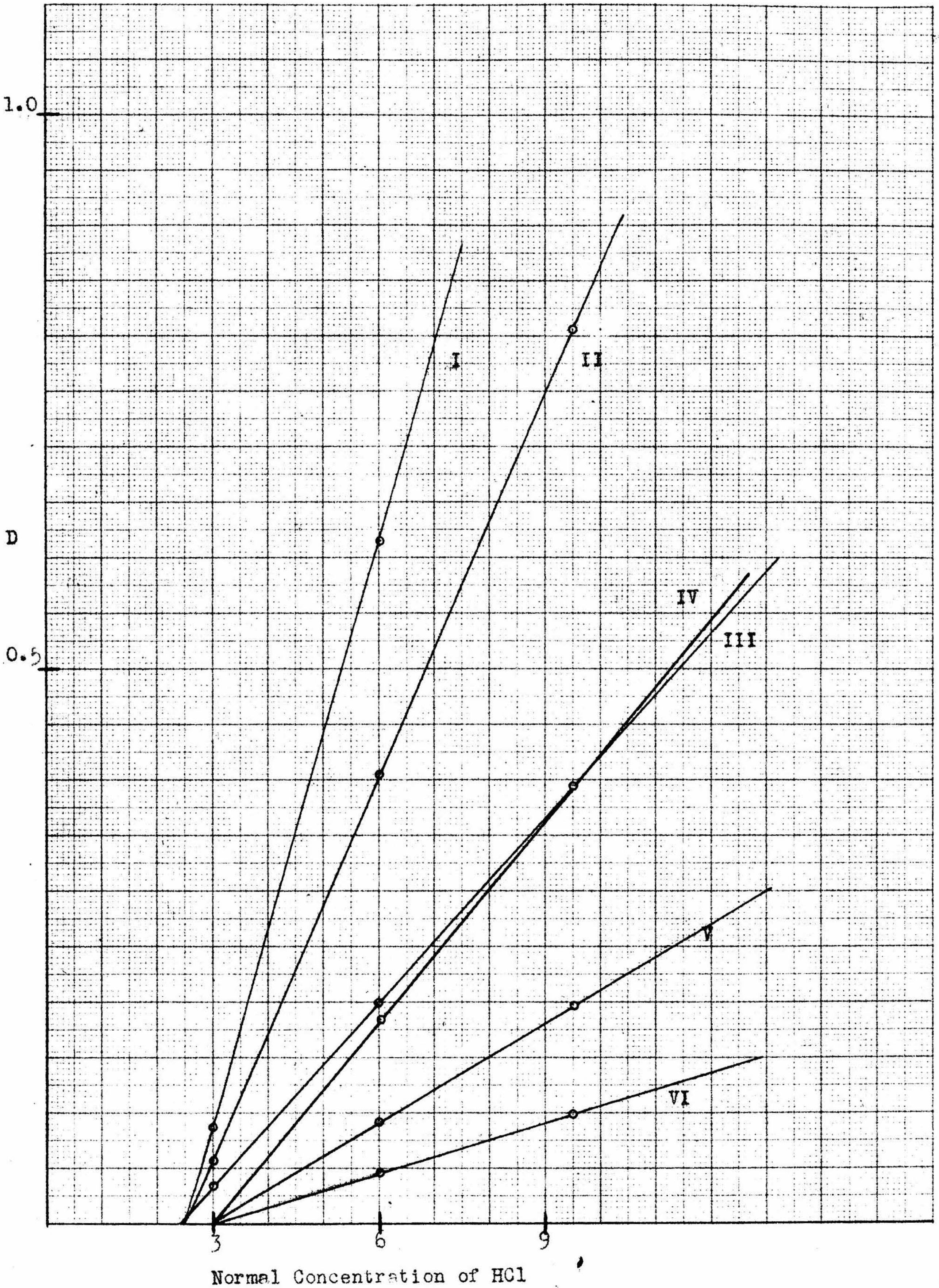


Figure XIV

Spectra of Sb^{III} and Sb^{V} in Alkaline Solution

