I. THE IODOMETRIC DETERMINATION OF ZINC

II. INVESTIGATIONS IN THE CHEMISTRY OF RHENIUM

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Eugene K. Maun

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Abstract

Part I describes a study of the iodometric determination of zinc. The equilibrium of the ferricyanide-ferrocyanide and iodide-iodine couples is shifted far to the right by zinc ion, which precipitates ferrocyanide and hence causes iodine liberation. Conditions based on this principle were developed for a rapid, accurate titration of zinc.

The results of a series of investigations of the reactions of oxidation states of rhenium in aqueous solution are presented in Part II. These reactions were studied by spectrophotometric and analytical experiments for the states Re^{VII}, Re^{V}, Re^{IV}, Re^{I}, and Re^{-I}.

Re^{V} was formed rapidly in a light green solution by addition of 1 or 2 equivalents of stannous chloride to solutions of perrhenic acid, $HReO_4$, in 4 $\underline{F}$ hydrochloric acid; this oxidation state has been previously reported. Similarly, yellow-brown Re^{IV} was verified as the product with further addition of stannous chloride. Brown Re^{IV} prepared from hydrochloric acid with rhenium dioxide had reactivity similar to the stannous chloride preparations, but yellow-green $Re^{IV}Cl_6^{=}$ was very resistant against a wide variety of oxidizing agents.

It was confirmed that Re^{-I} was formed by treatment of dilute solutions of perrhenic acid, in hydrochloric acid, by amalgamated zinc. Oxidation of Re^{-I} by $HReO_4$ or O_2 formed first brown Re^{+I} and then yellow Re^{IV}. Titration of Re^{-I} with Cu^{II} gave Re^{+I} and copper metal.

PART I: THE IODOMETRIC DETERMINATION OF ZINC

PART II. INVESTIGATIONS IN THE CHEMISTRY OF RHENIUM

Part I: The Iodometric Determination of Zinc

I. Introduction

In the course of an investigation of the zinc ferricyanides, the need arose for a method, preferably volumetric, for the determination of zinc. As a result of considerable experience with various modifications of the conventional titration with ferrocyanide, the method first proposed by Lang (1, 2) and subsequently investigated by various others (3, 4, 5) was tried. This method involves the addition of an excess of ferricyanide and iodide to the zinc solution, whereupon a combination of precipitation and oxidation-reduction reactions take place which can be expressed by the following overall equation:

$$3\ Zn^{++} + 2\ K^{+} + 2\ Fe(CN)_6^{\equiv} + 3\ I^{-} = K_2Zn_3(Fe(CN)_6)_2(s) + I_3^{-}. \quad (1)$$

The iodine is titrated with thiosulfate to the conventional starch-iodine end-point. The advantages of this end-point over the various end-point methods used in the direct titration of zinc with ferrocyanide were obvious, however certain features of the iodometric method were found to be inconvenient or troublesome. Thus, the necessity for addition of the ferricyanide in small portions, followed by titration with thiosulfate after each addition, made the titration tedious and time consuming. Also it was found that unless the excess of ferricyanide was carefully controlled there was a return of the end-point because of oxidation of iodide by the excess of ferricyanide. Finally, previous workers had found necessary an empirical factor of considerable magnitude, equation (1) not being stoichiometric.

Because of these facts there seemed justification for undertaking an investigation of the various factors and conditions involved in the method. The results of this study and a modified procedure are given below.

II. Discussion of the Method and of Previous Work

The overall equation given above (Equation 1) represents a combination of the two following reactions:

$$2\ \mathrm{Fe(CN)}_6^{---} + 3\ \mathrm{I}^- = 2\ \mathrm{Fe(CN)}_6^{----} + \mathrm{I}_3^- \qquad (2)$$

and

$$2\ \mathrm{Fe(CN)}_6^{----} + 3\ \mathrm{Zn}^{++} + 2\ \mathrm{K}^+ = \mathrm{K}_2\mathrm{Zn}_3(\mathrm{Fe(CN)}_6)_2\ (s). \qquad (3)$$

An obvious requirement of the method is that Reaction 2 shall proceed from left to right only when the ferrocyanide concentration is kept at an exceedingly small value by precipitation of the potassium zinc ferrocyanide. That this requirement has not been met satisfactorily in the previous methods is shown by a pronounced tendency for a return of the starch-iodine color after completion of the titration in spite of the expedient of successive additions of ferricyanide in order to keep its concentration at a low value.

The value of the formal potential for the half-cell reaction

$$\mathrm{Fe(CN)}_6^{----} = \mathrm{Fe(CN)}_6^{---} + e^- \qquad (4)$$

has been found to be approximately -0.71 v. in 1 formal sulfuric, perchloric, or hydrochloric acids; -0.56 in 0.1 formal and -0.48 in 0.01 formal hydrochloric; and -0.46 v. in 0.01 formal sodium hydroxide (6, 7). These data indicate that pH control would play an important part in the equilibrium established in solutions containing ferricyanide and iodide. In addition, a rate effect is known to be involved, it having been established that the rate of Reaction 2 is first order with respect to ferricyanide concentration and second order with respect to iodide concentration (8, 9, 10, 11). As a result of these considerations studies have been made of the effect upon the volumetric method of dilution, of the iodide and ferricyanide concentrations, of the pH of the solution, and of the time elapsing during and after the titration.

As a result of his first investigation, in which the titrations were made in essentially neutral solutions, Lang (1) reported reproducible values which were 1.65% low. This deviation was attributed to the formation of a 6.6% solid solution of zinc ferrocyanide in potassium zinc ferrocyanide. That zinc ferrocyanide is formed during the precipitation has also been confirmed by de Koninck and Prost (12, 1) and by Saito (13, 14). In subsequent titrations, made in sulfuric acid solutions, Lang (2) found values 1.60% low. Aster (3), Hibbard (5), and Casto and Boyle (4) have used this value as the basis for an empirical correction factor. In this study no conditions have been found under which the necessity for such a correction factor is eliminated, although as will be seen later, its value is somewhat dependent upon the conditions of the titration.

III. Experimental. Reagents and Solutions

Where not otherwise specified, reagent grade chemicals were used. Approximately 0.1 formal solutions of sodium thiosulfate containing 0.01% sodium carbonate were prepared, boiled distilled water being used, and were standardized against Bureau of Standards potassium dichromate.

Approximately 0.1 formal solutions of potassium ferricyanide were prepared by dissolving the solid in distilled water at room temperature. These solutions were stored in dark bottles and kept out of the light when not in use.

Potassium iodide free from iodate was used. Saturated solutions of potassium hydrogen phthalate, approximately 0.45 formal and with a pH of 3.9, were prepared either by heating an excess of the solid in distilled water, then cooling and filtering, or by stirring an excess of the reagent with distilled water and allowing the mixture to stand several hours. This reagent gave identical results with material prepared by heating phthalic anhydride with KOH and bringing this mixture to the same pH and formality.

Most of the standard solutions of zinc were prepared by dissolving weighed amounts of shavings of Bureau of Standards "freezing point" zinc in excess HCl or HNO_3, and boiling to destroy nitrite in the case of HNO_3. One solution was prepared by dissolving reagent grade $ZnSO_4 \cdot 7\ H_2O$ in distilled water, then analyzing for zinc by precipitation as ZnS and ignition to $ZnSO_4$ according to the procedure of Jeffreys and Swift (15). Another solution was made from zinc oxide previously heated to dull redness for several hours in the electric oven, weighed, and dissolved in an excess of 6 F HCl. Additional solutions of approximately known zinc concentration were made from the hydrated zinc sulfate or from zinc oxide, and the zinc content determined by Lang's procedure or the modification of it developed in this work; these solutions were used to determine the relative effect caused by various changes of conditions.

IV. Recommended Procedure

As a result of the numerous experiments which are summarized in the Tables below, the following procedure was finally developed, applicable to 100-250 mg. quantities of zinc (solutions 0.05 to 0.15 F):

> Pipet 25.00 ml. of the zinc solution into a 500 ml. conical flask, and neutralize with NH_4OH to incipient precipitation of zinc hydroxide (the pH should be between 4 and 6). Wash down the walls of the flask with 100-150 ml. of distilled water, and add a freshly prepared solution of 3 g. of potassium iodide in 50 ml. of distilled water. Add twenty-five milliliters of saturated (0.45 F) potassium hydrogen phthalate solution, followed by 6 ml. of 0.5 F sulfuric acid. Add 30 to 35 ml. of 0.1 F potassium ferricyanide, swirl the solution, cover the flask with a watch glass, and place it in the dark for 5 minutes. Titrate with 0.1 F thiosulfate, swirling the contents of the flask, till the iodine color is indistinct (approximately 2 ml. before the end-point), and the yellow ferricyanide color predominates. Add five milliliters of 0.4% starch solution and titrate slowly to the end-point, a change from a brownish-yellow solution to a clear bright yellow solution. If unfamiliar with the titration, prepare a comparison solution by dissolving $\frac{1}{2}$-1 g. of $ZnSO_4 \cdot 7H_2O$ in 25

ml. of distilled water, and treating this solution by the above procedure, except that an excess of 0.02-0.5 ml. of thiosulfate should be added.

Multiply the amount of zinc calculated on the basis of Equation 1 by the factor 1.019; that is, one liter of one-tenth formal thiosulfate solution corresponds to 10.00 grams of zinc.

V. Explanation of Tables and Data

Where not otherwise stated the recommended procedure was used in obtaining the data. The pH measurements were made with a Beckman pH meter after completion of the titration; pH values in brackets, as (3.0), were estimated from previous measurements on the same buffer system. Where the concentration of ferricyanide is reported this refers to the ferricyanide after Reaction (1) has occurred but before titration of the iodine--hence in most cases at a volume of 250 ml.

In the tables the following abbreviations or symbols are used: "% error" designates percentage deviation from a calculated value based on the assumption that Reaction (1) is stoichiometric; an error of -1.6% represents results in agreement with the correction factor mentioned above. "V_5 $Na_2S_2O_3$" indicates the volume of 0.1 F thiosulfate required to titrate the iodine present five minutes after reaching the end-point. "KI, formal concentration, before titration," represents the concentration of iodide calculated on the assumption that Reaction (1) has proceeded quantitatively with formation of tri-iodide; this concentration remains roughly constant during the titration, since the dilution factor is roughly equivalent to that caused by increase in iodide by reduction of the tri-iodide. "Unstable" means that recurrence of starch-iodine color occurred within a few minutes after reaching the end-point; "KHPhth" represents potassium hydrogen phthalate.

VI. The Effect of Dilution

The effect of the volume of the solution during the time the reactions of Equation (1) are taking place is shown in Table I.

Comparison of Expt. 1 with 2, and Expt. 3 with 4, indicates that when the volume is relatively small, iodine tends to be formed after the end-point because of Reaction (2). With small volumes, and moderate to large amounts of reactants such as ferricyanide, an error of less than -1.6% is obtained; this is attributed to the compensatory effect of Reaction (2), as shown by Expts. 9-13. With small volumes or at lower pH values, 1.5-2.5, high results are obtained if the amount of zinc is small and leaves a large

Table I

The Effect of Dilution

The recommended procedure was used with the modifications noted, except that a sulfate buffer instead of phthalate was used, and the solutions were not allowed to stand before beginning the titration.

In Expts. 1 and 2 no acid was added and the final pH was 6-7; in Expts. 3 to 7 from 3 to 4.5 millimols of HCl were added and the final pH ranged from 1.5 to 2; 20 millimols of sulfate and from 0.5 to 4.5 millimols of HCl were used in Expts. 8 to 19 resulting in pH values from 2 to 2.5. In many cases the value "% Error" is the average of several closely agreeing titrations.

Expt. No.	Volume before Titration (ml.)	Millimols Present		% Error	Remarks
		Zinc	$K_3Fe(CN)_6$		
1	25	0	3	--	I_2 evolved immediately.
2	135	0	"	--	40 millimols KI. Faint starch test.
3	125	3.757	"	-1.8	V_5 $Na_2S_2O_3$ 0.13 ml.
4	175	3.757	"	-1.6	40 millimols KI.
5	125	3.757	"	-1.6	V_5 $Na_2S_2O_3$ 0.03 ml.
6	125	5.902	4.5	-1.6	End-pt. recurred.
7	150	5.902	"	-1.6	25 millimols KI.
8	250	5.902	4.3	-1.65	
9	100	1.178	4.5	0.3	Let stand 1 min. before titration.
10	100	1.178	"	-0.8	End-point unstable.
11	125	1.178	"	-0.8	
12	150	1.178	"	-0.8	
13	140	1.178	1.5	-0.9	

Table I (cont.)

Expt. No.	Volume before Titration (ml.)	Millimols Present		% Error	Remarks
		Zinc	$K_3Fe(CN)_6$		
14	210	1.178	0.8	-1.7	
15	200	2.479	2.0	-1.7	
16	140	5.000	4.0	-1.4	
17	175	5.000	4.0	-1.6	
18	200	5.000	4.0	-1.6	
19	250	5.000	4.0	-1.6	

excess of ferricyanide. Dilution tends to overcome this effect as shown by comparisons of Expt. 1 with 2, Expt. 14 with 10-13, and Expt. 16 with 17-19. Because of these results, in most later experiments such quantities of solutions and water were used that the volume before beginning the titration of the liberated iodine was at least 200 ml., usually 250 ml.

VII. The Effect of Iodide Concentration

The results of experiments which show the effect of the iodide concentration have been summarized in Table II. As mentioned before, high acidity and high concentration of ferricyanide favor Reaction (2) causing a rapid recurrence of the end-point. For this reason, the data in Table II are arranged within each range of pH in decreasing order of concentration of ferricyanide. That high concentrations of iodide cause high values for zinc or cause instability of the end-point is shown (in the second part of the table) by Expts. 1-5 and 7. Results obtained at a lower pH are shown by Expts. 8-10. As a result of these experiments, the amount of iodide to be used has been fixed at 3 g. in a volume of 250 ml. Although this is lower than the concentration usually recommended (16), no evidence of loss of iodine was observed in these or any other experiments.

Table II

The Effect of Iodide Concentration

Amounts of Reactants Taken

Expt. No.	Millimols KI Taken	Millimols K_3 $Fe(CN)_6$ taken	Millimols Zinc Taken	Volume before Titration (ml.)
1	18	4.5	0	130
2	30	10	5.000	500
3	18	10	"	"
4	30	"	"	600
5	30	"	"	700
6	18	1.5	0	270
7	18	3	3.757	125
8	18	3	0	25
9	36	"	"	135
10	18	"	3.757	125

Table II (cont.)

The solution was titrated immediately after mixing the reagents, otherwise the recommended procedure was used with the modifications noted in the previous part of the table.

Expt. No.	Formal Concentration before Titration		pH at End-Point	% Error	$V_5 Na_2S_2O_3$
	KI	$K_3Fe(CN)_6$			
1	0.14	0.034	2.5	--	0.3
2	0.050	0.013	2	-1.1	0.16
3	0.026	0.013	"	-1.2	0.06
4	0.042	0.011	"	-1.2	0.08
5	0.036	0.0096	"	-1.2	0.06
6	0.066	0.0056	2.5	--	0.02
7	0.11	0.004	1.5	-1.8	0.13
8	0.72	0.12	7	--	0.5
9	0.29	0.022	"	--	0.02
10	0.11	0.004	6	-1.9	0.03

VIII. The Effect of Concentration of Excess Ferricyanide

The results of experiments made to test the effect of concentration of ferricyanide are given in Table III for solutions buffered by a hydrogensulfate-sulfate system. Large concentrations of excess ferricyanide are seen to cause higher values for zinc and instability of the end-point. In general, the error is of the order of that found by Lang, that is -1.6%, thus justifying his correction factor.

As is shown in Table IV, better reproducibility and less difficulty because of recurrent end-points are achieved in solutions buffered to a pH of approximately 3 by a phthalic acid-hydrogenphthalate system. Under these conditions the average error is nearer -1.85% than to that found by Lang. It seems probably that under the conditions used by Lang and others, Reaction (2) may have operated as a compensating factor, possibly because of the effect of the lower pH.

IX. The Effect of the Time of Standing Before a Titration

The experiments recorded in Table V were made for the purpose of determining the effect of allowing the reactants to stand before beginning the titration. The work of Saito (13, 14) indicates that a precipitate of more uniform

Table III

The Effect of Excess Ferricyanide in Hydrogensulfate-Sulfate Buffered Solutions

Amounts of Reactants Taken

Expt. No.	Millimols $K_3Fe(CN)_6$ Taken	Millimols Zinc Taken	Volume before Titration (ml.)
1	1	1.178	100
2	4.5	"	"
3	1.5	"	140
4	4.5	"	150
5	1.169	"	200
6	1.556	"	200
7	3.5	5.000	250
8	3.6	"	"
9	4.0	"	"
10	"	"	"
11	"	"	"
12	"	"	"
13	3.8	"	"
14	5.0	"	"
15	4.5	0	130
16	3	3.757	125
17	3	"	"

Table III (cont.)

The solution was titrated immediately after mixing the reagents; otherwise except for the modifications given in the previous part of the table, the recommended procedure was used.

Expt. No.	Formal Concentration before Titration		pH at End-Point	% Error	V_5 $Na_2S_2O_3$	Remarks
	$K_3Fe(CN)_6$	KI				
1	0.0022	0.17	2	-0.8		
2	0.037	"	"	-0.7	0.05	End-point unstable.
3	0.0051	0.12	"	-0.9		
4	0.026	0.11	"	-0.8	0.05	End-point unstable.
5	0.0020	0.085	"	-1.9		
6	0.0039	"	"	-1.8		
7	0.0007	0.052	"	-1.8		17.6 millimols chloride.
8	0.0011	"	"	-1.85		"
9	0.0027	"	"	-1.6		"
10	"	"	"	-1.6		"
11	"	"	"	-1.8		"
12	"	"	"	-1.8		"
13	0.0019	"	"	-1.8		"
14	0.0067	"	"	-1.6	0.02	"
15	0.034	0.14	2.5	--	0.3	
16	0.004	0.11	1.5	-1.8	0.13	
17	0.004	0.11	6	-1.9	0.03	

Table IV

The Effect of Excess Ferricyanide in Phthalic Acid-Hydrogenphthalate Buffered Solutions

The recommended procedure was used except that the solution was titrated immediately after mixing in Expts. 1-7; 8-17 let stand as indicated under Remarks.

Expt. No	$K_3Fe(CN)_6$, Formal Concentration before Titration	Millimols Taken		pH at End-point	% Error	Remarks
		$K_3Fe(CN)_6$	Zinc			
1	0.0051	5.0	5.595	3.07	-1.85	
2	0.0051	"	"	3.12	-1.9	$V_5Na_2S_2O_3$ 0.016 ml.
3	0.0092	6.0	"	3.19	-1.8	
4	0.0011	2.8	3.822	(3.45)	-1.75	End-point recurred in ½ min.
5	0.0018	3.0	"	(3.85)	-2.0	End-point recurred in 3 min.
6	0.0018	3.0	"	(2.9)	-1.75	
7	0.0026	3.2	"	(3.50)	-1.85	
8	0.0005	2.5	3.559	(3.0)	-1.95	Let stand in dark 5 min.
9	0.0025	3.0	"	(3.3)	-1.8	Let react 7 min.
10	0.0014	5.0	"	"	-1.75	" 5 min.
11	0.0025	3.0	"	"	-1.8	" 6 min.
12	0.0025	"	"	(3.0)	-1.9	" 5 min. $V_5Na_2S_2O_3$ 0.007 ml.

Table IV (cont.)

Expt. No.	$K_2Fe(CN)_6$, Formal Concentration before Titration	Millimols Taken		pH at End-point	% Error	Remarks
		$K_3Fe(CN)_6$	Zinc			
13	0.0025	3.0	3.559	(3.0)	-1.85	Let react in dark 5 min.
14	0.0013	2.7	"	"	-1.85	" "
15	0.0017	2.8	"	"	-1.85	" "
16	0.0045	3.5	"	"	-1.8	" "End-point recurs in 15 sec. Stable after one additional titration.
17	0.0049	3.6	"	"	-1.8	" "End-point recurs in 1 min. Stable after one additional titration.