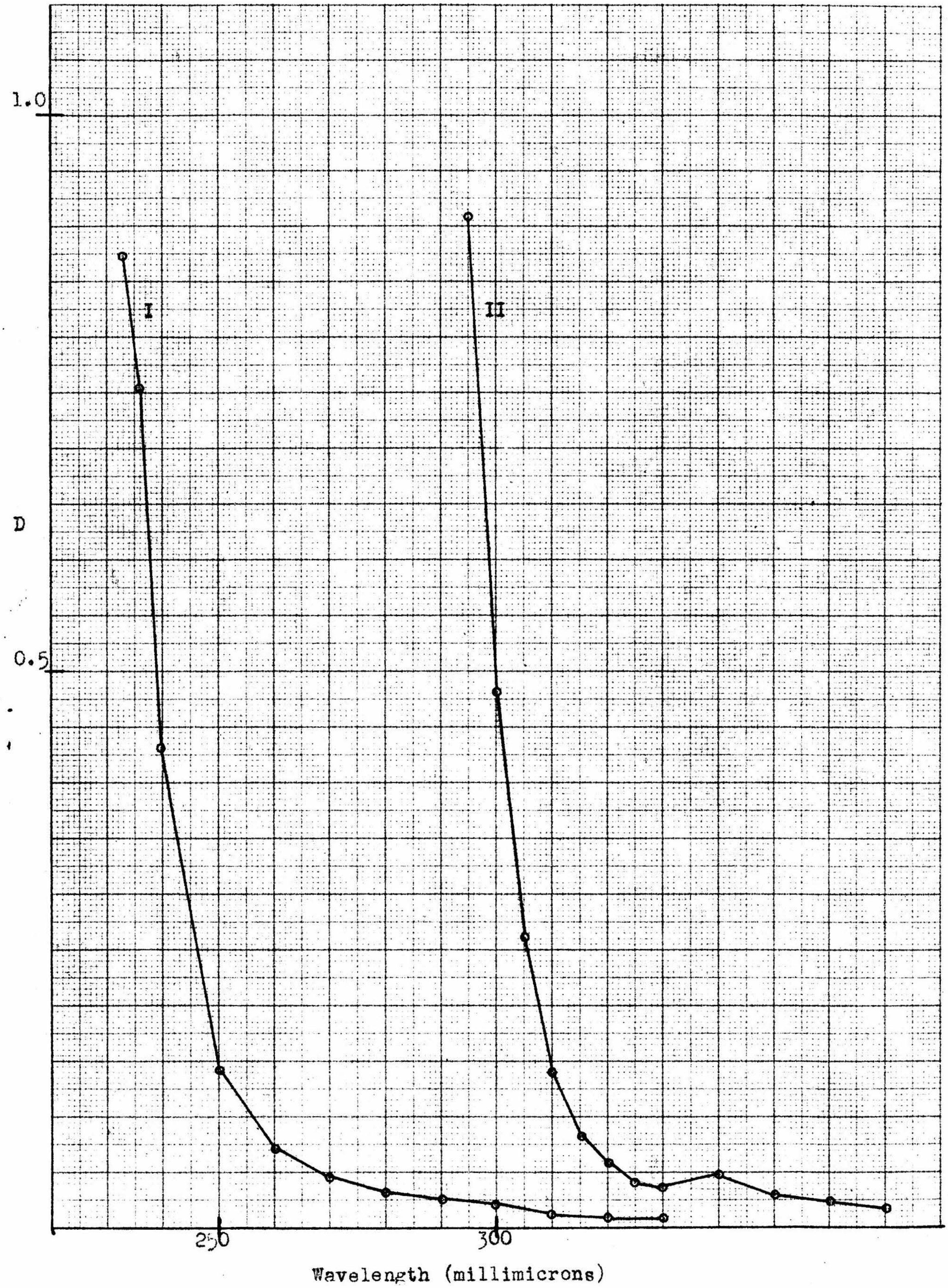


Figure XV

Spectra of Cu^{I}, Cu^{II}, and Mixtures