Table V

The Effect of the Time of Standing before Titration

24.96 ml. of a 0.1426 F zinc sulfate solution were taken and treated by the standard procedure. The volume before titration was 250 ml. and 11 millimols of potassium hydrogen phthalate were present in all experiments. The pH at the end-point was approximately 3.

Expt. No.	Time in dark before titration (min.)	$K_3Fe(CN)_6$ millimols added	% Error	Stability of end-points
1	0	2.5	-1.9	Recurs.
2	0	3.0	-1.85	Recurs, $V_2\ Na_2S_2O_3$ 0.01 ml.
3	0	"	-2.0	Recurs.
4	0	"	-1.8	
5	5	"	-1.8	
6	5	"	-1.8	
7	0	3.5	-2.1	Recurs in 2 min.
8	10	"	-1.85	
9	0	5.0	-2.0	Recurs.
10	10	"	-1.8	

composition should result; also, since Reaction (1) is probably somewhat slow, there should be less tendency toward low titration values and recurrent end-points. On the other hand there would be more tendency toward high values because of Reaction (2) or because of oxidation of iodide by oxygen. Photochemical catalysis of these reactions was minimized by storage in the dark during the time of standing, and Expts. 8 and 10 show that air oxidation was successfully minimized.

The improvement when the solution is allowed to stand five minutes before titration is shown by a comparison of Expt. 9 with 10, or 7 with 8, or 3 with 5 and 6.

X. The Effect of Potassium Salts

As has been mentioned earlier, the necessity for use of a correction factor is attributed to the formation of a solid solution of potassium zinc ferrocyanide with some zinc ferrocyanide. It would be expected that the concentration of potassium ion used would influence the nature of this precipitate and hence influence the correction factor. The data in Table VI show that the amount of potassium ion present can be varied over a wide range with but little effect.

XI. The Effect of Chloride

Lang (1, 2) found low results for titrations in nearly neutral solution containing chloride, which were probably caused by complex-ion formation. The data in Table VII show that large amounts of chloride can be tolerated in the present procedure.

XII. The Effect of the pH of the Solution and of Certain Anions

An inspection of Table VIII again shows that in the sulfate-buffered solutions, with pH values around 2, the error ranges from -1.6% to -1.8%, and that in the phthalate-buffered solutions, with pH values around 3, the error is much more constant and in general ranges from -1.8% to -1.9%. In addition, recurrence of the end-point is more pronounced at the lower pH values (see Expts. 1-4 and 7). In order to facilitate inspection of the tables, the amount of zinc and of potassium ferricyanide are given in Table VIIIA while the pH and anions are in VIIIB. No specific effect of the zinc was found, and it will be shown in the next section that the amount of zinc taken is without influence on the results; no effect of the ferricyanide was found when more than 4 millimols was used. In Table VIIIB the potassium ferricyanide was at

Table VI

The Effect of Potassium Salts

Fifty milliliters of 0.1000 F zinc chloride in 0.152 F hydrochloric acid were treated with the amount of potassium sulfate shown. The recommended procedure was used except that no phthalate was added. The pH was 2.

Expt. No.	$K_3Fe(CN)_6$ Millimols added	K_2SO_4 Millimols added	% Error
1	4.0	10	-1.6
2	"	"	-1.6
3	"	"	-1.8
4	"	"	-1.8
5	"	20	-1.6
6	5.0	10	-1.6
7	"	20	-1.6
8	"	40	-1.4
9	"	40	-1.5

Table VII

The Effect of Chloride

The recommended procedure with a phthalic acid-hydrogen-phthalate buffer system was used with the noted exceptions in the amounts of reactants taken. In Expts. 1 and 2, 24.96 ml. of 0.1392 F zinc chloride in 0.04 F hydrochloric acid were used, in Expts. 3 and 4, 24.96 ml. of 0.2000 F zinc chloride in 1.1 F ammonium chloride, and in Expts. 5 and 6, 24.96 ml. of 0.2000 F zinc chloride in 0.4 F hydrochloric acid and 0.8 F ammonium chloride.

Expt. No.	H_2SO_4 Milli-formula weights	pH of Titrated Solution	$K_3Fe(CN)_6$ Millimols added	% Error	Chloride Millimols present	Remarks
1	3	3.01	4.0	-1.8	17	$V_5 Na_2S_2O_3$ 0.01 ml. Neutralized by 5.5 meq. NH_4OH.
2	"	2.99	"	-1.8	"	" "
3	0	3.42	5.0	-1.8	37	$V_5 Na_2S_2O_3$ 0.02 ml.
4	15	2.90	"	-1.8	"	Neutralized by 28 meq. NH_4OH.
5	0	3.72	"	-1.8	40	Neutralized by 8.7 meq. NH_4OH.
6	0	3.78	"	-1.9	"	$V_5 Na_2S_2O_3$ 0.008 ml. End-point recurred in 1 min.

Table VIIIA

The Effect of the pH of the Solution and of Certain Anions

Expt. No.	Zinc Taken Millimols	$K_3Fe(CN)_6$ Taken Millimols
1	4.992	5.0
2	3.475	4.0
3	5.000	4.0
4	4.992	5.0
5	3.475	4.0
6	6.700	5.0
7	3.475	4.0
8	4.002	5.0
9	3.822	3.0
10	3.559	3.5
11	7.130	5.0
12	5.595	5.0
13	5.205	5.0
14	5.595	5.0
15	4.992	5.0
16	3.822	2.8
17	3.559	2.5
18	4.992	5.0
19	4.393	5.0
20	4.992	5.0

Table VIIIA (cont.)

Expt. No.	Zinc Taken Millimols	$K_3Fe(CN)_6$ Taken Millimols
21	3.822	2.5
22	4.992	5.0
23	4.992	5.0
24	3.475	4.0
25	4.992	5.0
26	3.475	4.0
27	4.992	5.0
28	4.992	5.0
29	4.992	5.0
30	4.992	5.0
31	4.992	5.0

Table VIIIB

The Effect of the pH of the Solution and of Certain Anions

Expt. No.	pH at End-point	Millimols Present			% Error	$V_{Na_2S_2O_3}^5$	Remarks
		$SO_4^=$	KHPhth	Cl^-			
1	1.70	4.5	0	40	--	0.09 0.10	
2	1.88	8.7	0	17	-1.8	0.13	
3	2	12.5	0	17	-1.6	0.02 0.10	
4	2.10	0	10.3	40	-1.9	0.03	
5	2.24	7.4	0	17	-1.85		
6	2.45	23.4	0	0	-1.6		
7	2.69	7.2	2.5	17	-1.8	0.02	
8	2.98	0	20.8	40	-1.8	0.020	
9	(3.0)	6.8	11	0	-1.75		Low $K_3Fe(CN)_6$. Recurs in 5 min.
10	(3.0)	6.6	11	0	-2.1		Low $K_3Fe(CN)_6$. Recurs 2 min.
11	(3.0)	10.1	11	0	-1.9		
12	3.17	95	25	0	-1.6		
13	3.29	10.2	11	0	-1.7		
14	3.30	95	0	0	-1.55	0.011	
15	3.43	0	58.5	40	-2.6		
16	(3.45)	5.3	11	0	-1.75		Low $K_3Fe(CN)_6$. Recurs ½ min.

Table VIIIB (cont.)

Expt. No.	pH at End-point	Millimols Present			% Error	V_5 $Na_2S_2O_3$	Remarks
		$SO_4^=$	KHPhth	$Cl^=$			
17	(3.45)	5.1	11	0	-2.3	-	Low $K_3Fe(CN)_6$. Recurs.
18	3.50	0	0	40	-1.9		
19	3.71	9.9	11	0	-1.8		
20	3.80	0.8	2	40	-1.8	0.007 0.005	
21	(3.85)	3.8	11	0	-2.1		Low $K_3Fe(CN)_6$. Recurs.
22	3.95	0	0	40*	-1.75	0.01	* 37 mm. acetate. End-point recurs slightly.
23	4.00	0	0	40*	-1.6	0.017 0.018	* 75 mm. acetate.
24	4.09	5.5	0	17	-1.8	0.004	
25	4.17	95	1.8	40	-1.9		
26	4.43	5.6	2.5	17	-1.8		End-point recurred in 8 min.
27	4.68	0	0	40*	-2.4	0.02 0.01 0.015	66 mm. acetate. End-point recurred slowly.
28	5.01	22	0.5	40	-2.0	0.013	
29	5.21	0	2.5	40	-2.5		
30	5.82	0	0	40	-2.1	0.005 0.002	
31	5.82	0	0	40	-1.8	0.03	

least 4 millimols for each experiment unless otherwise noted. It is seen that higher pH values than 3 do not appear to give substantial improvement in the stability of the end-point.

Effects due to high concentrations of phthalate, chloride, or acetate are observed in solutions of low hydrogen ion concentration. These effects (also noticed by Lang) are probably caused by complex-ion formation and result in low values for zinc and recurrence of the end-point. The specific effect of acetate is apparent at pH 4.7 but not at pH 3 or 4 (see Expts. 22, 23, 27).

A comparison of Expts. 9 and 21 with 15, and of Expt. 26 and 5, 7, and 24 indicates that the effect of phthalate is minimized by lower pH, by excess ferricyanide, and by allowing the solution to stand before the titration.

XIII. The Effect of the Amount of Zinc Taken

The amount of zinc taken may affect: (1) the composition of the precipitate and hence the value of the empirical factor; (2) the time required for completion of Reaction (1); and (3) the visibility of the end-point. No such effects were observed with quantities of zinc varying from 1 to 7.5 millimols, data in Tables IX and X. The data in these tables are also presented in order to show the reproducibility of the method. Thus the average error for the values obtained in hydrogensulfate-sulfate solutions over the range of conditions shown in Table IX is -1.63%, but the average deviation from this value is only 0.07%. The average error for the phthalic acid-hydrogenphthalate buffered solutions, Table X, is -1.8%, with an average deviation of 0.06%.

Experiments were also made in which solutions containing a known amount of zinc were titrated to the end-point according to the recommended procedure, then known quantities of iodine were added and the solution again titrated. In all cases the recovery of the iodine was quantitative within the experimental methods involved. In another experiment a potassium zinc ferrocyanide precipitate was prepared by titrating a sample of zinc according to the recommended procedure and then adding excess zinc solution (to remove all ferricyanide) and again titrating. The precipitate obtained was washed by decantation till it was free of zinc ion. A portion of this precipitate was then introduced into a reaction mixture prepared according to the recommended procedure except that only 10-15 ml. of 0.1 F ferricyanide solution was added. A known quantity of iodine was then added and titrated by thiosulfate; again the iodine was completely recovered.

Table IX

The Effect of the Amount of Zinc Taken in Hydrogensulfate-Sulfate Buffered Solutions

The solution was titrated immediately after mixing, and the volume after mixing was 250 ml. unless noted otherwise.

Expt. No.	No. of Expts.	Millimols Added		pH at End-point	% Error	Remarks
		Zinc	$K_3Fe(CN)_6$			
1	4	1.178	0.816	2	-1.7	Volume 210 ml.
2	2	2.945	2.725	2	-1.6	Volume 225 ml.
3	2	3.475	4.0	2.24 2.42	-1.85	
4	1	4.992	5.0	2	-1.6	
5	1	"	"	3.20	-1.75	
6	2	5.000	4.0	2	-1.6	
7	1	5.000	5.0	2	-1.6	
8	1	"	"	"	-1.6	
9	1	"	6.0	"	-1.4	
10	1	"	3.6	"	-1.8	
11	2	5.595	5.0	3.30	-1.6	$V_5Na_2S_2O_3$ 0.01 ml.
12	1	5.902	4.5	2	-1.6	Volume 150 ml.
13	3	"	"	"	-1.55	" "
14	4	6.700	5.0	2.44	-1.6	
15	2	7.505	"	3.5 2.90	-1.6	

Table X

The Effect of the Amount of Zinc Taken in Phthalic Acid-Hydrogenphthalate Buffered Solutions

The volume after mixing was 250 ml. in all experiments, and the solution was titrated immediately unless noted otherwise.

Expt. No.	No. of Expts.	Millimols Added Zinc	Millimols Added $K_3Fe(CN)_6$	pH at End-point	% Error	Remarks
1	3	3.475	4.0	2.69	-1.8	$V_5 Na_2S_2O_3$ 0.01 ml.
2	1	3.475	4.0	3.63	-1.9	" " End-point recurred .
3	1	3.559	3.5	(3.0)	-1.85	
4	1	"	"	"	-1.9	
5	2	"	4.0	"	-1.85	
6	1	3.767	3.0	(2.9)	-1.8	In dark 5 min.
7	2	"	"	"	-1.9	
8	1	3.822	2.8	(3.45)	-1.8	End-point recurred in ½ min.
9	1	"	3.0	(2.9)	-1.8	
10	2	"	"	(3.0)	-1.7	
11	1	"	3.2	(3.5)	-1.85	
12	2	4.128	3.0	(2.9)	-1.0	In dark 5 min.
13	3	4.393	5.0	3.4-3.7	-1.7	$V_5 Na_2S_2O_3$ 0.005 ml.
14	1	"	"	3.82	-1.9	End-point recurred.

Table X (cont.)

Expt. No.	No. of Expts.	Millimols Added Zinc	 $K_3Fe(CN)_6$	pH at End-point	% Error	Remarks
15	1	4.992	"	3.72	-1.8	
16	4	"	"	3.61- 3.78	-1.9	
17	1	5.265	5.0	3.29	-1.7	
18	1	"	"	3.98	-1.9	
19	2	5.595	"	3.07 3.21	-1.85	
20	2	"	"	3.12 3.52	-1.9	$V_5Na_2S_2O_3$ 0.016 ml.
21	2	6.700	"	3.30	-1.8	$V_5Na_2S_2O_3$ 0.005, 0.002 ml.
22	2	7.130	"	(3.0)	-1.85	
23	1	"	"	"	-1.9	
24	1	7.505	"	3.00	-1.6	
25	2	"	"	3.31	-1.8	
26	2	7.653	"	(3.0)	-1.87	

XIV. Confirmatory Analyses

The data obtained from several series of confirmatory analyses have been collected in Table XI. On the basis of these analyses (and of numerous other experiments) the recommendation is made that the empirical factor 1.019 be used when calculating the quantity of zinc found by titrations by the recommended procedure. Considering the magnitude of this factor the reproducibility of the values is surprisingly good, being better than 0.1%.

It is to be noted that as much as 40 millimols of chloride is without apparent effect; as shown in Table VIII, acetate is without effect when the pH is maintained at a value of 3 or less. The effect of other ions should be essentially the same as that found by Lang (1, 2) and by Casto and Boyle (4).

XV. Summary

A study has been made of the iodometric determination of zinc. Under the conditions recommended (a volume of 250 ml. and use of a phthalic acid-hydrogenphthalate buffer system), the necessity for stepwise addition of ferricyanide and successive titrations of iodine has been eliminated and a stable end-point obtained, even with

Table XI

Confirmatory Analyses

In Series 4, 17 millimols of chloride were present. In Series 6, 40 millimols of chloride were present, of which 10 were HCl; no H_2SO_4 was added. Series 7 was the same as Series 6 but with the addition of 8.7 millimols of NH_4OH. The amount of potassium ferricyanide used was 3.0 millimols in Series 1-3, 4.0 in Series 4, and 5.0 in Series 6-7. With these exceptions, the recommended procedure was used.

Expt. No.	pH at End-point	Millimols Zinc Taken	Millimols Zinc Found	% Error	V_5 $Na_2S_2O_3$ (ml.)	Remarks
1 a	(3.0)	3.822	3.756	-1.75		Recurs in 5 min.
b	"	"	"	-1.75		
2 a	(2.9)	3.767	3.697	-1.9		
b	"	"	3.700	-1.8		
c	"	"	3.695	-1.9		
3 a	"	4.128	4.049	-1.9		
b	"	"	4.049	-1.9	0.05	
4 a	3.01	3.475	3.414	-1.8	0.01	
b	2.99	"	3.414	-1.8	0.01	Recurs in 3 min.
5 a	(3.0)	7.653	7.510	-1.87		
b	"	"	"	-1.87		
6 a	2.10	4.992	4.896	-1.9	0.03	
b	2.50	"	4.898	-1.9	0.025	
7 a	3.72	4.992	4.902	-1.8		
b	3.78	"	4.896	-1.9	0.008	Recurs in 1 min.

greater variability in the amounts of reagents used. It is necessary to increase by an empirical factor of 1.019 the theoretically calculated amount of zinc. The titration for macro amounts of zinc is fast, requires no previous experience, and has a sharp end-point; a precision of 1-2 parts per thousand has been obtained.

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PART II: INVESTIGATIONS IN THE CHEMISTRY OF RHENIUM

Introduction

Part of the interest of the chemistry of rhenium, atomic number 75, is due to the large number of oxidation states in which this element occurs--in fact, compounds of rhenium for all oxidation numbers between +7 and -1 have been reported. In this research, an attempt has been made to characterize more precisely some of the oxidation states of rhenium in aqueous solution.

Since many of the rhenium compounds encountered were colored, they were studied by measuring their light absorption in the visible region with a Beckman spectrophotometer. These substances, as well as colorless preparations such as the interesting uni-negative rhenium, were also studied by their behavior with common oxidizing and reducing agents.

Because of the complex chemistry and conflicting literature of rhenium, some of the literature has been summarized, and for clarity the results obtained in the present work are stated for comparison with the literature and then later are summarized.

Because results of early investigators have often not been confirmed by later workers, sometimes because of differences in experimental conditions, the conditions of the analytical determinations and of the other experimental work have been given in considerable detail in the present research.

I. MATERIALS

A. Rhenium Compounds

A ten-gram sample and a five-gram sample of rhenium metal powder and a ten-gram sample of potassium perrhenate were obtained from the University of Tennessee. The rhenium metal was reported to assay 99.5% or better, the chief impurity being silver introduced during its preparation by reduction of potassium perrhenate in a silver tube. The potassium perrhenate was stated to assay 99.8% or better, the chief impurity being rubidium possibly as rubidium perrhenate.

Additional tests of the purity are described in Section III-1, The Chemistry of Re^{VII}.

B. Oxidizing and Reducing Agents

Approximately 0.05 F solutions of ceric ammonium sulfate in 0.5 F sulfuric acid were prepared. A 0.05 F ferrous ammonium sulfate solution in 0.3 F sulfuric acid was prepared by weighing out Mohr's salt and was standardized against a solution of Bureau of Standards potassium dichromate using diphenylamine as indicator. The normality found in this way was the same as that calculated by weight. Hence the ceric sulfate solutions were standardized against this freshly prepared ferrous solution, using o-phenanthroline ferrous complex indicator.

Ferrous ammonium sulfate solutions 0.05 F in 0.3 F sulfuric acid were standardized before each day's use against standard ceric sulfate solutions. New ferrous solutions were made up if air oxidation had decreased the ferrous concentration by 5% from its value in the freshly prepared solution.

Some ceric titrations were done in hydrochloric acid solutions. When it was necessary to minimize reaction of the ceric sulfate with the chloride, the concentrations of hydrogen ion and of chloride were kept less than 4 formal.

Potassium iodate solutions 0.015 F, or 0.090 N, for use in iodine titrations, were prepared from the dried reagent. Use of iodate in solutions stronger than 6 F in hydrochloric acid was avoided to minimize oxidation of chloride by iodate. From the 0.090 N solutions of iodate, solutions of 0.045 N concentration were prepared by dilution as needed.

Sodium thiosulfate solutions 0.1 F were prepared in boiled distilled water containing 0.01% sodium carbonate. They were standardized frequently against the standard solutions of potassium iodate, using starch solution as indicator. Fresh solutions were prepared if the solution had changed concentration by ½%, or if it was six weeks old. Titrations were done in solutions containing 3% potassium iodide (free from iodate) to prevent loss of iodine. By dilution of the 0.1 F thiosulfate, 0.05 F

(0.05 N) solutions were prepared. These solutions were then restandardized against iodate.