thereof in 6N HCl

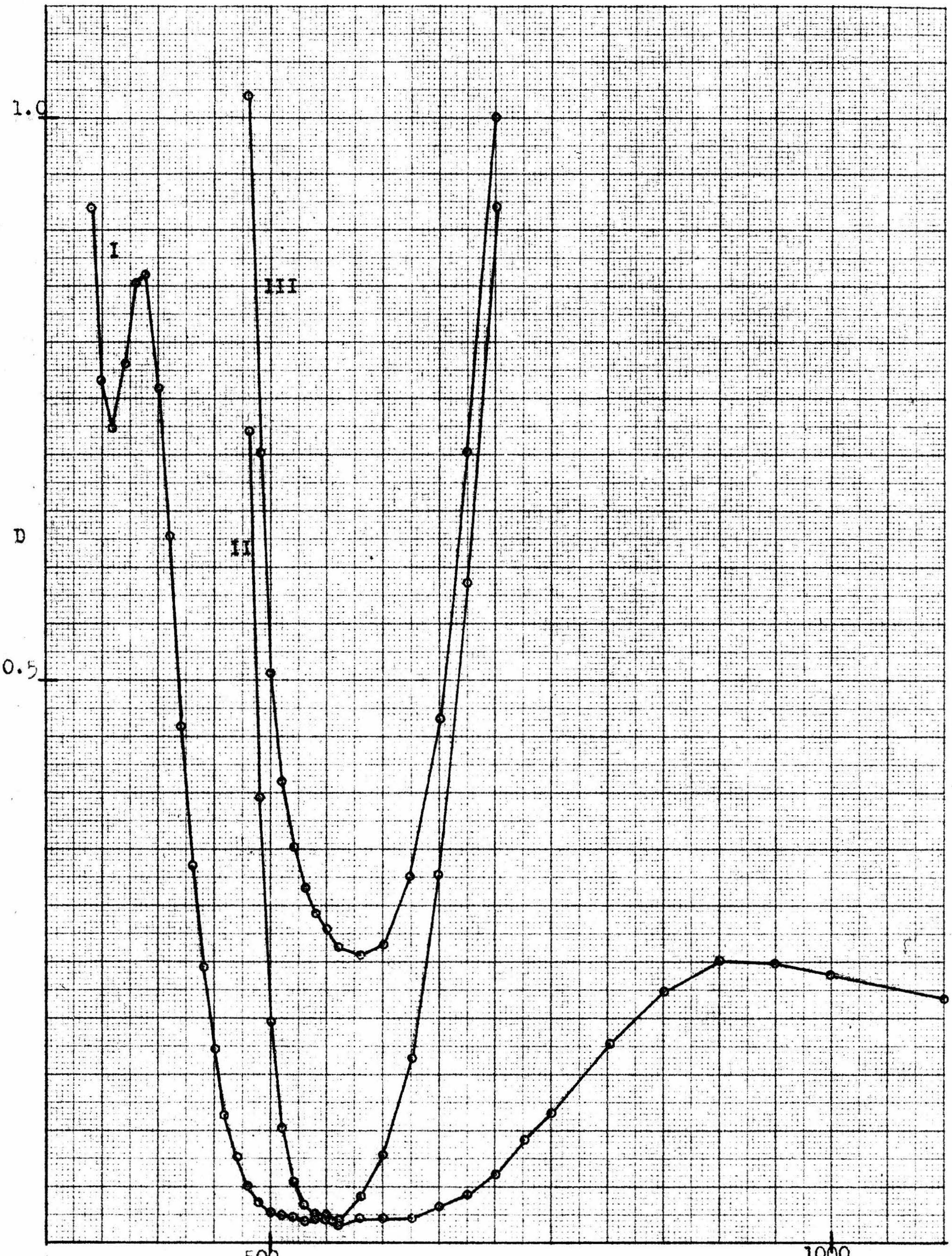


Figure XVI

Al Absorption Curve of Radiation