A 0.3 F (0.3 N) iodine solution in 7.5% potassium iodide was prepared by dissolving 75 g. of potassium iodide in 75 ml. of water, adding 38 g. of iodine and stirring till all the iodine was dissolved, then diluting slowly to 1 liter. The iodine solution was stored in a bottle covered with paper, and was kept in the dark when not in use. Whenever it was needed, it was standardized against a standard thiosulfate solution.

A 0.07 F copper sulfate solution, prepared from reagent copper sulfate pentahydrate, was standardized by adding a known volume to excess 3% potassium iodide solution and titrating the iodine with standard thiosulfate.

Solutions of ferric ammonium sulfate 0.15 or 0.06 F in 0.1 F sulfuric acid were prepared from reagent grade iron alum. These solutions were standardized iodometrically using the optimum conditions given by Swift (1).

A 0.05 F (0.1 N) titanous sulfate solution in 4 F hydrochloric acid was prepared from 20% titanous sulfate solution. It was standardized against ceric sulfate as well as by potassium iodate. The titanous sulfate solution in hydrochloric acid was kept out of air when not in use, and was restandardized before use.

Stannous chloride solutions 0.05 F (0.1 N) were prepared by dissolving the solid in 4 or 6 F hydrochloric acid. The solution was kept stored in a desiccator filled with carbon dioxide. During use, a stream of carbon dioxide was kept flowing through the desiccator by a side inlet and out a top outlet. To standardize the stannous, excess iodine solution was prepared from iodate and iodide, and a known volume of stannous chloride was then introduced under the iodine by a pipette rinsed with carbon dioxide. The iodine remaining after reaction with the stannous chloride was then titrated with standard thiosulfate. No stannous chloride solution was used after its concentration had been decreased by air oxidation by 10-15% from its initial value.

Solutions of cuprous chloride in 4 F hydrochloric acid were prepared fresh when needed, as follows. Cuprous chloride (85%) was dissolved in a small volume of concentrated hydrochloric acid, and poured into a large volume of distilled water. The white precipitate of CuCl was centrifuged and washed, and enough was dissolved in concentrated hydrochloric acid to give a 0.1 F solution after diluting the acid to 4 F. These solutions contained only a few percent of cupric ion, and the cuprous concentration could be determined with ceric sulfate.

A 0.1 F chromic chloride solution was prepared in 4 F hydrochloric acid from an approximately weighed amount of the solid.

C. Other Reagents

Pure acids and bases were used. A 0.1 formal potassium hydroxide solution was standardized against potassium hydrogen phthalate; to avoid error due to carbonate, the solution was boiled just short of the phenolphthalein end-point. Hydrochloric acid solutions were standardized against this fresh potassium hydroxide or against sodium carbonate. Other basic solutions were standardized against the hydrochloric acid solutions.

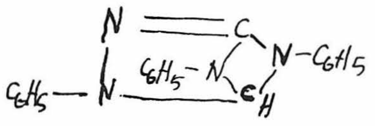
C. P. zinc, reagent mercuric nitrate, and pure distilled mercury were used. Reagent cesium chloride was used in some experiments.

Cylinders of common gases were available. These included hydrogen, nitrogen, oxygen, carbon dioxide, argon, carbon monoxide, and chlorine. In a few experiments, Linde dry nitrogen, 99.99%, was used from a cylinder.

Chlorine solutions 0.03-0.05 F (0.06-0.1 N) were prepared by passing the gas through 4 F hydrochloric acid, and were standardized before use by pipetting a small volume of the chlorine solution into excess 3% potassium iodide solution, and titrating the iodine by standard thiosulfate.

Hydrogen peroxide stock solution, 30%, was used. It was shown by a titration with base that the titer of a perchloric acid solution was not changed when hydrogen peroxide was added and then destroyed by boiling; this proves the absence of basic or acidic non-volatile impurities in the hydrogen peroxide.

For use in analysis of perrhenate, a 5% nitron acetate solution was prepared from nitron,



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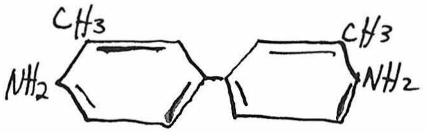
as described by Geilmann and Voigt (2). It was stored in the dark. A 0.1% solution of o-tolidine,



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was prepared in 1.2 F hydrochloric acid for detection of chlorine, following the instructions of Welcher (3). It was kept in a bottle covered with paper and stored in the dark.

II. SPECTROPHOTOMETRY

The light absorption for solutions in the near ultraviolet and visible regions was measured using a Beckman photoelectric quartz spectrophotometer, Model DU. Quartz cells were used in the ultraviolet, and corex cells were used from 320 to 1000 millimicrons (mμ). The path length of the rectangular cells was 1.00 cm., and their volume was 3 ml. The cells were checked against one another by measuring their absorption when filled with water and when filled with 0.1 N potassium dichromate solution. In this way their path lengths were shown to be equal.

For protection of solutions from oxygen of the air, a number of long-stemmed corex cells capped with ground joints were used. Solutions could be measured into the cells by use of graduated pipettes drawn out fine enough to slip inside the joint.

Measurement was done at room temperature. The absorption of the solvent (usually water or hydrochloric acid) was automatically subtracted and correction made for reflection and scattering by measuring the absorption relative to a blank of the solvent in a similar cell. The values of the extinction coefficient ϵ are calculated from the observed readings of optical density d at a given wave-length by knowing the concentration c and the path length l of 1.00 cm.,

$$d = \log_{10} \frac{I_0}{I} = \epsilon cl . \qquad (1)$$

Formal concentrations were used throughout since the constitution of some of the substances investigated is indefinite. Readings were taken consecutively from short wave-lengths (usually 320 mμ) to long wave-lengths (1000 mμ). A filter was used with the tungsten light source from 320 to 425 mμ , and a pause was made for several minutes at 625 mμ when changing from a blue sensitive phototube to a cesium oxide phototube.

In many cases uncertainty in the concentration was the chief source of error.

In order to ensure best reproduction of peaks, it is desirable to use a narrow band width. This was done by operating the instrument at low potentiometer scale sensitivity which corresponded to narrow slit widths and hence narrow band widths. The galvanometer was found to respond when the optical density scale setting was changed the smallest measurable amount for the region of wave-lengths used. In the region of optical density from 0 to 0.400, a change in d of 0.001 unit caused the galvanometer reading to be changed significantly. From optical density values 0.400 to 0.800, the uncertainty in d is 0.003; from 0.800 to 1.00, it is 0.005; and from 1.00 to 1.50, 0.02.

In using a spectrophotometer it is usually necessary to compromise between using a small slit width with a narrow band of wave-length to ensure best reproduction of peaks, or using a large slit width with high light intensity and hence strong phototube response. Operation of the instrument at high potentiometer scale sensitivity requires a large phototube current and hence high illumination and large slit-width. With the instrument used and weakly absorbing blanks, it was shown that the instrument could actually be operated at minimum potentiometer scale sensitivity (and hence small slit-width) and yet have enough light intensity for accurate readings.

The minimum spectral band width necessary to give sufficient light intensity for scale readings to 0.1%, $\Delta\lambda$min., has been given by Cary and Beckman (4) as a function of wave-length. Another graph was available which gave as a function of wave-length the actual band width when the spectrophotometer slit was open one millimeter, $\Delta\lambda$/mm. Then for any given slit width in millimeters, S(mm), the band width $\Delta\lambda$ is given by

$$\Delta\lambda = \Delta\lambda/\text{mm} \cdot S\ (\text{mm}) \quad . \qquad (2)$$

In order to have sufficient light for 0.1% scale readings, it is necessary that

$$\Delta\lambda \geqslant \Delta\lambda\text{min.} \quad . \qquad (3)$$

However it is also necessary to keep $\Delta\lambda$ small in order that peaks be followed closely. Data in Table I show that $\Delta\lambda$ was in almost all cases equal to or slightly greater than $\Delta\lambda$ min. for low potentiometer scale sensitivity. This method of operating the instrument is therefore the optimum method. It is the optimum method because any increase in potentiometer scale sensitivity corresponds to increase in slit-width and widening of the band-width, causing poorer reproduction of peaks. In tabulating the slit-widths for Table I, a correction of 0.02 millimeter was added to the experimentally observed slit-width because Cary and Beckman (4) state that aberration produced by the collimator is equivalent to an increase in slit of 0.02 millimeter.

The data in Table I also show that good reproducibility can be achieved for separate measurements. However, optical density values below 0.010 are not significant unless particular care has been taken to match the blank solution with the solvent used for the absorbing species. For optical density values greater than 0.05, the instrumental errors are only a few percent, and the chief source of error becomes the accuracy with which the concentration is known. The wave-length could be reproduced to better than 1 millimicron; for consideration of other experimental factors, reference is made to Cary and Beckman's article (4).

Since the blanks used in later solutions were weakly absorbing, usually water or hydrochloric acid, they had slit-widths comparable with those given in Table I. Therefore slit-widths are not given for later measurements.

Table I

Light Absorption Data for Potassium Rhenichloride

Wave-length millimicrons	Optical Density 0.010_0 F K_2ReCl_6 4 F HCl	Slit Width corrected mm	Band Width for 1 mm Slit	Actual Band Width	Smallest Band Width for 0.1% Readings
(mμ)	d	S(mm)	$\Delta\lambda$/mm	$\Delta\lambda$	$\Delta\lambda_{min.}$
320		0.30	5.0	1.5	1.0
350		0.12	6.8	0.8	0.5
400	0.386*	0.095	10	1.0	0.4
400	0.384	0.10	"	1.0	0.4
400	0.380	0.09	"	0.9	"
450	0.071	0.039	15	0.6	0.5
450	0.070	0.039	"	0.6	"
450	0.071	0.038	"	0.6	"
500	0.020	0.031	20	0.6	0.6
500	0.019	0.032	"	0.6	"
500	0.017	0.030	"	0.6	"
550	0.009	0.03	26.5	0.8	0.9
550	0.009	0.03	"	0.8	"
550	0.008	0.030	"	0.8	"
600	0.010	0.036	34	1.2	1.2
600	0.009	0.037	"	1.2	"
600	0.008	0.037	"	1.2	"
650	0.034	0.05	41	2.0	1.6
650	0.034	0.05	"	2.0	"
650	0.033	0.05	"	2.0	"
700	0.028	0.04	49	2.0	1.7
700	0.026	0.04	"	2.0	"
700	0.025	0.041	"	2.0	"

* In each set, the second measurement was made 15 minutes after the first, Then the lamp was turned off till 3 hours later when the third measurement was made.

Table I (cont.)

Wave-length millimicrons	Optical Density 0.010_0 F K_2ReCl_6 4 F HCl	Slit Width correct-ed mm	Band Width for 1 mm Slit	Actual Band Width	Smallest Band Width for 0.1% Readings
(mμ)	d	S(mm)	$\Delta\lambda$/mm	$\Delta\lambda$	$\Delta\lambda$ min.
750	0.009	0.039	57	2.2	1.9
750	0.007	0.04	"	2.2	"
750	0.008	0.04	"	2.2	"
800	0.008	0.037	64	2.4	2.0
800	0.009	0.038	"	2.4	"
800	0.006	0.037	"	2.4	"
850	0.010	0.036	71	2.6	2.2
850	0.006	0.035	"	2.5	"
850	0.008	0.035	"	2.5	"
900	0.008	0.035	77	2.7	2.6
900	0.005	0.034	"	2.6	"
900	0.006	0.034	"	2.6	"
950	0.008	0.036	83	3.0	3.5
950	0.007	0.036	"	3.0	"
950	0.008	0.035	"	2.9	"
1000	0.009	0.04	87	3.5	4.5
1000	0.009	0.04	"	3.5	"
1000	0.009	0.04	"	3.5	"

III. THE CHEMISTRY OF RHENIUM (VII)

It was desirable to find suitable qualitative and quantitative tests for the important valence states of rhenium in order to be able to characterize these states in solution. Heptavalent rhenium has as its representative in aqueous solution the perrhenate ion, ReO_4^-. Hence a study was made of perrhenic acid.

1. Preparation of Perrhenic Acid

Solutions of perrhenic acid, $HReO_4$, were prepared by heating powdered rhenium metal with an excess of 30% hydrogen peroxide until all the rhenium was dissolved (5, 6),

$$2\ Re + 7\ H_2O_2 = 2\ ReO_4^- + 2\ H^+ + 6\ H_2O. \qquad (4)$$

The solution was heated until the excess peroxide was destroyed as proved by lack of color with ammonium molybdate solution or titanic sulfate solution.

One solution of $HReO_4$ was prepared from 0.515 g. of rhenium in a flask covered with a watch glass, heating with 10 ml. of 30% hydrogen peroxide for an hour on a sand bath. The solution was then diluted to 100 ml., and the concentration of acid determined by titration with standard potassium hydroxide to a methyl red end-point, making indicator end-point corrections. A volume of 2.005 ml. of the perrhenic acid solution required 6.83 ml. of 0.00776 F base, giving 0.02645 formal as the concentration of the acid, 4.6% less than the value expected from the weight of rhenium powder used.

Analysis of the hydrogen peroxide as discussed in Section I-C proved the discrepancy was not due to basic impurities in the peroxide.

The concentration of perrhenate was checked by precipitation as nitron perrhenate (2). Two samples of 2.005 ml. were used, giving results 5.2% and 4.3% less than the value expected from the weight of rhenium, but in agreement with the results found by titration with potassium hydroxide.

The perrhenate solution contained no molybdenum as molybdate because no yellow color was produced with the hydrogen peroxide when dissolving the rhenium.

In order to determine whether the rhenium possibly contained oxides as impurity, it was treated with hydrogen. A sample of 100 mg. of rhenium metal when treated with hydrogen at 1000°C and cooled in an atmosphere of pure nitrogen lost 1.5 mg. in weight; this indicates that the 4.6% deficit in the amount of perrhenic acid obtained from rhenium metal was not due to oxygen impurity in the latter.

In view of these experiments and the stated purity of the rhenium, it appears that the loss is due to either

(a) volatility of perrhenic acid or (b) loss of rhenium in a spray under the conditions of reaction of the rhenium with the hydrogen peroxide. A similar conclusion about preparation of perrhenic acid in this way was reached by Hölemann (7). Geilmann and Weibke (8) also observed losses of rhenium from hot perrhenic acid solutions.

Table II shows the results of analyses on various preparations of perrhenic acid made by treating rhenium powder with 30% hydrogen peroxide and water. Titration of the $HReO_4$ formed was done with 0.01 F base standardized against standard acid under the same conditions used in titrating the perrhenic acid. The entire rhenium sample was titrated in Experiments 1 and 2; in the others, aliquot portions were used.

2. Qualitative Tests for Perrhenic Acid

The nitron test previously referred to in the literature (2, 9, 10) was verified to be quite sensitive for perrhenate, but cannot be used effectively in solutions containing chloride. An appreciable white precipitate of nitron perrhenate was given when a drop (0.05 ml.) of 5% nitron acetate was added to a drop of 0.02 F $HReO_4$ solution. However, the nitron acetate reagent gave a bulky, gelatinous precipitate with hydrochloric acid more concentrated than 0.5 formal, or with ammonium chloride solution.

Table II

Analyses of Perrhenic Acid

Expt. No.	Rhenium Taken milligrams	Volume 30% H_2O_2 added (ml.)	Volume H_2O added (ml.)	Treatment	Rhenium Found milligrams	% error
1	12.31	0.15	4	Let stand 45 min. Heated close to boiling point 80 min. Titrated to methyl red end-point.	11.48	-6.6
2	12.69	0.15	4	"	12.04	-5.1
3	51.48	0.15 0.35	2	Warmed 5 min. Warmed 2 hrs. maintaining volume. Diluted to 5 ml. Titrated to bromthymol blue end-point.	49.9_5	-3.0
4	466	0.5	5	Allowed to stand overnight. Kept at boiling pt. 3 hrs. Diluted to 50 ml. Bromthymol blue indicator.	450	-3.4
5	462.5	2	5	Kept close to boiling pt. 4 hrs. Evaporated to 1 ml. Bromthymol blue.	446	-3.7
6	469	0.5 1.7	12	Let react 10 min. Boiled several hrs. Diluted to 50 ml. Bromthymol blue.	445	-3.0

Cesium perrhenate is sparingly soluble, 7.8 grams per liter at 19 °C (11), or solubility product 4×10^{-4}. However when 0.10 F cesium ion was present with 0.011 F perrhenate no precipitate was observed upon centrifuging before or after addition of an equal volume of 6 F HCl. This may be explainable by reported formation of supersaturated solutions (9).

The lack of formation of a visible precipitate when cesium chloride is added to dilute $HReO_4$ is significant because Re^{IV} in the ion $Re^{IV}Cl_6^=$ forms an insoluble cesium salt (12) and CsCl may be used to distinguish ReO_4^- and $ReCl_6^=$.

3. Light Absorption of Perrhenic Acid

In Table III are given the optical density data measured for two solutions of perrhenic acid against a blank of water. For comparison, the data of Custers (13) are included. Good agreement is found between Custers' measurements and the present work. The light absorption was practically zero from 330 to 1000 mμ and therefore absorption of perrhenic acid is negligible compared to that of colored compounds. No color formed when 6 F HCl was added to $HReO_4$.

4. Summary of the Chemistry of Re^{VII}

Dilute perrhenic acid solutions may be prepared by treatment of rhenium with hydrogen peroxide. The acid

Table III

Light Absorption of Perrhenic Acid

Wave-length (mμ)	Optical Density		Calculated Extinction Coefficient		Extinction Coefficient Reported by Custers
	0.02645 F $HReO_4$	0.0535 F $HReO_4$	0.02645 F $HReO_4$	0.0535 F $HReO_4$	
280.4					57.5
285	0.88	1.75	33.2	32.8	
289.4					17.7
290	0.47	1.00	17.8	18.7	
295	0.255	0.53	9.7	9.9	
296.7					6.59
300	0.138	0.283	5.2	5.3	
302.2					3.00
305	0.071	0.154	2.7	2.9	
310	0.042	0.098	1.6	1.8	
313.4					0.55
315	0.027	0.062	1.0	1.1	
320	0.020	0.046	0.8	0.9	
325	0.018	0.040	0.7	0.7	
330	0.015	0.036	0.6	0.7	
335	0.013	0.031	0.5	0.6	
340	0.012	0.025	0.5	0.5	
345	0.012	0.028	0.5	0.5	
350	0.012	0.025	0.5	0.5	

Table III (cont.)

Wave-length (mμ)	Optical Density 0.02645 F $HReO_4$	Optical Density 0.0535 F $HReO_4$	Calculated Extinction Coefficient 0.02645 F $HReO_4$	Calculated Extinction Coefficient 0.0535 F $HReO_4$	Extinction Coefficient Reported by Custers
350	0.012	0.025	0.5	0.5	
375	0.009	0.021	0.3	0.4	
400	0.008	0.020	0.3	0.4	
420	0.008	0.019	0.3	0.4	

concentration obtained is about 3-4% less than expected from the weight of rhenium taken. This error seems to be attributable to loss of rhenium by volatility of $HReO_4$ rather than due to impurities in the rhenium.

The nitron test for perrhenate is sensitive but not applicable in solutions containing chloride. Perrhenic acid gives no visible precipitate with small quantities of dilute cesium chloride solution.

IV. THE CHEMISTRY OF RHENIUM (V)

This section describes the preparation of pentavalent rhenium in solution.

Turkiewicz (14), by potentiometric study of mixtures of stannous chloride with perrhenate, found evidence for the formation of pentavalent rhenium. At room temperature in 4.4 <u>F</u> HCl, after each addition of stannous chloride he observed a drop of indicator electrode potential, which gradually rose again. After two equivalents had been added, the potential remained down and did not change appreciably with addition of more stannous chloride.