from Sn Separated from Sample

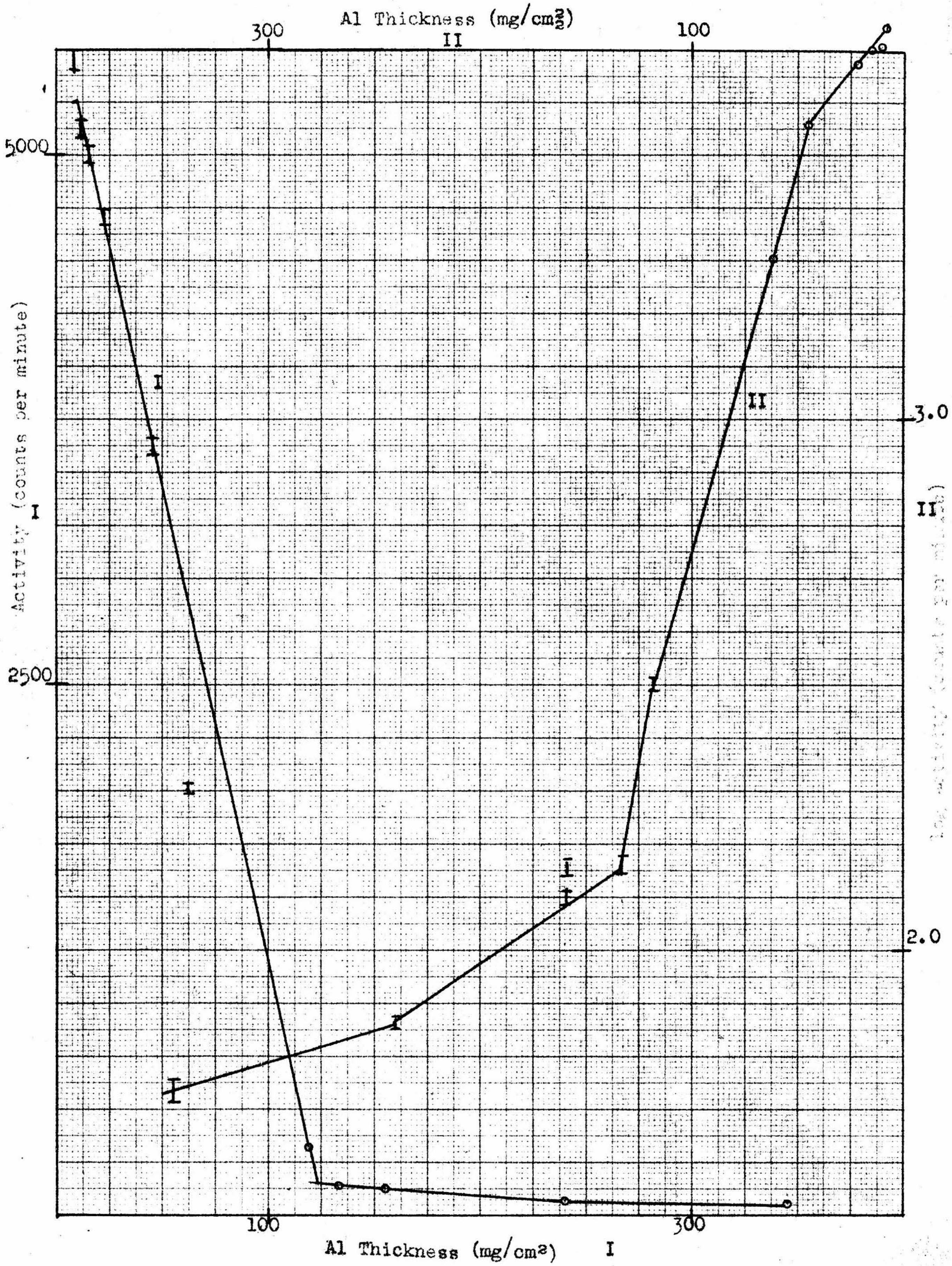


Figure XVII

Al Absprption