Jacob and Jezowska (15, 16, 17) isolated the compound K_2ReOCl_5 from solutions of potassium perrhenate in 6 or 8 <u>F</u> hydrochloric acid, electrolytically reducing the rhenium at a palladium cathode. The compound was analyzed for potassium, rhenium, and chlorine. The valence of rhenium was established by the observations that 2.00 equivalents of permanganate were used to oxidize an amount of the compound containing one mole of rhenium (the highest verified state of rhenium is VII); in hot HCl solution the compound liberated one equivalent of iodine when treated with potassium iodide.

The K_2ReOCl_5 of Jacob and Jezowska gave greenish or yellowish colored solutions. A black oxide was precipitated by alkalies; the oxide was easily oxidized by air, $KMnO_4$, H_2O_2, or HNO_3 to perrhenate. Upon long heating of dilute HCl solutions, there resulted K_2ReCl_6 and $KReO_4$ in a disproportionation,

$$H_2O + 3\ ReOCl_5^{=} = 2\ ReCl_6^{=} + ReO_4^{-} + 3\ Cl^{-} + 2\ H^{+} \qquad (5).$$

The K_2ReOCl_5 gave an intensive green color with potassium thiocyanate, the color being extracted by ether. No silver salt of the compound could be precipitated. Another method of preparation by reduction of perrhenate with cold iodide solutions was given; this will be discussed in Section V-D. The yellow green crystals had unlimited stability in dry air. In moist air, complete hydrolysis was reported after 24 hours. Strongly acidic solutions were stable in air at room temperature, but upon dilution a black oxide formed with simultaneous part decomposition into Re^{IV} and Re^{VII}. The acidic solution was easily oxidized by ferric salts, $KMnO_4$, or H_2O_2. The compound could be dissolved in 6 F HCl but not in 2 F without hydrolysis.

Jacob and Jezowska (16) also reported the inverse process of disproportionation, because when rhenichloride and perrhenate were allowed to stand in strong HCl, slowly a constant potential was achieved, the mixture gave the same color with KSCN as did Re^{V}, and it was oxidized by Fe^{III} in distinction to $ReCl_6^{=}$,

$$2\ ReCl_6^{=} + ReO_4^{-} + 2\ H^{+} + 3\ Cl^{-} = H_2O + 3\ ReOCl_5^{=}. \qquad (6)$$

Hölemann (18) investigated the action of stannous chloride on perrhenate, by potentiometric methods. A break in potential was found after addition of two equivalents of perrhenate, corresponding to formation of Re^{V}, in 4.3 F HCl at 80 °C under a protective atmosphere of nitrogen. In the presence of thiocyanate, three equivalents of $SnCl_2$ were required, thus forming Re^{IV}, but in the absence of CNS^{-} it was not possible to determine by the potential whether Re^{IV} was formed too. Hölemann found that it was possible to potentiometrically titrate ReO_4^{-} by $SnCl_2$ to formation of Re^{V}. He concluded that in a short period of time only Re^{V} was formed with the $SnCl_2$. The Noddacks (12) stated that Re^{IV} was formed by $SnCl_2$ with ReO_4^{-}, but excess stannous was present in their experiments.

In later work, Hölemann (19) investigated the action of other reducing agents on perrhenate. He found that in strong sulfuric acid solutions free of halogen, reduction to Re^{V} was given by $Ti_2(SO_4)_3$, $SnSO_4$, and $FeSO_4$. He found indications of intermediate formation of hexavalent rhenium, Re^{VI}, because an intermediate violet color was obtained which went to the blue of Re^{V} in sulfuric acid. $CrSO_4$ gave reduction to Re^{IV}; the formation of Re^{VI} and Re^{V} could be identified as intermediates by the potentiometric method only in strong acid.

Hölemann (20) also synthesized K_2ReOCl_5 by the method of reduction of perrhenate by iodide (17). By X-ray powder photographs he was able to identify the presence of this new compound, and show its non-identity with $KReO_4$, K_2ReCl_6, or KCl. He gave qualitative tests to distinguish it from K_2ReCl_6. When heated with KI, separation of iodine occurs; cyanide gives a red coloration which is not changed by ammonia. With cesium and rubidium salts, no precipitate is formed. Ferrocyanide gives a dark red color which becomes weakly yellow with ammonia, ferricyanide gives a weak red color. No precipitate forms with mercurous salts, but mercuric salts and ammonia gave a gray black precipitate. Hölemann reported a yellow-green color in dilute solution with thiocyanate, and a red brown color with ammonia. The cold solution hydrolyzed, while cold K_2ReCl_6 is stable.

Tribalat (21, 22, 23) confirmed the formation of Re^{V} by potentiometric titration of perrhenate with stannous chloride. She reported Re^{V} to be unstable and to disproportionate to compounds of Re^{IV} and Re^{VII}, as was also stated by W. and I. Noddack (12). Jezowska (24) and Jacob and Jezowska (17) reported that K_2ReOCl_5 was stable in strong HCl but that upon dilution disproportionation occurred. Tribalat found a slow disproportionation of Re^{V} in 4 F HCl because the emerald green solution of Re^{V} turned brown and deposited a black precipitate after 24 hours. She decided that perrhenate had reformed, because addition of more $SnCl_2$ gave a test for Re^{V} with KCN. She found it was possible to continue the reduction of Re^{V} with a third equivalent of stannous chloride if portions were added slowly over a period of hours. More vigorous reducing agents, Cr^{II} or Ti^{III}, reduced the ReO_4^- directly to the black oxide of Re^{IV}.

In her later experiments (22), Tribalat found that the same results were obtained at higher acidities, but that in 1 F HCl the disproportionation of Re^{V} was accelerated by the formation of hydrated ReO_2, which precipitated with the first addition of $SnCl_2$ to the ReO_4^-. In dilute HCl, the Re^{V} was found stabilized by oxalate (a blue complex) or tartrate (blue). In 4 F HCl the tartrate complex was clear green and its disproportionation was not observed after 24 hours.

In the present research the action of stannous chloride on perrhenate in 4 F HCl was studied by spectrophotometric observation, with some information from qualitative and quantitative analyses. It was first shown that the same green substance forms when one equivalent of stannous chloride is added to one mol of perrhenate as when two equivalents are used, but that a new yellow-brown substance forms if more than two equivalents are used. Therefore Re^{V} is formed if the amount of stannous chloride is less than or equal to two equivalents per mol of perrhenate. The green Re^{V} solution has the same absorption when measured several hours after addition of the stannous chloride as when measured immediately, proving that the rate of formation is high and that there is no rapid loss due to oxidation by traces of O_2 or due to rapid disproportionation. Next it is found that the same substance is formed in different experiments. Since it is reproducible, it is a well-defined species. On the other hand, the absorption of the solutions with 3, 4, or 5 equivalents of stannous chloride per mol of rhenium (VII) increases gradually over a period of hours, but finally reaches the same value for the various solutions. This shows that Re^{IV} is the product, that its rate of formation is low, and that there is no serious difficulty due to disturbing influences such as possible oxidation or change in form.

The green solutions of Re^{V} are found to be slowly oxidized by prolonged treatment of oxygen. Since the effects of air and of time are then known, it is possible to interpret other experiments.

It is found by analysis that Re^{V} is completely oxidized to perrhenate by ceric sulfate or by potassium iodate, and largely if not completely oxidized to perrhenate by iodine in dilute HCl. Re^{V} is instantly decolorized by hydrogen peroxide, oxidation to colorless ReO_4^- being the explanation. Re^{V} reduces $HgCl_2$ in HCl to Hg_2Cl_2. By spectrophotometric data, it is shown that chlorine oxidizes Re^{V} rapidly and quantitatively to ReO_4^-. Heating a solution of Re^{V} in 4 F HCl at 60 °C for an hour does not cause disproportionation or any other change in the concentration of the Re^{V}.

Since the light absorption of Re^{V} in 4 F HCl decreases slightly after a long time, it cannot be undergoing disproportionation into any of the colored forms of Re^{IV}. The proof that it also does not undergo disproportionation to a colorless form of Re^{IV} is deferred until the discussion of Re^{IV}, when it is shown that the observed decrease in light absorption of Re^{V} after a long time can be explained on the basis of oxidation to $Re^{VII}O_4^-$. It is shown that in 2 F HCl, Re^{V} rapidly disproportionates, giving $Re^{VII}O_4^-$ and a black precipitate. The properties of the precipitate are found to be the same as later found for $ReO_2 \cdot x\, H_2O$.

1. Preparation of Re^V from Perrhenate with Stannous Chloride

Portions of dilute perrhenic acid and hydrochloric acid were mixed in corex cells with water, and stannous chloride in hydrochloric acid was added. Preliminary experiments showed that in low acidity, as 2 F HCl, a yellow-brown color resulted when $SnCl_2$ was added to $HReO_4$, followed by gradual settling out of a brown-black precipitate. If the acid was 4 F, no precipitate formed. In 4 F HCl, small quantities of stannous chloride with perrhenate gave light green solutions while larger amounts gradually developed a yellow-brown color. The volumes and concentration of reactants taken were such as to give a resultant volume of 3 ml. of 0.010 F rhenium with $SnCl_2$ in a resultant acidity of 4 F HCl.

It was desirable to follow the solutions over considerable lengths of time, which might give opportunity for air oxidation of rhenium compounds or of stannous chloride. In all work the stannous chloride was pipetted into the cells containing the $HReO_4$ and HCl while keeping the cells protected in a desiccator filled with carbon dioxide. The pipette and the cell filled with $HReO_4$ and HCl were rinsed out with CO_2. Early experiments were done in long-stemmed corex cells, 3 ml. volume and stem radius 0.2 cm., but it was found that when these cells were merely capped with rubber policemen, considerable air oxidation of $SnCl_2$ occurred after a period of hours. Therefore the cells were modified by being equipped with glass caps which slid over ground joints. Blank experiments with 0.017 F $SnCl_2$ in these cells showed not more than 10-20% oxidation after 1-2 days.

The hydrochloric acid was available as concentrated acid, approximately 12 F, or as dilute acid, 6 F. A check on a number of samples showed the concentrations usually were slightly higher than these values, but within 5%. Unless stated otherwise, the acidity in the perrhenic acid before adding the stannous chloride was 3-4 F HCl, and correspondingly the acidity in the 0.05 F stannous chloride was 6-4 F HCl to give a resultant mixture of 3 ml. of 0.01 F $HReO_4$ in 4 F HCl. The assumption of 4 F HCl after addition of the volumes is based upon no volume change upon dilution. Experiments were performed in which known volumes of concentrated hydrochloric acid and of water were mixed, and this assumption was found valid within a few percent.

2. Light Absorption of Re^V

A series of experiments was carried out in which various amounts of stannous chloride were added to 0.030 millimols of $HReO_4$ solution. The amounts of stannous chloride used were 0.030 milliequivalents (0.015 millimols), 0.060 meq., 0.075 meq., 0.090 meq., and 0.121 meq. Light absorption measurements were made within an hour. The observed optical densities have been plotted against wave-length to give the absorption curves of Figure 1. Actually the optical densities were divided by the formal concentration of the rhenium, 0.010 F, to give a quantity which may be termed the "formal apparent extinction coefficient," (see Section II, Equation 1, also Section VII-2). It is seen that the absorption of solutions with 1 or 2 meq. $SnCl_2$ per mm. $HReO_4$ was considerably lower than for solutions with any greater amount of stannous chloride, which already shows that the solution with 2 meq. $SnCl_2$ per mm. $HReO_4$ contained Re^V while a lower oxidation state was formed with excess stannous chloride.

The light green solutions with 1 or 2 meq. $SnCl_2$ per mm. $HReO_4$ were shown to have nearly the same absorption for 5 minutes to 16 hours after preparation. This proves that the rate of formation of the absorbing species is rapid, and that either oxygen was successfully excluded from the cells (which has already been mentioned in Section IV-1) or that it does not rapidly or extensively affect the light green substance. This latter possibility was later shown correct also. Table IV contains the data showing the stability of the green solutions. In distinction, the absorption of solutions with any excess stannous chloride beyond the amount required to form Re^V increased for hours before reaching a limiting value.

Table IV

Effect of Time upon Light Absorption of Re^{V}

a. 0.030 mm. $HReO_4$ and 0.030 meq. $SnCl_2$ in 3 ml. 4 F HCl

Time after Preparation	5-25 min.	25-170 min.	$15\frac{1}{2}$-$16\frac{1}{2}$ hrs.	38 hrs.
Wave-length (mμ)	Optical Density d	Optical Density d	Optical Density d	Optical Density d
350	-0.037	-0.040	-0.05	+0.044
400	+0.054	+0.051	+0.025	+0.055
450	+0.058	+0.056	+0.045	+0.043
500	0.038	0.039	0.038	0.026
550	0.013	0.014	0.013	0.010
600	0.031		0.026	0.022
650	0.060		0.049	0.041
700	0.082		0.068	0.055
750	0.092	0.090	0.074	
800	0.084		0.070	0.058
850	0.071		0.057	0.048
900	0.065	0.064	0.051	0.043
950	0.070			
1000		0.080	0.066	0.056

Table IV (cont.)

b. 0.030 mm. $HReO_4$ and 0.060 meq. $SnCl_2$ in 3 ml. 4 F HCl

Time after Preparation	5-25 min.	25-170 min.	$15\frac{1}{2}$-$16\frac{1}{2}$ hrs.	38 hrs.
Wave-length (mμ)	Optical Density d	Optical Density d	Optical Density d	Optical Density d
350	0.062	0.048	0.020	0.127
400	0.158	0.150	0.135	0.165
450	0.121	0.119	0.116	0.112
500	0.075	0.079	0.074	0.069
550	0.024	0.023	0.021	0.020
600	0.058		0.054	0.051
650	0.117		0.110	0.104
700	0.163		0.157	0.147
750	0.182	0.184	0.175	
800	0.162		0.164	0.154
850	0.135		0.136	0.128
900	0.128	0.127	0.122	0.115
950	0.138			
1000		0.160	0.156	0.145

The increase in absorption with time for solutions with excess stannous chloride was not only observed by spectrophotometric methods, but was also evident by visual inspection. These solutions changed color gradually from green to yellow-green to yellow-brown.

Although this proves the solution with 2 meq. $SnCl_2$ per mm. $HReO_4$ contained Re^V, it does not prove that Re^V was the product when only one milliequivalent of stannous chloride was added to one millimol of perrhenic acid. Data in Table V show the absorption of the solution with 2 meq. $SnCl_2$ per mm. $HReO_4$ was just twice the absorption of the solution with only 1 meq. $SnCl_2$ per mm. $HReO_4$. Therefore the 1:1 ratio also produced Re^V. Since the time was previously shown to have little effect, values of optical densities in Table V were either readings at 5-25 minutes after preparation of the solutions, or at 25-170 minutes, or an average in cases where there was a (small) difference. The stannous chloride used had only 0.5 F HCl, but the acidity reached 4 F immediately after mixing and was greater than 4 F always in the phase containing the rhenium solution. The agreement of the data show that no objectionable effect resulted due to influence of acidity.

Although the data just given are consistent, they are not the best for determining the extinction coefficients

Table V

Comparison of Light Absorption for Solutions with $SnCl_2$(meq.):$HReO_4$(mm.) 1:1 and 2:1

Wave-length (mμ)	Optical Density 0.030 mm. $HReO_4$ + 0.030 meq. $SnCl_2$ d	Optical Density 0.030 mm. $HReO_4$ + 0.060 meq. $SnCl_2$ d	$\frac{\text{d 2:1 ratio}}{\text{d 1:1 ratio}}$
380	0.020	0.115	5.75
390	.040	.140	3.5
400	.052$_5$	.154	2.9
410	.058	.150	2.6
420	.062	.148	2.38
430	.063	.134	2.12
440	.058	.125	2.15
450	.057	.120	2.10
460	.056	.118	2.10
470	.055	.115	2.09
480	.055	.113	2.05
490	.050	.100	2.00
500	.038$_5$	.077	2.05
530	.014	.033	2.35
540	.013	.022	1.69
550	.013$_5$	.023$_5$	1.74
560	.015	.027	1.80
600	.031	.058	1.87
650	.060	.117	1.95
700	.082	.163	1.99
730	.088	.178	2.02
740	.090	.180	2.00
750	.091	.183	2.01
760	.092	.184	2.00
770	.090	.180	2.00
780	.088	.177	2.01
800	.084	.162	1.93
850	.071	.135	1.90
900	.064$_5$	.127$_5$	1.98
920	.064	.130	2.03
940	.068	.135	1.98
950	.070	.138	1.97
960	.071	.142	2.00
980	.075	.150	2.00
1000	.080	.160	2.00

of Re^{V} because the stannous chloride had not been recently standardized and was about 20% less than its initial value. Since this $SnCl_2$ solution was used to prepare both of the solutions just described, this does not change the conclusion that they both contained Re^{V}. In Table VI extinction coefficients for two good experiments with freshly standardized stannous chloride are given. None of the product formed with excess stannous chloride was present, because its absorption is much higher than that of Re^{V} at 550 mμ, Figure 1, but both the Re^{V} solutions agreed beyond 450 mμ. The values for one solution are considered slightly better than for the other because of more accurate standardization of the stannous chloride. Recalculation of the coefficients of the second solution to give best average fit gave 3% difference from the uncorrected values. Browne (25) has shown that absorption of stannous or of stannic in 3-6 F HCl first becomes appreciable for wave-lengths below 330 mμ but that an interaction complex between the two tin valences is formed with significant absorption below 400 mμ. The absorption of perrhenic acid has been shown negligible beyond 330 mμ, Sec. III-3. No attempt was made to analyze results below 350 or 400 millimicrons. For longer wave-lengths the absorption of the stannic chloride and the perrhenic acid was neglected (actually no $HReO_4$ remained after reaction) and the absorption was measured against a blank of 4 F HCl.

Table VI

Extinction Coefficients for Two Re^V Solutions

Wave-length ($m\mu$)	Solution 1 0.0100 F Re^V Extinction Coefficient ϵ	Solution 2 0.010_0 F Re^V Extinction Coefficient ϵ	Solution 2 0.0097 F Re^V (Assumed conc.) Extinction Coefficient ϵ
350	103	35.0	
400	55.6	29.5	30
450	19.9	16.5	17.0
500	11.8	9.6	9.9
550	3.0	3.1	3.2
600	7.0	7.4	7.6
650	13.5	14.0	14.4
700	19.5	19.4	20.0
750	22.0	21.6	22.2
800	21.1	19.8	20.4
850	17.7	16.6	17.1
900	15.4	15.0	15.5
950	16.8	16.6	17.1
1000	19.3	18.7	19.3

A number of other Re^V solutions made with less reliable stannous chloride solutions were found to give absorption curves which could be brought into agreement with the good solutions if correction was made for decrease in the stannous chloride due to gradual air oxidation. These solutions were also considered in preparing a table of the best values for the extinction coefficients of Re^V at various wave-lengths, Table VII, values believed good to 5%. The absorption curve of Re^V in 4 F hydrochloric acid is plotted in Figure 2 from the values in Table VII.

The evidence that a well-defined species is formed rests on the agreement of the absorption for two good solutions, on the observation that doubling the amount of stannous chloride (always less than 2:1 ratio with perrhenic acid) doubled the absorption, and on the fact that all observed curves could be made to coincide if allowance was made for decrease in stannous chloride concentration due to gradual oxidation of old stannous chloride solutions. Since the species was well-defined, suggesting a compound, and since all of its observed properties agreed with those reported for $ReOCl_5^=$ in solution as described in the introduction to this section, it is believed to have been very similar to the solutions for K_2ReOCl_5.

Table VII

Best Value of Extinction Coefficient of Re^V

Wave-length ($m\mu$)	Extinction Coefficient ϵ
400	20
410	19
420	17
425	15
430	16
440	15
450	15.0
460	14.3
470	13.7
480	13.6
490	12.2
500	9.1
510	6.0
520	4.5
530	3.7
540	3.0
550	3.0
560	3.5
570	3.9
580	4.9
590	5.5
600	7.2
650	14.1
700	19.9
730	21.7
740	22.1
750	22.1
760	22.4
770	22.0
780	21.5
800	20.5
850	17.2
900	15.6
920	15.7
940	16.5
950	16.9
960	17.3
980	18.3
1000	19.4
1050	21
1100	20

3. Effect of Oxidizing Agents upon Re^{V}

a. Oxygen

Oxygen was bubbled through 3 ml. of 0.0059 F Re^{V} solution whose concentration was determined from its observed optical densities using Equation 1, Sec. II and the coefficients in Table VII; the solution contained no excess $SnCl_2$ because none of the brown product with high absorption at 550 $m\mu$ was observed. After one minute of oxidation, the light absorption was measured again and found the same. Oxygen was then bubbled through in a fine stream for 35 minutes. The observed optical densities after this indicated a decrease to 0.0034 F Re^{V} with formation of a colorless product of oxidation. Since no Re^{VI} compound stable in solution has been reported, while Re^{VII} is the highest oxidation state and is stable, the product of oxidation was ReO_4^-. This experiment shows that the rate of oxidation was low.

b. Ceric Sulfate

Table VIII shows that the Re^{V} formed by reaction of stannous chloride with perrhenate was completely oxidized to Re^{VII} by ceric sulfate. Experimental variables found to have no effect such as the exact volumes taken are given in the appendix, Supplementary Data to Table VIII.

Table VIII

Analysis of Re^{V} by Ceric Sulfate

Solution number	Meq. Reducing Agent Added	Meq. $Ce(SO_4)_2$ Used	Remarks
1 a)	0.0100	0.0105	
2 a)	0.0105	0.0113	
3 a)	0.0105	0.0110	
3	0.0105	0.0110	
4	0.0149	0.0153	
1	0.0100	0.0105	Bubbled O_2 thru rhenium soln. 1 minute, then added to excess $Ce(SO_4)_2$.
2	0.0102	0.0111	Bubbled O_2 thru 5 min. before adding to excess $Ce(SO_4)_2$.

a) calculated from light absorption data to contain:

1 0.0100 $\underline{F}$ Re^{V}

2 0.0087 $\underline{F}$ Re^{V}, 0.0010 $\underline{F}$ Re^{IV}, 0.0002 $\underline{F}$ $SnCl_2$

3 0.0096 $\underline{F}$ Re^{V}, 0.0005 $\underline{F}$ Re^{IV}, 0.0001 $\underline{F}$ $SnCl_2$

4 0.0064 $\underline{F}$ Re^{V}, 0.0039 $\underline{F}$ Re^{IV}, 0.0027 $\underline{F}$ $SnCl_2$

The Re^{V} solution was added to excess ceric sulfate and the unreacted excess determined by titration with ferrous sulfate to an o-phenanthroline end-point, unless another order of mixing is indicated in Table VIII. Blank experiments showed no serious error due to oxidation of the HCl by the ceric sulfate.

Solution 1 of Table VIII contained Re^{V} with no excess stannous chloride. In the other solutions, a slight excess of stannous chloride was used and some of the yellow-brown lower oxidation state of rhenium was formed. The experiments for these solutions prove merely that all the reducing agent added as stannous chloride was recovered. However later work, Sec. V, showed that the yellow-brown lower oxidation state was Re^{IV} formed in a well-defined species. This work enabled the concentrations of both Re^{V} and Re^{IV} to be determined in these solutions. It is seen from the footnotes to Table VIII that the rhenium was nearly all Re^{V} in most of these solutions. Therefore from the data in Table VIII the Re^{V} was completely oxidized to Re^{VII}.

c. Iodine

Analysis by iodine was done by adding the Re^{V} solution to excess iodine in 3% potassium iodide. The unreacted iodine was determined by titration with thiosulfate to a starch end-point. Table IX contains the results of iodine analysis upon the two good Re^{V} solutions with no excess stannous chloride whose light absorption has

Table IX

Analysis of Re^{V} by Iodine

Solution Number	Meq. Re^{V} Added	Meq. Iodine Used	Remarks
1	0.0100	0.0073	
1	0.0100	0.0093	
1	0.0100	0.0091	
2	0.0194	0.0145	Left colorless solution after titration.

been given in Table VI. Supplementary data are in the appendix. It is seen from Table IX that the Re^{V} was largely, if not completely, oxidized to ReO_4^- by iodine.

d. Potassium Iodate

Analysis by iodate was done by pipetting the rhenium solution under excess iodate, and determining the unreacted excess by addition of potassium iodide followed by titration with thiosulfate. Table X shows that oxidation of Re^{V} to Re^{VII} was complete. The numbering of solutions enables comparison with Table VIII. Since a slight green color remained after mixing the iodate and rhenium solutions and before adding potassium iodide, while the final solution after thiosulfate titration was clear, the reduction product of the iodate was ICl_2^- in the hydrochloric acid furnished by the rhenium solution. (Acidity etc. in Supplementary Data, Appendix.)

e. Mercuric Chloride

Solutions of Re^{V} containing no excess stannous chloride gave a white precipitate with mercuric chloride, and the green color of the Re^{V} disappeared. The reaction is therefore

$$Re^{V} + 2\ HgCl_2 + 4\ H_2O = ReO_4^- + Hg_2Cl_2(s) + 8\ H^+ + 2\ Cl^-. \quad (7)$$

Re^{V} solutions were also instantly decolorized by H_2O_2.

Table X

Analysis of Re^{V} by Potassium Iodate

Solution Number	Meq. Reducing Agent Added	Meq. KIO_3 Used	Remarks
2 a)	0.0105	0.0115	
3 a)	0.0125	0.0132	Colorless after titration.
5 a)	0.0194	0.0180	The mixture of KIO_3 and rhenium solution had a slight color before titration. Solution was clear after titration.

a) calculated from light absorption to contain:

2 0.0087 F Re^{V}, 0.0010 F Re^{IV}, 0.0002 F $SnCl_2$

3 0.0096 F Re^{V}, 0.0005 F Re^{IV}, 0.0001 F $SnCl_2$

5 0.0097 F Re^{V}

4. Effect of Time upon Re^{V}

The light absorption of Re^{V} in 4 F HCl was found to slowly decrease after a period of days. This shows that it cannot have been disproportionating into any colored form of Re^{IV}. Later in this Section observation of disproportionation in 2 F HCl showed intermediate colored compounds. In Section V it is shown that the decrease with time of Re^{V} in 4 F HCl was due to oxidation rather than disproportionation.

5. Oxidation of Re^{V} by Chlorine

Excess chlorine completely decolorized Re^{V} thus forming $Re^{VII}O_4^-$. It was shown that a limited amount of chlorine oxidized part of the Re^{V} to ReO_4^-. Although the Re^{V} was an old solution, no interference was found due to age.

To 2.76 ml. of Re^{V} solution found 0.0036_2 F by light absorption was added 0.24 ml. of 0.031_5 F (0.063 N) chlorine solution in 4 F HCl. The light absorption of the resulting solution showed the Re^{V} to be present in 0.0010_8 F concentration. It was also shown that no colored products formed and that the reaction was finished at least in a minute or so, because measurements at all wave-lengths gave this same Re^{V} concentration for a 10-15 minute period after preparation of the mixture. Finally a test with o-tolidine was made and showed that no unreacted chlorine remained.

On the basis of oxidation to ReO_4^- with the quantities of reactants present, the reaction is

$$\mathrm{Re^{V}} \quad + \quad \mathrm{Cl_2} \quad = \quad \mathrm{Re^{VII}} \quad + \quad 2\ \mathrm{Cl^{-}}. \qquad (8)$$

	Re^{V}	Cl_2	Re^{VII}	$2\ Cl^{-}$
Initial	0.0100 mm.	0.0150 meq.		
Final (calc.)	0.0025 mm.	0	0.0075 mm.	0.0150 mm.

The observed quantity of 0.0032 mm. unreacted Re^{V} agrees satisfactorily with 0.0025 mm. expected.

6. Disproportionation of Re^{V}

It was found that when 0.060 meq. of stannous chloride was added to 0.030 mm. of perrhenic acid to give a mixture at a resultant acidity of 1.9 F HCl, light green Re^{V} was not the final product. Instead, the solution became first yellow and then dark as a black precipitate settled. Upon centrifuging the solution, the precipitate was carried down completely and the colorless supernatant solution found to give no test with mercuric chloride. The lack of color or of formation of a precipitate upon addition of mercuric chloride showed the absence of Re^{V} in the supernatant liquid, as well as the absence of $SnCl_2$.

Some of the clear supernatant liquid was treated with stannous chloride to give a reaction mixture in 4 F hydrochloric acid. A light green color formed, and overnight became yellow in the presence of excess stannous chloride. Hence ReO_4^- was present in the supernatant liquid. But the original reaction mixture contained $HReO_4$ and $SnCl_2$ in just the right proportions to convert all the ReO_4^- to Re^V, and the reaction went to completion because no excess $SnCl_2$ remained. Therefore the black precipitate must have contained some lower valence state of rhenium than Re^V.

The black precipitate did not dissolve in 4.5 F hydrochloric acid, but did largely in 6 F and dissolved completely in 12 F. The solution in 12 F hydrochloric acid could be diluted to 4 F without reprecipitation. These observations are similar to those made for hydrated rhenium dioxide in Sec. V-C. Furthermore, the light absorption of the black precipitate in hydrochloric acid had the qualitative features observed for a solution of rhenium dioxide in hydrochloric acid. The observation that a yellow solution resulted before all of the black precipitate formed shows that the precipitate formed through a colored valence state of rhenium; Re^{IV} of Sec. V-A had this color.

Further similarities to hydrated rhenium dioxide in hydrochloric acid (see Sec. V-D) were observed in analyses of the black precipitate, dissolved in hydrochloric acid, by ceric sulfate and potassium iodate (the same results) or by iodine (lower amount of reducing agent found).

Some of the clear supernatant liquid was treated with stannous chloride to give a reaction mixture in 3 F HCl. Additional brown-black precipitate resulted, showing that disproportionation occurs in 3 F hydrochloric acid.

No influence of temperature upon the stability of Re^V solutions was found because the solution with 0.030 meq. stannous chloride and 0.030 mm. perrhenic acid in 3 ml. of 4 F hydrochloric acid was kept at 55 ± 5 °C for an hour, but had the same light absorption after this treatment as initially.

The critical acidity at which Re^V disproportionates to give hydrated rhenium dioxide and perrhenate is unknown, but must lie between 3 and 4 F hydrochloric acid from the work just described. It appears likely that the slow disproportionation reported by Tribalat (21, 22) was due to acidity somewhat lower than in the present investigation. She reported disproportionation over a period of 24 hours in 4 F hydrochloric acid, while rapid disproportionation was found in the present work in 2 F hydrochloric acid.

As discussed in Sec. IV-1, the acid used in this work was within 5% of 4.0 F, perhaps slightly higher than 4.0. If the acid used in Tribalat's work had been 10% low, or 3.6 F, it might account for slow disproportionation.

7. Summary of the Chemistry of Re^{V}

Light green Re^{V} is formed quickly in 4 F hydrochloric acid if less than two equivalents of stannous chloride is added to one mol of perrhenic acid. Further addition of stannous chloride slowly forms a yellow-brown state later identified as Re^{IV}. The Re^{V} is probably present as a compound since it may be made reproducibly with the same light absorption in different experiments. Solutions of Re^{V} may be kept for hours, and it is not affected by heating an hour at 55 °C. Re^{V} is slowly oxidized by treatment with oxygen, and completely oxidized to perrhenate by ceric sulfate, potassium iodate, or hydrogen peroxide. It is also largely oxidized to perrhenate by iodine, and it reduces mercuric chloride to mercurous chloride. Re^{V} in 4 F hydrochloric acid does not disproportionate, though disproportionation occurs in 1.9 or 3 F hydrochloric acid. Chlorine oxidizes Re^{V} rapidly and completely to ReO_4^-.

V. THE CHEMISTRY OF RHENIUM (IV)

A. Re^{IV} Prepared from Perrhenate with Excess Stannous Chloride

Hölemann (18) found that it was possible to potentiometrically titrate perrhenate to form Re^{IV} if thiocyanate was present, but in the absence of CNS^- it was not possible to determine by the potential whether Re^{IV} was formed. This was in 4.3_5 F hydrochloric acid at 80 °C under nitrogen.

Tribalat (21, 22, 23) found it was possible to continue reduction of perrhenate through Re^V to Re^{IV} with a third equivalent of stannous chloride if portions of the stannous chloride were added slowly over a period of hours. The same results were obtained at higher acidities. In 4 F hydrochloric acid, she reported slow disproportionation of Re^V into ReO_4^- and Re^{IV}. In 1 F hydrochloric acid, the disproportionation of Re^V was accelerated by the formation of hydrated rhenium dioxide, which precipitated with the first addition of stannous chloride. In this lower acidity, reduction to Re^{IV} was not quantitative.

In the present research, it is found that addition of more than two equivalents of stannous chloride per mol of perrhenic acid gives a yellow-brown solution. The absorption of the solutions with 3, 4, or 5 equivalents of stannous chloride per mol of perrhenate increases gradually over a period of hours, but finally reaches the same limiting value in all cases. This shows that Re^{IV} is the product, that its rate of formation is low, and that disturbing influences such as possible change in form or oxidation have no serious effect.

It is found that definite values can be given for the absorption of the Re^{IV}, indicating a well-defined species. Re^{IV} is oxidized completely to perrhenate by ceric sulfate or potassium iodate, and is at most but slightly affected by iodine. It is instantly decolorized by hydrogen peroxide, but does not appear to react with mercuric chloride.

Analysis of the absorption data of an old solution of Re^{IV} before and after the addition of more stannous chloride indicates the likelihood that a slight observed decrease in concentration of the colored Re^{IV} after a long time is due to conversion of the colored Re^{IV} into a colorless or weakly absorbing form rather than into ReO_4^- by oxidation. Similar experiments for Re^{V}, however, show that in this case the change is to be attributed to oxidation and not to disproportionation into a colorless form of Re^{IV} and ReO_4^-.

By analytical data, it is shown that chlorine oxidizes Re^{IV} rapidly, and that the product of oxidation is Re^{VII}, not Re^{V}.

1. Preparation of Re^{IV} from Perrhenate

The solutions were prepared in the same way as described in Section IV-2, with the difference that larger amounts of stannous chloride were used in order to form Re^{IV} and not just Re^{V}. The final mixture of perrhenic acid, stannous chloride, and hydrochloric acid had volume 3 ml. and was 0.010_0 F in rhenium, in 4 F hydrochloric acid. Unless stated otherwise, the acidity in the mixture of perrhenic acid and hydrochloric acid was 3-4 F before adding the stannous chloride in 6-4 F hydrochloric acid to give a resultant of 4 F.

2. Light Absorption of Re^{IV}

It has been mentioned in Section IV-2 that the light absorption of solutions with excess stannous chloride beyond the ratio 2 meq. $SnCl_2$ per mm. $HReO_4$ increased for hours, and that the solutions changed color initially from green to yellow-green and later to yellow-brown. The absorption within the first hour has been given in Figure 1 for solutions with ratios of 2.5:1 milliequivalents of stannous chloride per millimol of rhenium, and also 3:1 and 4:1. After 15 hours, the absorption was found to remain constant with time for a period of several days in the closed cells.

Figure 3 shows agreement between a solution with a 3:1 ratio of stannous chloride to perrhenic acid, and for a solution with 4:1 ratio. The data for the 3:1 ratio were taken on a 22 hour old solution, those for the 4:1 ratio on a 64 hour old solution. Comparison of these two is justified because of experiments showing the constancy of optical densities from 15 hours to several days. Agreement was also found for other solutions with a 3:1 ratio and for a solution with a 3.74:1 ratio. This proves that the product is Re^{IV} in a well-defined species.

The absorption curve for a solution with 4:1 ratio is also included in Figure 3 to show the effect of low acidity. The perrhenic acid was in 2.4_7 $\underline{F}$ hydrochloric acid before adding the stannous chloride, and an incipient brown precipitate was noticed at the interface before mixing the reactants thoroughly, although no precipitate settled from the solution.

Optical density data for other solutions of 0.030 millimols of rhenium with 0.090 milliequivalents of stannous chloride were examined, and the presence of a small amount of Re^V was indicated by the fact that the absorption curves were slightly lower than the curve for 0.030 millimols of rhenium and 0.121 milliequivalents of stannous chloride at 550 mμ where Re^V is non-absorbing, but better agreement was obtained at longer wave-lengths where the absorption of Re^{V} and Re^{IV} is more comparable, Figures 1 and 3. The reason for this is not known, but it could be due to very low rate of reaction of stannous chloride and Re^{V} in equivalent quantities near the end of the reaction. The possibility was considered that the stannous chloride decreased somewhat in concentration after a long time, either due to leakage of air or to photochemical reaction of the stannous chloride with the 4 F hydrochloric acid. Experiments with ceric sulfate to be described showed that complete recovery of the reducing agent added was found even after 64 hours, which shows that oxidation was not the cause of the observed low light absorption. Another possibility is change of Re^{IV} into another less absorbing form, but this does not easily explain why the assumption of some Re^{V} gave agreement with the observed absorption with the total rhenium being 0.0100 F as required.

Absorption data were taken on four solutions of Re^{IV} prepared with the equivalent amounts of reactants and with the acidity in both the perrhenic acid and the stannous chloride 4 F. From data in Table VII, tables of the optical densities for Re^{V} solutions at 500, 550, 600,..., 1000 millimicrons were prepared, and proved very useful. The extinction coefficients of Re^{IV} were taken from the solution with 0.030 mm. perrhenic acid and 0.121 meq. stannous chloride assuming that after 64 hours with the excess stannous all the rhenium was Re^{IV}.

For the four good solutions, the concentration of Re^{IV} was estimated from the absorption at 550 and 600 mμ where Re^{V} has low absorption. At longer wave-lengths a first approximation to the Re^{V} concentration could be made. After finding approximate concentrations in this way, the concentration of Re^{IV} at each of ten wave-lengths was calculated for various assumed Re^{V} values differing by 0.0001 F (using the tables of Re^{V} optical densities), and the best fit was taken as that Re^{V} value which gave the smallest average deviation for the Re^{IV} concentrations.

Table XI shows the results of these calculations. For all solutions, the formal concentration of Re^{V} plus Re^{IV} came out 0.0100 F with 80-95% of the rhenium as Re^{IV}. Data for Solution 1 of Table XI are given at two times, 6 hours after preparation and after 22 hours. Although reaction was not complete after 6 hours, the absorption change was negligible during the 15-30 minutes required to measure the optical densities. As expected, the Re^{V} decreases while the Re^{IV} increases with time, data for Solution 1.

For each of the wave-lengths, the calculated concentration was compared with the average of the calculations,

Table XI

Concentration of Re^{IV} in Mixtures with Re^{V}

Wave-length (mμ)	ε Re^{IV}	Solution 1 22 hr. old. F Re^{IV} for 0.0007 F Re^{V}	Solution 1' 6 hr. old. F Re^{IV} for 0.0011 F Re^{V}	Solution 2 64 hr. old. F Re^{IV} for 0.0013 F Re^{V}
500	180	0.00966	0.00895	0.00916X
550	73.9	0.00930	.00891	.00823
600	81.2	.00940	.00876	.00831
650	55.0	.00951	.00889	.00859
700	38.6	.00950	.00900	.00862
750	36.8	.00925	.00865	.00815
800	33.7	.00940	.00881	.00819
850	31.1	.00939	.00886	.00794
900	33.4	.00940	.00892	.00809
1000	19.8	.00945	.00935	.00828
Average		0.00943	0.00891	0.00827
Average Deviation		8.4	11.6	16.3

Wave-length (mμ)	Solution 3 64 hr. old. F Re^{IV} for 0.0017 F Re^{V}	Solution 4 92 hr. old. F Re^{IV} for 0.0013 F Re^{V}
500	0.00872X	0.00922X
550	.00767	.00805
600	.00785	.00816
650	.00806	.00859
700	.00777	.00826
750	.00759	.00785
800	.00771	.00805
850	.00743	.00781
900	.00758	.00800
1000	.00773	.00813
Average	0.00771	0.00810
Average Deviation	12.7	16.4

X indicates value omitted from the average and where trends were found, small corrections were made to get the extinction coefficients at 550, 600,..., mμ, Table XII, values believed good to a few percent. The value at 450 mμ is 20%, at 500, 5-10%. Other values to 5% were estimated by comparison with less reliable solutions in which the perrhenic acid was in less than 4 F hydrochloric acid before adding the stannous chloride. The absorption curves of Re^{IV} and Re^{V} are given in Figure 4.