Curve of Radiation from Sb Separated from Sample

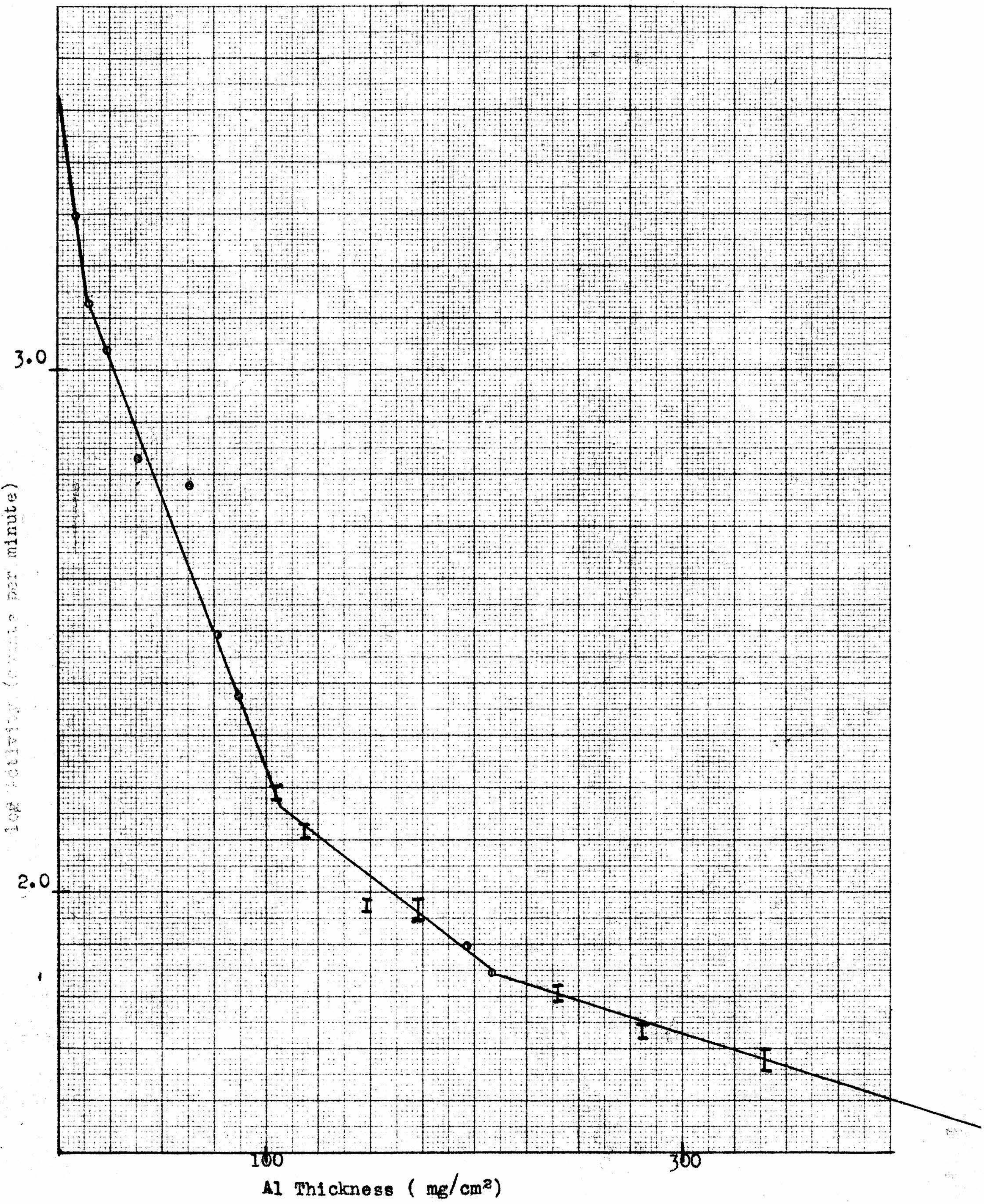


Figure XVIII