3. Effect of Oxidizing Agents upon Re^{IV}

a. Oxygen

Oxygen was bubbled through a Re^{IV} solution for 35 minutes, after which the optical densities decreased about 20%. No Re^{V} had been present because the solution was made with excess stannous chloride (4:1 ratio). It is not possible to prove rigorously that the Re^{IV} in solution form was oxidized because the solution was one for which incipient precipitation was observed because of low initial acidity; the experiment shows that a long time would be required for complete oxidation.

Table XII

Best Values of Extinction Coefficients of Re^{IV}

Wave-lengths ($m\mu$)	Extinction Coefficient ϵ
450	500
500	195
520	110
550	73.5
560	65
570	62.5
580	64
600	81.2
620	78
630	70
650	56.6
670	45
700	39.3
720	39.5
750	36.0
770	35
800	33.5
850	30.5
880	30
900	33.1
920	33.5
950	32.5
970	27
1000	19.8

b. Ceric Sulfate

Analysis by ceric sulfate was done in a manner similar to that described in Sec. IV-3-b. Table XIII contains the results of these analyses. The rhenium solution was pipetted under the surface of the ceric sulfate unless noted otherwise. The concentrations of the colored Re^{IV} and Re^{V} were determined by light absorption, using the best fit method described in Sec. V-2, at a time when the absorption was not changing rapidly, and the ceric sulfate analyses were made directly after the absorption measurements.

The a) experiments for Solutions 1-3 and 5 of Table XIII prove that all the reducing agent added as stannous chloride to form the colored rhenium compounds was recovered in the ceric sulfate analysis. From the supplementary data in the appendix for Table XIII, the last three solutions were 64 hours old when analyzed, so this proves that no leakage of air into the cell or other oxidation occurred over this length of time. The numbering of solutions is the same as in Table XI where their light absorption was treated. Solution 5 is the good Re^{IV} solution prepared with excess stannous chloride whose extinction coefficients are in Table XI.

It was desired to remove the small amounts of stannous chloride remaining in cases of incomplete reaction and thus verify the sum of the milliequivalents of Re^{IV} and Re^{V} found by light absorption. Experiments on 0.005 F stannous chloride solutions in 4 F hydrochloric acid showed that the stannous chloride was not quite all oxidized to stannic after bubbling oxygen through three milliliters of the solution for one minute, but that oxidation was complete after 5 minutes. It has been shown in Sec. IV-3-a that Re^{V} is only slowly oxidized, and in Sec. V-3-a that Re^{IV} is also not rapidly oxidized by oxygen. Data for two Re^{V} experiments in Table VIII of Sec. IV-b show that the Re^{V} was not appreciably affected after 5 minutes treatment with oxygen. The b) experiments in Table XIII, this section, for Solutions 1 and 1' show that the milliequivalents of reducing agent found after 5 minutes oxidation is just that expected for complete oxidation of the stannous chloride calculated present; the amount of stannous chloride was computed by difference from the amount added and the milliequivalents of Re^{IV} and Re^{V} observed by light absorption. These experiments show the presence of stannous chloride in these solutions, and also agree with the concentrations of Re^{IV} with Re^{V} found by light absorption.

Oxidation of stannous chloride in the rhenium solutions was not complete after only one minute treatment with oxygen, Solution 3b) while some of the rhenium was oxidized after 4 hours exposure to air, b) experiments, Solutions 3, 5.

c. Iodine

Analysis by iodine was done by adding the rhenium to excess iodine in potassium iodide as in Sec. IV-3-c. The data in Table XIV, (supplementary data are in the appendix), show that the observed small effect of iodine agrees roughly with the assumption that all the Re^V and stannous chloride present were oxidized, and the data show that the iodine had little if any effect on the Re^{IV}. This was also shown by the yellow color of the Re^{IV} remaining in the solution after titration of the excess iodine with thiosulfate.

d. Potassium Iodate

An indication that Re^{IV} is oxidized by iodate has already been obtained for Re^V solutions containing some Re^{IV}, Table X, Sec. IV-3-d. In another experiment, 1.00 ml. of a 12 hr. old solution whose absorption showed 0.0276 meq. Re^{IV}, 0.0016 meq. Re^V, and no $SnCl_2$, was added to 2.74 ml. of solution containing 0.0624 meq. of potassium iodate, giving 1.07 $\underline{F}$ HCl due to the Re^{IV} solution. After addition of excess iodide, it was found by thiosulfate titration that 0.0263 meq. of the iodate

Table XIII

Analysis of Re^{IV} by Ceric Sulfate

Solution Number	Meq. Reducing Agent Added	Meq. $Ce(SO_4)_2$ Used	Remarks
1 a)	0.0149	0.0151	
2 a)	0.0300	0.0300	
3 a)	0.0300	0.0298	
5 a)	0.0403	0.0398	
1 b)	0.0146	0.0144	Bubbled O_2 5 min., added $Ce(SO_4)_2$.
1 b)	0.0117	0.0118	"
1' b)	0.0145	0.0146	"
3 b)	0.0265	0.0289	Bubbled O_2 thru solution 1 minute, added $Ce(SO_4)_2$.
3 b)	0.0132	0.0115	Exposed to air 4 hrs., added to $Ce(SO_4)_2$.
5 b)	0.0150	0.0125	

a) calculated from light absorption data to contain:

1 0.0094_3 $\underline{F}$ Re^{IV}, 0.0007 $\underline{F}$ Re^{V}

1' 0.0089_1 $\underline{F}$ Re^{IV}, 0.0011 $\underline{F}$ Re^{V}, 0.0005 $\underline{F}$ $SnCl_2$

2 0.0082_7 $\underline{F}$ Re^{IV}, 0.0013 $\underline{F}$ Re^{V}, 0.0013 $\underline{F}$ $SnCl_2$

3 0.0077_1 $\underline{F}$ Re^{IV}, 0.0017 $\underline{F}$ Re^{V}, 0.0017 $\underline{F}$ $SnCl_2$

5 0.0100 $\underline{F}$ Re^{IV} , 0.0051 $\underline{F}$ $SnCl_2$

b) Meq. Reducing Agent Added assumes no $SnCl_2$ left had been used. When the brown Re^{IV} was added to the iodate, the color faded to light green, showing the product of reduction was ICl_2^-.

e. Mercuric Chloride

There is indication that Re^{IV} may not be affected by mercuric chloride, because a solution prepared with excess stannous chloride and therefore containing no Re^{V}, was exposed to the air four hours, after which it gave no mercuric chloride test.

4. Effect of Time upon Re^{IV}

There was some indication that Re^{IV} is converted into a weakly absorbing form after days. For Re^{V}, however, observed decreases in the absorption were shown due to oxidation.

The light absorption of a 3½ week old Re^{IV} solution showed only half the Re^{IV} expected; some Re^{V} was present because the solution had been made with only the equivalent amounts of reactants. Additional stannous chloride was added and the absorption indicated that the Re^{V} decreased and more Re^{IV} formed. If ReO_4^- had been present due to air oxidation, an initial increase in Re^{V} would have been expected, followed by gradual formation of Re^{IV}.

Table XIV

Effect of Iodine upon Re^{IV}

Solution Number	Meq. Reducing Agent Present			Meq. Re^{V} $SnCl_2$ Present	Meq. I_2 Used	Remarks
	Re^{IV}	Re^{V}	$SnCl_2$			
1	0.0148	0.0007	0.0000	0.0007	0.0017	
1	0.0085	0.0004	0.0000	0.0004	0.0010	
1	0.0113	0.0006	0.0000	0.0006	0.0009	
1'	0.0134	0.0011	0.0004	0.0015	-0.0005	
5	0.0300	0.0000	0.0103	0.0103	0.0075	Yellow color left after titration.
5	0.0120	0.0000	0.0041	0.0041	0.0026	
1	0.0142	0.0007	0.0000	0.0007	0.0000	Bubbled O_2 5 min.

Re^{V} was found to decrease in concentration after a long time. A 0.0082 F solution was 0.0059 F after 138 hours according to its light absorption. Since this solution was in a cell capped with a rubber policeman, this could be attributed to air leakage. However, a Re^{V} solution initially 0.010 F and kept always in a cell closed with a ground joint cover was 0.0085 F after 21 days. If the loss of millimoles of Re^{V} were due to disproportionation,

$$3\ Re^{V} = 2\ Re^{IV} + Re^{VII}, \qquad (9)$$

the amount of ReO_4^- in the solution would be one-third the observed loss of Re^{V}, whereas if the loss were due to oxidation, all the Re^{V} would be converted into Re^{VII}.

In order to determine the amount of $Re^{VII}O_4^-$ in the solution, more stannous chloride was added and the light absorption measured. As work described earlier shows, the initial reaction of ReO_4^- and stannous is immediate formation of Re^{V},

$$Re^{VII} + Sn^{II} = Re^{V} + Sn^{IV}, \qquad (10)$$

followed by formation of Re^{IV} over a time of 15 hours if excess stannous is present,

$$2\ Re^{V} + Sn^{II} = 2\ Re^{IV} + Sn^{IV}. \qquad (11)$$

A 1.50 ml. portion of the 0.0085 F Re^{V} was left in the cell and 1.40 ml. of 4 F hydrochloric acid added, after which light absorption gave 0.0038_2 F Re^{V} (0.0044 expected if no oxidation occurred when the cell was opened). Then 0.10 ml. of 0.0480 F stannous chloride in 4 F hydrochloric acid was added to the 2.90 ml. The light absorption after 3¼ hours showed 0.0046 F Re^{V} and 0.0004_3 F Re^{IV}. Table XV contains the quantities of Re^{V} and Re^{IV} expected under the assumptions a) all of the 0.0039 mm. loss of Re^{V} from the 1.50 ml. of 0.0100 F rhenium solution was due to air oxidation, b) all of the loss was due to disproportionation into colorless forms of Re^{IV}, but addition of stannous chloride caused the ReO_4^- present to give colored Re^{IV}, and c) the decrease from 0.0100 F Re^{V} to 0.0085 F in the stock solution was due to disproportionation, but the rest of the loss was due to air oxidation when the cell was opened. Table XV shows that only the assumption of all loss due to air oxidation is compatible with the observed absorption.

The experiment was continued by adding another 0.10 ml. of 0.0480 F stannous chloride to the 3 ml. at 16 hours and measuring the absorption immediately afterward and again after another 27½ hours. The calculations in Table XV show that the absorption at these times also requires the assumption that all the Re^{V} loss was due to

Table XV

Effect of Stannous Chloride upon Re^{V} Solution

Time (hr.)	0	3¼	16	43½
Re^{V} observed (mm.)	0.0111	0.0138	0.0127	0.0046
Re^{V} a) (mm.)	0.0111	0.0150-0.0132	0.0132	0.0036+
Re^{V} b) (mm.)	0.0111	0.0124-0.0054	0.0054	0.0000
Re^{V} c) (mm.)	0.0111	0.0135-0.0087	0.0087	0.0000
Colored Re^{IV} Observed (mm.)	0	0.0013	0.0025	0.0107
Re^{IV} a) (mm.)	0	0.0000-0.0018	0.0018	0.0114-
Re^{IV} b) (mm.)	0	0.0000-0.0070	0.0070	0.0124
Re^{IV} c) (mm.)	0	0.0000-0.0048	0.0048	0.0135
Re^{V} plus colored Re^{IV} observed (mm.)	0.0111	0.0151	0.0152	0.0153
Re^{V} Re^{IV} a) (mm.)	0.0111	0.0150	0.0150	0.0150
Re^{V} Re^{IV} b) (mm.)	0.0111	0.0124	0.0124	0.0124
Re^{V} Re^{IV} c)	0.0111	0.0135	0.0135	0.0135

Table XV (cont.)

a) Calculated assuming all loss of Re^{V} due to air oxidation, and solution initially 0.0111 mm. Re^{V}, 0.0039 mm. Re^{VII}.

b) Calculated assuming all loss of Re^{V} disproportionation, solution initially 0.0111 mm. Re^{V}, 0.0013 mm. Re^{VII}, 0.0026 mm. colorless Re^{IV}.

c) Calculated assuming 0.0022 mm. loss of Re^{V} due to disproportionation, 0.0017 mm. loss due to air oxidation. Assumed initially 0.0111 mm. Re^{V}, 0.0024 mm. Re^{VII}, 0.0015 mm. colorless Re^{IV}.

oxidation. It is not clear whether the oxidation was due to slow leakage of air into the cell over a period of weeks, or whether due to photochemical or other reaction. The data prove finally that Re^{V} in 4 F hydrochloric acid is perfectly stable with respect to disproportionation.

5. Oxidation of Re^{IV} by Chlorine

A Re^{IV} solution was prepared with excess stannous chloride and therefore contained no Re^{V}. Preliminary experiments showed that the yellow-brown color was rapidly decolorized by excess chlorine, therefore forming ReO_4^- with the excess Cl_2. Analysis with iodine showed that the solution in 4 F hydrochloric acid had less than 0.003 milliequivalents per milliliter of stannous; the Re^{IV} is known by Sec. V-3-c to undergo little reaction with I_2. Analysis by ceric sulfate confirmed this amount of stannous with 0.010_0 F Re^{IV}. A 0.50 ml. portion of the solution was treated with 0.005 meq. of chlorine. The solution was still yellow-brown, but when potassium iodide and starch solution were added, no starch-iodine color developed, showing that the chlorine had reacted completely. Two possible explanations for the reaction of the chlorine are

$$2\ Re^{IV} + Cl_2 = 2\ Re^{VII} + 2\ Cl^- . \qquad (12)$$

Initial	0.005 mm.	0.005 meq.	0	
	0	0	0.005 mm.	0.005 mm.

and

$$2\ \mathrm{Re}^{IV} + 3\ \mathrm{Cl}_2 = 2\ \mathrm{Re}^{VII} + 6\ \mathrm{Cl}^- . \qquad (13)$$

Initial	0.005 mm.	0.005 meq.	0	
Final	0.0033 mm.	0	0.0017	0.005 mm.

On the basis of Reaction 12, the solution would contain 0.005 mm. Re^V and no Re^{IV} after reaction with chlorine, while for Reaction 13 it would still contain considerable Re^{IV}. The observation that the color did not decrease greatly already favors Reaction (13). An analysis was done with iodine since it is known that Re^V is largely oxidized to Re^{VII} by iodine, Sec. IV-3-c, while Re^{IV} is but little affected, Sec. V-3-c. Excess potassium iodate was added to the mixture of rhenium solution and chlorine in 3% potassium iodide. Titration with thiosulfate showed that 0.0032 meq. of iodine had been used, best explained by slight reaction of the Re^{IV} rather than oxidation by iodine of 0.005 mm. Re^V to Re^{VII}. Therefore the experimental observations are best explained on the basis of oxidation of Re^{IV} directly to Re^{VII} with no intermediate formation of Re^V.

6. Summary of the Chemistry of Re^{IV} from Perrhenate

Addition of 3 or more equivalents of stannous chloride to perrhenic acid forms yellow-brown Re^{IV} in a well-defined species. The solutions are stable for hours. Re^{IV} is oxidized completely to perrhenate by ceric sulfate or potassium iodate, but is not much affected by iodine. Chlorine oxidizes Re^{IV} rapidly, forming Re^{VII}, not Re^{V}. There is some indication that after standing for days the yellow Re^{IV} is somewhat converted into a colorless form. Change after days for Re^{V} was due to oxidation, not disproportionation.

B. Re^{IV} Prepared from Perrhenate with Chromous Chloride or Titanous Chloride

Turkiewicz (14) reported that reduction of perrhenate with chromous chloride in 4.4 F hydrochloric acid formed Re^{IV}. Hölemann (19) found by potentiometric study that chromous sulfate in sulfuric acid reduced perrhenate to Re^{IV}. Chromous in chloride was more satisfactory because the chromous reduced the sulfuric acid to sulfur dioxide. Only in strong acid could intermediate Re^{VI} or Re^{V} be identified with chromous.

Tribalat (21, 22) reported that the first drop of chromous chloride added to perrhenate in 4 F hydrochloric acid gave Re^{IV}. Titanous chloride gave the same result more slowly. Eventual formation of a black precipitate similar to the precipitate formed by disproportionation of Re^{V} was reported. Chromous chloride in 10 F hydrochloric acid was found by potentiometric study to form Re^{III}.

In the present work, analysis by ceric sulfate proved that the yellow-brown solution obtained by reduction of perrhenate in 4 F hydrochloric acid by chromous chloride contained Re^{IV}. A yellow-brown product was also observed when titanous chloride was added to perrhenate.

The method used in studying the reduction of perrhenic acid by chromous chloride was to add excess chromous, destroy the excess by bubbling oxygen through the solution 1 or 2 minutes, and determine the reducing agent formed, by ceric sulfate. The chromous chloride was prepared by shaking 0.1 F $CrCl_3$ in 4 F hydrochloric acid with 30 mesh zinc in a loosely stoppered vessel. Known volumes of the resulting light blue solution were pipetted under excess ceric sulfate, showing that the solutions were 0.035-0.055 N in reducing agent. After oxygen was bubbled through the chromous solution for 1 to 2 minutes, titration with ceric sulfate to an o-phenanthroline end-point showed only 0.0005-0.0010 meq. of chromous left unoxidized. A similar treatment with air was not satisfactory.

The experiments in Table XVI prove that Re^{IV} was the product when 2 or 3 times excess chromous chloride was added to perrhenic acid in 4 F hydrochloric acid. The excess $CrCl_2$ was removed by 1 or 2 minutes treatment with oxygen as indicated in the supplementary data in the

Table XVI

Formation of Re^{IV} by Chromous Chloride with Perrhenate

Expt. No.	Meq. $CrCl_2$ added	Meq. $Ce(SO_4)_2$ added	Meq. $Ce(SO_4)_2$ used	Meq. HReO present	% error based on theoretical reduction to Re^{IV}
1	0.056	0.0231	0.0155	0.0150	+3
2	0.090	0.0500	0.0295	0.0300	-2
3	0.22	0.0273	0.0273	0.0290	-6
4	0.22	0.0273	0.0273	0.0290	-6
5	0.22	0.0462	0.0289	0.0290	0
6	0.13	0.0273	0.0273	0.0290	-6
7	0.13	0.0237	0.0237	0.0290	-18
8	0.22	0.0282	0.0282	0.0290	-3
9	0.13	0.0300	0.0286	0.0290	-1
10	0.22	0.0924	0.0750	0.0756	-1
11	0.22	0.0750	0.0721	0.0756	-5
12	0.22	0.0695	0.0659	0.0756	-8
13	0.22	0.0831	0.0715	0.0756	-5
14	0.22	0.0761	0.0694	0.0756	-8
15	0.22	0.0680	0.0680	0.0756	-10
16	0.22	0.0660	0.0645	0.0720	-10
17	0.22	0.0655	0.0655	0.0720	-9
18	0.22	0.0660	0.0660	0.0720	-8

appendix. Titration with ceric sulfate was to a direct o-phenanthroline end-point if the meq. $Ce(SO_4)_2$ added is the same as that used. Otherwise excess ceric sulfate was added and the excess determined with ferrous sulfate. The experiments are not very reproducible, running 5% less than theoretical formation of Re^{IV}; some oxidation of the Re^{IV} by O_2 may have occurred.

Addition of 0.1 N titanous sulfate in 4 F hydrochloric acid to perrhenic acid solutions formed yellow-brown products. Attempts with oxygen or with iodine to remove the excess titanous ion and leave only the Re^{IV} were not successful.

It is believed that this form of Re^{IV} is substantially identical with the product formed by excess stannous chloride and perrhenate.

C. $Re^{IV}Cl_6^=$ Prepared from Perrhenate by Heating with Iodide

A study of the chemical reactivity of potassium rhenichloride (potassium hexachlororhenate (IV)) proved it markedly different from the reactive Re^{IV} prepared by stannous chloride reduction of perrhenate.

1. Preparation of K_2ReCl_6

Potassium rhenichloride was prepared by reduction with potassium iodide of two grams of potassium perrhenate in concentrated hydrochloric acid, Inorganic Syntheses (26)

$$12\ Cl^- + 2\ ReO_4^- + 9\ I^- + 16\ H^+ = 2\ ReCl_6^= + 3\ I_3^- + 8\ H_2O. \quad (14)$$

The product contained no free iodine as shown by a test with starch solution and with carbon tetrachloride. A test with sodium nitrite solution and carbon tetrachloride showed the absence of iodide.

2. Qualitative Tests for K_2ReCl_6

Microscopic examination of the preparation of K_2ReCl_6 showed small yellow-green crystals having isotropic extinction and octahedral habit. This salt has the K_2PtCl_6 crystal structure (27).

It was found that cesium chloride was a good reagent for qualitative and quantitative estimation of rhenichloride. By working in a small centrifuge cone, it was possible to observe the light yellow Cs_2ReCl_6 precipitate when 0.5 F cesium chloride was added dropwise to 0.05 ml. of 0.005 F potassium rhenichloride solution.

Addition of silver nitrate solution to 0.05 F K_2ReCl_6 in 4 F hydrochloric acid gave a mixture of white silver chloride and red-brown Ag_2ReCl_6 precipitates. Nitron acetate reagent gave a yellowish precipitate; the hydrochloric acid was kept less than 0.5 F to prevent chloride interference. The reaction of nitron with $ReCl_6^=$ was previously reported by Geilmann and Wrigge (28), and excludes the use of nitron as a characteristic reagent in solutions possible containing both $ReCl_6^=$ and ReO_4^-, since ReO_4^- also gives a precipitate, Sec. III-2.

The $ReCl_6^=$ in a 0.005 F solution in 4 F hydrochloric acid gave only a faint brown color with silver nitrate, and the nitron test was indefinite for this concentration.

No test was obtained with potassium ferrocyanide solutions, with or without addition of ammonium hydroxide before or after the test.

3. Analysis of K_2ReCl_6

A check of the purity of the K_2ReCl_6 was made in two ways: the amount of reducing agent, Re^{IV} plus any impurity, was determined, and the amount of rhenichloride ion was determined.

The Re^{IV} in the preparation was determined with hot ceric sulfate by the procedure of Geilmann and Wrigge (29),

$$ReCl_6^= + 3\ Ce^{IV} + 4\ H_2O = ReO_4^- + 3\ Ce^{III} + 6\ Cl^- + 8\ H^+ \quad (15)$$

A quantity of 24.71 mg. of potassium rhenichloride was warmed with 8 ml. of 0.05 F ceric sulfate in 0.5 F sulfuric acid with 4 ml. added 3 F sulfuric acid. The mixture was kept gently boiling for 20 minutes, then the excess ceric was titrated by ferrous sulfate, giving 0.125 milliequivalents used. In a blank, an amount of chloride equal to that of the $ReCl_6^=$ was heated with 0.275 meq. Ce^{IV} in equal volume and found to consume 0.003 meq. of ceric sulfate. The corrected value for the K_2ReCl_6 is then 0.122 meq., theory 0.120 meq.

To a 0.30_0 ml. solution containing 0.0505 F K_2ReCl_6 was added 0.10 ml. of 0.5 F cesium chloride solution. The resulting heavy Cs_2ReCl_6 was centrifuged, the supernatant tested with more cesium ion and removed. The precipitate was washed by stirring with 0.5 ml. of concentrated hydrochloric acid, and dried an hour at 120 °C after removing the liquid. Its weight was 10.0 mg., theory 10.1 mg. (12).

4. Light Absorption of K_2ReCl_6

Table I, Section II, contains data which prove the stability of K_2ReCl_6 in 4 F hydrochloric acid in a closed cell. Extinction coefficients calculated from optical density data for a 0.05 F solution in 4 F hydrochloric acid are plotted in Figure 5. Within the errors for the weakly-absorbing solutions, the extinction coefficients were independent of concentration for 0.01-0.05 F rhenichloride in 4-6 F hydrochloric acid. For comparison, the data of Schmid (30) are also plotted. Only rough agreement is found; his data show only one measurement between 600 and 700 mμ. The measurements of Schmid shown were for 0.04 F K_2ReCl_6 in 3 F acid; other data are given in 6 F acid (30) with no improvement.

5. Effect of Oxidizing or Reducing Agents upon K_2ReCl_6

Potassium rhenichloride is known to be resistant to reaction with oxidizing or reducing agents. The Noddacks (12) report that acidic solutions are very stable against H_2O_2. Geilmann and Wrigge (29) found complete oxidation by ceric sulfate in 1 F sulfuric acid only after 20 minutes' boiling. Potassium permanganate in sulfuric acid is not decolorized by rhenichloride (31). The acidic solutions are very resistant towards dichromate or ferric ions, though gradually some oxidation occurs upon heating (12, 29).

The effect of amalgamated zinc or of molten potassium is described in this thesis in Section VI. In the following, it is shown that none of the following affect K_2ReCl_6 solutions at room temperature: oxygen, stannous chloride, ceric sulfate, ferrous or ferric ions, chlorine, iodine or potassium iodide, potassium iodate, cupric or cuprous ions.

a. Oxygen

Measurement of the absorption of a solution exposed to air showed that not more than 5-10% of the rhenichloride could have reacted. Concentrations and other experimental conditions are in Table XVII, Experiment 1.

b. Stannous Chloride

Measurement of the absorption showed not more than 5-10% reaction, Experiment 2, Table XVII.

c. Ceric Sulfate

Although hot ceric sulfate quantitatively oxidizes K_2ReCl_6 after 20 minutes boiling, Sec. V-C-3, rhenichloride is not affected by standing one or two minutes with ceric sulfate at room temperature. The ceric sulfate added was titrated with ferrous sulfate to an o-phenanthroline end-point and found to be completely recovered, Table XVII, Experiments 3-5.

d. Ferrous or Ferric Ions

The preceding experiments also indicate that $ReCl_6^=$ does not react at an appreciable rate with ferrous or ferric ions, since the end-points in the ceric titration were stable. Rhenichloride and ferric gave a strong red color with thiocyanate, though $ReCl_6^=$ alone did not affect SCN^-, Table XVII, Experiment 6.

e. Chlorine

The light absorption showed not more than 5-10% reaction. Strong tests were obtained for the unreacted

Table XVII

Effect of Oxidizing or Reducing Agents upon K_2ReCl_6

Expt. No.	Agent Used	Concentrations in Mixture			Total Volume (ml.)	Observations
		Agent F	K_2ReCl_6 F	Acid F		
1	O_2	(air)	0.010	4 (HCl)	3.0	Absorption same after 11 hrs. exposure.
2	Sn^{II}	0.018	0.0064	4.7 (HCl)	2.8	Absorption same.
3	Ce^{IV}	0.0119	0.00210	0.6 (HCl) 0.1 (H_2SO_4)	1.55	All Ce^{IV} recovered.
4	Ce^{IV}	0.0398	0.00720	0.6 (HCl) 0.4 (H_2SO_4)	0.35	All Ce^{IV} recovered.
5	Ce^{IV}	0.0084	0.0092	0.8 (HCl) 0.6 (H_2SO_4)	1.10	All Ce^{IV} re-recovered.
6	Fe^{III}	0.0069	0.0091	0.1 (H_2SO_4)	0.565	Strong red with KCNS.
7	Cl^0	0.01	0.010	4 (HCl)	3.0	Absorption same. Strong Cl^0 tests. with o-tolidine, starch-iodide.
8	KI	0.18	0.0033	Neutral	1.5	No color.
9	KI I^0	0.0032 0.18	0.00059	0.01 (HCl)	17	All I^0 recovered.
10	KIO_3	0.0076	0.0025	1.5 (HCl)	2.0	All KIO_3 recovered.
11	KIO_3	0.0050	0.00278	2 (HCl)	3	All KIO_3 recovered.
12	KIO_3	0.0076	0.00418	Neutral	2	All KIO_3 recovered.
13	Cu^{II}	0.0257	0.0065	Neutral	0.79	No color change, no precipitate. No ppt. with KSCN.
14	Cu^{I}	0.0220	0.0085	0.7 (HCl)	1.22	No Cu^{II} formed.

chlorine, Table XVII, Experiment 7.

f. Iodine or Iodide Ion

In view of its synthesis using iodide and forming iodine, it would be expected that K_2ReCl_6 would be unaffected by these agents. No color was given with iodide solution, Table XVII, Experiment 8, and all the iodine in a mixture of rhenichloride and iodine was recovered by thiosulfate, Table XVII, Experiment 9.

g. Potassium Iodate

Potassium rhenichloride was unaffected by several minutes' standing with iodate because addition of iodide followed by thiosulfate titration gave complete recovery,

$$IO_3^- + 8\ I^- + 6\ H^+ = 3\ I_3^- + 3\ H_2O, \qquad (16)$$

Table XVII, Experiments 10-12.

h. Cupric or Cuprous Ions

Cupric sulfate added to rhenichloride gave no precipitate or other visible change. As mentioned in Sec. V-C-5-d, $ReCl_6^=$ is not affected by thiocyanate, so a test was made with thiocyanate; no precipitate formed, therefore no cuprous was present, Experiment 13, Table XVII.

Cuprous ion was added to rhenichloride, and a test made for cupric by adding iodide,

$$2\ Cu^{II} + 5\ I^- = 2\ \underline{CuI} + I_3^-. \qquad (17)$$

No Cu^{II} was found by thiosulfate titration other than a small impurity originally in the cuprous, Table XVII, Experiment 14.

6. Summary of $Re^{IV}Cl_6^=$ Chemistry

The absorption spectrum of the rather weakly absorbing $ReCl_6^=$ has been recorded. Cesium chloride has been found to be a satisfactory reagent for qualitative and quantitative estimation of rhenichloride in hydrochloric acid or in water. Potassium rhenichloride was found very resistant to a wide variety of oxidizing and reducing agents. Quantitative oxidation to perrhenate by hot cerium (IV) (29) was verified.

D. Re^{IV} Prepared from Rhenium Dioxide

The hypothesis was considered that the more strongly colored yellow-brown form of Re^{IV} differs from $Re^{IV}Cl_6^=$ by containing some rhenium-oxygen bonds instead of only rhenium-chlorine bonds and that possibly there is polymerization because of rhenium-oxygen-rhenium bonds. These ideas suggested that the kind of rhenium (IV) obtained by dissolving hydrated rhenium dioxide in acid be studied.

It is the object of this section to report that a Re^{IV} ion or ions markedly different in chemical properties from $Re^{IV}Cl_6^=$ are obtained when rhenium dioxide, precipitated by alkali from $ReCl_6^=$ solutions, is dissolved in hydrochloric acid. This "active Re^{IV}" is more strongly colored than the $ReCl_6^=$ ion, it is more readily attacked by oxidizing agents, and it may be converted to $ReCl_6^=$ by treatment with hot concentrated hydrochloric acid. It appears to be essentially the same kind of reactive Re^{IV} formed by action of excess stannous chloride with perrhenate. The absorption spectrum of the ReO_2 solutions in HCl is similar to, but not identical with, the absorption spectrum of the rhenium (IV) obtained by reduction with stannous chloride.

Some qualitative observations by the Noddacks (12) upon solutions of ReO_2 in hydrochloric acid support the assumption of rhenium-oxygen bonding. These experiments have been confirmed and extended in the present research. The reported preparation of $K_2Re^{IV}Cl_5OH$ and $K_4Re_2^{IV}OCl_{10}$ (33, 34) gives an indication of the type of solid compounds which may be expected. To account for the observation of several forms of Re^{IV} in solution found in the present research, oxygen coordination may be assumed as follows: (1) a series of hydroxo ions of the type $ReCl_{6-n}(OH)_n^=$ may be assumed, or (2) a series of polymers with rhenium-oxygen-rhenium bonds may be assumed.

1. Preparation of Active Re^{IV}

Rhenium dioxide has been reported to form upon addition of sodium hydroxide solution to potassium rhenichloride (11, 17, 12, 24, 32),

$$ReCl_6^{=} + 4\ OH^- + (x-2)H_2O = ReO_2 \cdot xH_2O + 6\ Cl^-. \qquad (18)$$

Most of the rhenium dioxide preparations were made by addition of sodium hydroxide to rhenichloride; a product with identical properties was formed with excess ammonium hydroxide.

The brown-black ReO_2 precipitate was readily centrifuged, and gave no observable effect with 4 F hydrochloric acid. With 6 F acid, a slight brown color developed in the supernatant acid. Quantities up to 0.2 millimols were found to dissolve completely at room temperature upon stirring with 35 ml. of 12 F acid. Warming encouraged solution, but use of elevated temperatures was avoided because later work indicated changes in form. The reaction product in 12 F hydrochloric acid could be diluted to 4 F acid with no precipitation. The critical acidity at which rhenium dioxide precipitates from hydrochloric acid is unknown; W. and I. Noddack (12) state that potassium rhenichloride undergoes no hydrolysis even upon heating if the acid is higher than 3.4 F. The critical acidity for precipitation of rhenium dioxide would appear from Sec. IV-6, to be essentially the same as for disproportionation of Re^V.

2. Effect of Oxidizing or Reducing Agents upon Active Re^{IV}

Geilmann and Wrigge (29) studied the oxidation of rhenium dioxide prepared in the dry way (32),

$$2\ Re_2O_7 + 3\ Re = 7\ ReO_2. \qquad (19)$$

They found quick quantitative oxidation to ReO_4^- by ferric sulfate in 1 F sulfuric acid upon warming, in strong contrast to the behavior of potassium rhenichloride reported by them and confirmed in Sec. V-C-5-d. ReO_2 was also reported completely oxidized by heating with 0.1 N potassium dichromate in 1 F sulfuric acid, by 0.1 N chromate in weakly basic solution, by 0.1 N ceric sulfate in 1 F sulfuric acid, or with ferric sulfate in nearly neutral solution.

The "active Re^{IV}" prepared from hydrated rhenium dioxide in hydrochloric acid was found to react very similarly to the above behavior of solid rhenium dioxide. In the following paragraphs it will be shown that active Re^{IV} is completely oxidized by ceric sulfate or by potassium iodate, slightly oxidized by iodine, nearly completely oxidized by ferric sulfate, largely oxidized by cupric sulfate, and not affected by cuprous chloride, all at room temperature.

a. Ceric Sulfate or Potassium Iodate

Four formal hydrochloric acid solutions of the hydrated rhenium dioxide prepared from known quantities of potassium rhenichloride were analyzed by ceric sulfate. The rhenium solution was mixed with a small excess of ceric sulfate and the excess determined after $\frac{1}{2}$-2 min. by titration with ferrous sulfate to an o-phenanthroline end-point. This procedure was more satisfactory than direct titration because of sluggish reaction near the end-point. Analysis with iodate was done by pipetting the Re^{IV} into excess iodate and determining the excess after 1-2 min. with thiosulfate after addition of iodide, Reaction (16), Sec. V-C-5-g.

The results of these analyses are given in Table XVIII, supplementary data in appendix. The same results were obtained with ceric sulfate as with potassium iodate, but always somewhat lower than the amount of Re^{IV} expected from the K_2ReCl_6 taken to prepare the hydrated rhenium dioxide. Table XIX shows that the age of the solution has no definite effect on the results. The best explanation appears to be that some oxidation (especially of the precipitate) occurred while washing; there may also have been small losses of precipitate mechanically in washing. Biltz and Cornehl (32) in an investigation of preparation of hydrated rhenium dioxide by hydrolysis of aqueous rhenichloride concluded that partial oxidation of the product occurred. There is some indication from the "Remarks" of Table XVIII that 30 seconds is required for complete reaction of iodate with Re^{IV} but no other direct dependence on conditions was seen. The possibility was considered that some of the rhenium was in a form not oxidized by ceric or iodate. Although it was later found that active Re^{IV} can be converted into inert rhenichloride by heating with strong acid, Sec. V-D-5, there is no good evidence that this happens in cold solutions.

It can be stated that any inert form of Re^{IV} must be a weakly absorbing form, because the yellow-brown solutions were decolorized by the ceric or iodate (iodine monochloride was the product with the excess iodate). Therefore the correct concentration of colored Re^{IV} for later spectrophotometry is that found by ceric or iodate analysis.

Table XVIII

Analysis of Active Re^{IV} Solutions

Soln No.	Meq. Ox. Agent Present	Meq. Re^{IV} Theory all ReO_2 to ReO_4^-	Meq. Re^{IV} Found	Ratio of Meq. Found / Meq. Theory	Remarks
1 a)	0.0404 Ce^{IV}	0.0482	0.0398	0.83	
1	0.0912 KIO_3	"	0.0335	0.69	Added KI and titrated immediately.
1	0.1370 KIO_3	"	0.0420	0.87	Let react 2 min.
2 a)	0.0421 Ce^{IV}	0.0515	0.0415	0.82	
2	0.0912 KIO_3	"	0.0397	0.78	Let react 1 min.
2	0.0912 KIO_3	"	0.0427	0.83	Let react 5 min.
3 b)	0.0625 Ce^{IV}	0.0930	0.0617	0.66	
3 b)	0.0655 Ce^{IV}	"	0.0586	0.63	Let react 5 min.
3	0.0912 KIO_3	"	0.0431	0.45	
3	0.1189 KIO_3	"	0.0548	0.59	
3	0.1370 KIO_3	"	0.0500	0.54	

a) Added Ce^{IV} to Re^{IV}

b) Added Re^{IV} to Ce^{IV}

Table XIX

Effect of Age in Analysis of Active Re^{IV}

Soln. No.	Ox. Agent Used	Age of Soln. (min.)	Ratio of $\frac{\text{Meq. Found}}{\text{Meq. Theory}}$
1	Ce^{IV}	21	0.83
1	KIO_3	25	0.87
2	KIO_3	1	0.78
2	KIO_3	6	0.83
2	Ce^{IV}	8	0.82
3	KIO_3	1	0.45
3	Ce^{IV}	6	0.66
3	KIO_3	10	0.59
3	Ce^{IV}	16	0.66
3	KIO_3	20	0.54

b. Iodine

Solutions of Re^{IV} which had been analyzed by ceric sulfate and by potassium iodate were added to iodine, and unreacted iodine titrated by thiosulfate to a starch end-point. Table XX (supplementary data in appendix) shows that the Re^{IV} was somewhat oxidized by iodine, but not completely, to perrhenate. The Re^{IV} remaining gave a yellow-brown colloidal appearance to the solution after the titration to a starch end-point had been finished. The Re^{IV} was allowed to react 1 or 2 minutes with the iodine in these experiments; other experiments indicated that the rate of reaction is slow.

c. Ferric Sulfate

It was found that after several additions of ferric ion to Re^{IV}, a red color was obtained in a test with potassium thiocyanate, Experiment 1, Table XXI. To determine the extent of reaction between Re^{IV} and Fe^{III}, mixtures were allowed to react 1-2 minutes, and excess ferric determined by addition of iodide and titration of the iodine formed,

$$2\,Fe^{III} + 3\,I^- = 2\,Fe^{II} + I_3^-. \qquad (20)$$

Table XX

Analysis of Active Re^{IV} Solutions by Iodine

Expt. No.	Meq. I_2 Present	Meq. Re^{IV}		Ratio of $\frac{\text{Meq. by } I_2}{\text{Meq. by } Ce^{IV} \text{ and by } KIO_3}$	Remarks
		Found by Ce^{IV} by KIO_3	Found by I_2		
1	0.0178	0.0101	0.0013	0.13	Yellow color left in soln. after titration.
2	0.0134	0.0096	0.0046	0.48	Yellow color.
3	0.0134	"	0.0047	0.49	Yellow color.
4	0.0455	0.0108	0.0040	0.37	Yellow color.
5	0.0089	0.0103	0.0016	0.16	
6	0.0178	0.0056	0.0012	0.21	
7	0.0912	0.0460	0.0125	0.27	Yellow color.
8	0.0912	0.0535	0.0050	0.09	Yellow color.

Table XXI

Analysis of Active Re^{IV} by Ferric Sulfate

Expt. No.	Meq. Fe^{III} Present	Meq. Re^{IV}		Ratio of	Remarks
		Found By Ce^{IV} and KIO_3	Found by Fe^{III}	$\frac{\text{Meq. by } Fe^{III}}{\text{Meq. by } Ce^{IV}}$	
1	0.0067	0.0108	0.0065	0.60	Mixture gave KSCN red color. No titration made.
2	0.0084	"	0.0079	0.73	
3	0.0446	0.0460	0.044	0.96	KSCN test.
4	0.0208	0.0184	0.018	0.9_8	Strong KSCN test.
5	0.0476	0.0400	0.036	0.90	KSCN test.
6	0.0595	"	0.040	1.00	Let react 5 min.
7	0.0446	0.0415	0.027	0.65	Added KI immediately, then titrated.
8	0.0446	"	0.037	0.89	Let react 5 min.
9	0.0893	"	0.039	0.94	Let react 5 min.

The ferric ion was allowed to react with the Re^{IV} in 4-5 F hydrochloric acid, concentrations in Table XXI, supplementary data in the appendix. Three percent potassium iodide solution was added to dilute the mixture to 15 ml., and the iodine formed was titrated after one minute. A small quantity formed in three minutes and was titrated, after which the end-point was stable for 5-10 minutes. The acidity of hydrochloric acid in the mixtures of iodide and ferric was usually 2 F, supplementary data to Table XXI. These conditions deviated from the optimum procedure (1) so blank experiments were made which showed that 0.003-0.005 meq. more thiosulfate was consumed than corresponded to the Fe^{III} present in typical cases. This has been corrected for in Table XXI. It is seen from Table XXI that substantially complete oxidation of the Re^{IV} to ReO_4^- resulted with ferric ion. There is some indication that the extent of oxidation depends upon the length of reaction time of Re^{IV} and Fe^{III}, Experiment 7.

d. Cupric or Cuprous Ions

Active Re^{IV} solutions analyzed by ceric or iodate were mixed with cupric sulfate and allowed to stand a few minutes. Then excess iodide was added and a thiosulfate titration made,

$$2\ \mathrm{Cu^{II}} + 5\ \mathrm{I^-} = 2\ \underline{\mathrm{CuI}} + \mathrm{I_3^-}. \qquad (17)$$

$\mathrm{Re^{IV}}$ and $\mathrm{Cu^{II}}$ were allowed to react in 4 F hydrochloric acid in two types of experiments; the cuprous ion formed was complexed in the acid. In one type of experiment, a slight excess of $\mathrm{Cu^{II}}$ was allowed to react 1-2 minutes. Then excess iodide was added, giving a small amount of iodine and considerable cuprous iodide precipitate, Reaction 17. Titration of the iodine showed that the $\mathrm{Cu^{II}}$ consumed was 60-75% of the number of milliequivalents of $\mathrm{Re^{IV}}$ present as determined by a ceric sulfate titration to $\mathrm{Re^{VII}}$. In another type of experiment, an appreciable excess of $\mathrm{Cu^{II}}$ was allowed to react ½-1 minute. Addition of iodide and titration of the iodine formed showed 60% of the $\mathrm{Re^{IV}}$ was oxidized. In both types, the conditions minimized air oxidation of $\mathrm{Cu^{I}}$ back to $\mathrm{Cu^{II}}$. Taken together they show that $\mathrm{Cu^{II}}$ largely, but not completely, oxidizes $\mathrm{Re^{IV}}$ to $\mathrm{Re^{VII}}$.

Large excesses of $\mathrm{Cu^{II}}$ were allowed to react 5 minutes with $\mathrm{Re^{IV}}$. The air oxidation of $\mathrm{Cu^{I}}$ was corrected for by knowing (1) the original milliequivalents of $\mathrm{Re^{IV}}$ taken found by a ceric sulfate titration, (2) the amount of ceric sulfate to titrate an aliquot portion of the 5 minute old reaction mixture, and (3) the amount of $\mathrm{Cu^{II}}$ in an aliquot portion of the 5 minute mixture as determined by Reaction 17. This experiment showed 85% oxidation of the Re^{IV} to Re^{VII}.

As expected, the brown color of Re^{IV} remained unchanged after addition of cuprous chloride. Addition of iodide then showed that a small impurity of Cu^{II} in the cuprous had been removed completely by reaction with the Re^{IV}.

3. Qualitative Tests for Active Re^{IV}

In decided contrast to the behavior of K_2ReCl_6, Sec. V-C-2, active Re^{IV} in 0.004 F solution, 6 F hydrochloric acid, gave no precipitate with cesium chloride; no precipitate with nitron, but a brown color; a yellowish color with silver nitrate; and a deep orange-brown coloration with ferrocyanide which faded upon exposure to ammonia.

4. Light Absorption of Active Re^{IV}

The strongly yellow-brown active Re^{IV} solutions had much higher absorption than potassium rhenichloride of Sec. V-C-4. The observed absorption had a general similarity to the absorption of Re^{IV} prepared by stannous chloride reduction of perrhenate, Sec. V-A-2. The light absorption of these solutions was constant for the first hour or so after putting them in capped cells, had decreased after 5 hours, and was considerably less after 45 hours. Analyses after 45 hours by iodate showed less reducing agent present than in the initial solutions. No definite tests for $ReCl_6^=$

were given on the old solutions by cesium chloride; the low concentrations involved would not have given much $ReCl_6^=$ in any case. These observations are similar to those for Re^{IV} prepared with stannous and perrhenate, Sec. V-A-4.

The active Re^{IV} solution whose concentration of Re^{IV} was 0.0080 N or 0.0026_7 F (calculated from Table XVIII of Sec. V-D-2-a and its supplementary data, Solution 1), was measured in the spectrophotometer 2 hours after preparation, and again after 49 hours. Analysis by iodate at this later time gave 0.0019_7 F active Re^{IV}. Since it is known that all colored forms of Re^{IV} are oxidized by iodate or ceric, Sec. V-D-2-a, the observed optical densities were divided by these formal concentrations to calculate extinction coefficients. Similar data were calculated for Solution 2 of Table XVIII, 0.0027_7 F initially (within 2 hours after preparation), and found to be 0.0020_3 F after 44 hours.

These extinction coefficients are plotted in Figure 6. Examination of Figure 6 shows the following facts: (1) the two solutions did not have the same absorption initially, although their concentrations were practically identical, (2) after correcting for the concentration changes over a 45 hour period, the absorption for each solution was different than for either initially, and (3) the absorptions of the two solutions are in near agreement after 45 hours although they were initially different. From this it is concluded that Re^{IV} exists in more than one absorbing form, that one or more of the initial colored forms is converted into less absorbing forms upon standing, and that since the initial forms are not reproducible, the substance is not one well-defined species.

5. Conversion of Active Re^{IV} into $Re^{IV}Cl_6^=$

The active Re^{IV} solutions of hydrated rhenium dioxide in hydrochloric acid were converted into rhenichloride, $Re^{IV}Cl_6^=$, by heating in strong acid overnight at 130 °C.

All air was removed from 0.0056 $\underline{F}$ Re^{IV} (ceric analyses) in 8 $\underline{F}$ hydrochloric acid by pumping on a vacuum line, and the solution sealed in a tube. After heating at 130 °C for half a day, the color intensity had decreased greatly. Addition of cesium chloride gave a considerable yellow precipitate, though the original Re^{IV} did not give this test, showing the formation of $ReCl_6^=$.

A deaerated 0.033 $\underline{F}$ active Re^{IV} solution in 12 $\underline{F}$ hydrochloric was heated a day at 130 °C. Twice the volume of water was added to the nearly colorless solution. Addition of cesium chloride to a milliliter of this diluted solution gave 6.8 milligrams of precipitate, corresponding to 0.0102 $\underline{F}$ $ReCl_6^=$ compared with 0.011 $\underline{F}$ for complete conversion.

The light absorption was measured and observed optical densities divided by 0.0102 F to calculate the extinction coefficients plotted in Figure 7. It is seen by comparison with the curve for K_2ReCl_6 in 4 F HCl, Figure 5, that the converted Re^{IV} is similar to $ReCl_6^=$ in light absorption; the higher values may be partly due to the presence of a small amount of highly absorbing unconverted active Re^{IV}.

6. Summary of Active Re^{IV} Chemistry

Strongly brown colored acid-soluble forms of Re^{IV} result if rhenium dioxide prepared from rhenichloride by addition of base is treated with concentrated hydrochloric acid. The brown form is reconverted to $ReCl_6^=$ by heating with strong hydrochloric acid.

The brown form is much more reactive than $Re^{IV}Cl_6^=$, and is completely oxidized to ReO_4^- by ceric sulfate or potassium iodate, and largely oxidized by ferric sulfate. Iodine oxidizes it slightly.

With various reagents, it gave different qualitative tests than rhenichloride, especially no precipitate with cesium ion. Active Re^{IV} is not one well-defined species and changes to other forms upon standing. It appears very similar to the Re^{IV} prepared from perrhenate with excess stannous ion.

The observation of several forms of Re^{IV}, having similar reactivity, supports the assumption of rhenium-oxygen bonds as discussed in the introduction to Sec. V-D. This is also strongly supported by conversion of the yellow-brown forms into $ReCl_6^=$ by heating with HCl.

E. Re^{IV} Prepared from Perrhenate by Iodide Reduction at Room Temperature

In view of the great differences found between the two types of quadrivalent rhenium, inert $Re^{IV}Cl_6^=$ and the reactive Re^{IV} from rhenium dioxide, a study was made of the reduction of perrhenate by iodide at room temperature to determine whether $ReCl_6^=$ was formed directly or through reactive Re^{IV}. It was found that a reactive intermediate formed.

The formation of Re^{IV} by reaction of perrhenate and iodide at room temperature was reported by Jezowska (24) and Jacob and Jezowska (17) and has been mentioned in Sec. IV. They reported fast formation of Re^{V} in cold solutions followed by slower formation of Re^{IV}. In later work (33, 34) these authors and co-workers reported isolating the compounds $K_2Re^{IV}Cl_5OH$ and $K_4Re^{IV}{}_2OCl_{10}$, prepared by iodide reduction of perrhenate at room temperature in high hydrochloric acid. The first reduction product was the K_2ReCl_5OH which easily gave $K_4Re_2OCl_{10}$ by hydrolysis. These compounds were described as brown, readily oxidized, and converted into K_2ReCl_6 gradually at room temperature in hydrochloric acid, and quickly converted upon heating. They therefore appear to be similar to the active Re^{IV} described in Sec. V-D prepared from hydrated rhenium dioxide.

The Noddacks (12) reported that Re^{IV} was formed quantitatively by addition of potassium iodide to potassium perrhenate in 25-33% hydrochloric acid at 15-65 °C with ratios of $KReO_4$:KI from 1.1 to 1.8 They also reported the product $K_4Re_2OCl_{10}$ but did not confirm K_2ReCl_5OH.

This section gives a few general observations on the product formed by reaction of cold perrhenate with iodide; extensive study was not made. The reduction product had all the chemical behavior of active Re^{IV} prepared by dissolving rhenium dioxide in hydrochloric acid, Sec. V-D, but had the remarkable property of an absorption spectrum very similar to that of rhenichloride.

1. Preparation of Re^{IV} from Perrhenate with Iodide

Equivalent quantities (for reduction to Re^{IV}) of powdered potassium perrhenate and potassium iodide were mixed in a tube. To this mixture of 0.881 mm. $KReO_4$ and 2.65 mm. KI was added 5 ml. 12 F hydrochloric acid, liberating iodine at once at room temperature. A blank showed no air oxidation of iodide for several minutes, hence the reaction of perrhenate and iodide was rapid. The tube was placed in a bath of dry ice and acetone, and the air evacuated. The reactants were shaken 15 minutes at room temperature and all the iodine was extracted by carbon tetrachloride. The reaction mixture was then diluted to 26 ml., acidity 6 F hydrochloric acid. Some unreacted solid was seen.

Five milliliters of the greenish-brown solution gave no precipitate with 1 ml. of 0.5 F cesium chloride, hence no $ReCl_6^=$ or $ReI_6^=$ was present (rheniiodides are less soluble than rhenichlorides (31)). Addition of Fe^{III} showed the presence of unreacted iodide.

The iodine extracted in CCl_4 was found to be 1.85 meq. by thiosulfate, which would correspond to 70% reaction based on Re^{IV} and give 0.071 N rhenium in reduced forms in the 26 ml. of 6 F HCl. Incomplete reaction may have been due to incomplete solution of the reactants.

2. Effect of Oxidizing Agents upon Re^{IV}

Since only one set of experiments was done, the exact details of the analyses will not be given. The methods used have been described in Sec. V-D-2; the determinations were made to always depend on a determination of iodine with thiosulfate. The reduced rhenium in initially 6 F hydrochloric acid behaved exactly like rhenium dioxide in 4 F hydrochloric acid, Sec. V-D, in that it was entirely oxidized by excess iodate, 22% oxidized by iodine, and 85% oxidized by excess Fe^{III}. By slow addition of iodate, extracting the iodine formed by carbon tetrachloride and determining the end-point by an external test with starch-iodide, the iodide present was found to be 0.013 F, less than expected if all the unreacted iodide had dissolved. It was also shown that both the Re^{IV} and the I^- formed I_2 when titrated by iodate. By addition of the mixture of rhenium and iodide to a limited amount of iodate, it was found that the iodide was oxidized faster than the Re^{IV}.

The experiments described do not prove quantitatively that the rhenium was in the quadrivalent state. If the rhenium is assumed to have been pentavalent, it would have to be a new form of Re^V which was not oxidized completely by iodine (see Sec. IV-3-c) and which had exactly the chemical reactivity of active Re^{IV} as prepared from rhenium dioxide.

The observations that perrhenate is rapidly reduced by iodide, giving iodine in 12 F hydrochloric acid, while the reduced product is oxidized somewhat by iodine in 0.6 F hydrochloric acid, show a strong dependence upon acidity. The Noddacks (12) reported that Re^{IV} was formed quantitatively by perrhenate with iodide in 8-11 F hydrochloric acid, and that noticeable reduction occurred slowly in 1.5 F acid.

3. Light Absorption of Re^{IV} from Perrhenate with Iodide

The observed optical densities of the 0.071 N greenish-brown solution were divided by 0.024, the formal concentration assuming the state was Re^{IV}, and these extinction coefficients plotted in Figure 8. Comparison with rhenichloride of Figure 5 shows decided similarity, but the curve was not similar to Re^{V}, Figure 2. Nevertheless the rhenium is not $ReCl_6^{=}$ because (1) it gave no cesium precipitate, Sec. V-E-1, and (2) it was easily oxidized by iodate and ferric, Sec. V-E-2. Comparison of the $ReCl_6^{=}$ curve in 4 F hydrochloric acid with the Re^{IV} of Figure 8 in 6 F is justifiable because the absorption of $ReCl_6^{=}$ is nearly the same in 4 as in 6 formal acid, Sec. V-D-4.

The light absorption data plotted in Figure 8 were taken for a 3 hour old solution. The absorption increased slightly with time.

Of the various quadrivalent rhenium complexes mentioned in the introduction to Sec. V-E, $ReCl_5OH^{=}$ (33, 34) suggests itself as the one most likely to correspond to the above light absorption and chemical reactivity.

4. Summary of the Chemistry of Re^{IV} from Perrhenate with Iodide

By reaction of perrhenate and iodide in 12 F hydrochloric acid, a solution was obtained containing reduced rhenium in a reactive form similar to hydrochloric acid solutions of hydrated rhenium dioxide. The light absorption was similar to $Re^{IV}Cl_6^=$ although $ReCl_6^=$ was shown absent.

VI. THE CHEMISTRY OF RHENIUM (-I)

This section describes the preparation and properties of uninegative rhenium in solution.

Lundell and Knowles (35) were the first to discover this interesting oxidation state of rhenium. They prepared Re^{-I} in 0.9 F sulfuric acid at 5 °C in an atmosphere of carbon dioxide. They ran a mixture of potassium perrhenate and acid through a Jones reductor with 20 mesh zinc amalgamated with 5 percent of mercury. Five hundred milliliters of solution 0.000093 to 0.000186 F in perrhenate were used, and the reductor was washed out with 100 ml. of 0.9 F sulfuric acid. The valence was found to be -1 by experiments in which the compound was caught in a CO_2-filled receiver and titrated directly with permanganate, caught in excess $Fe_2(SO_4)_3$, caught in excess H_2MoO_4, or caught in excess $KMnO_4$.

These authors reported that the reduced compound also reacted with Cu^{II} or Ag^{I} to yield the elements, and gave lower valence compounds with dichromate, vanadate, molybdate, and perrhenate. It even reacted with sulfuric acid if the concentration of the Re^{-I} were appreciable or the solution warm. Concentrations of 0.00028 or 0.00046 F rhenium were too great for complete reduction.

Tomicek and Tomicek (36) studied the preparation of Re^{-I} in H_2SO_4, HCl, and H_3PO_4 media, using saturated amalgams of zinc or cadmium in mercury as well as the amalgamated solid metals. They found complete formation of Re^{-I} after 5 minutes in the Jones reductor in 0.5 F sulfuric acid or in 3 F hydrochloric acid, with 0.002 F perrhenate. Re^{-I} was also formed from perrhenate in sulfuric or hydrochloric acid by saturated zinc amalgam, but cadmium carried the reduction only to Re^{IV}.

Lingane (37, 38) prepared Re^{-I} solutions for polarographic investigation by reducing perrhenate in dilute sulfuric acid with amalgamated zinc. He confirmed formation of Re^{-I} for 0.0001 to 0.0008 F potassium perrhenate solutions in 1 F sulfuric acid reduced 10 minutes at 5 °C under nitrogen. He recommended determination of the Re^{-I} by running the reduced solution into excess ceric sulfate, and titrating back with ferrous sulfate to an o-phenanthroline end-point.

In the present work it is shown that favorable conditions for the preparation of Re^{-I} by use of 5% amalgamated zinc in a Jones reductor are initial concentration of $HReO_4$ 0.001 <u>F</u> in 4-6 <u>F</u> hydrochloric acid, time of contact with the zinc several minutes. Poorer results are obtained with higher concentrations of perrhenate, though the acidity, time of contact, and volume of solution taken may be varied without great effect within wide limits. The temperature seemed to have but slight effect for reductions in hydrochloric acid; work was done at 0-5 °C. Oxidation of the Re^{-I} to perrhenate was complete with ceric sulfate or potassium iodate, and also with iodine for fresh solutions of Re^{-I}.

The reduced rhenium solution remained colorless for hours when protected from air, but when exposed to air gradually became brown. It reduced Cu^{II}, Hg^{II}, $MoO_4^{=}$, MnO_4^{-}, and VO_3^{-}. No volatility of Re^{-I} from hydrochloric acid solutions was found, and carbon monoxide had no effect upon the Re^{-I}.

Liquid amalgams were not as satisfactory for the reduction as the 5% amalgamated zinc. Other methods tried for making Re^{-I} are discussed.

In Section VII it is shown that oxidation of Re^{-I}

produces first Re^{+I}, then Re^{IV}. Some observations about potentiometric titration of the Re^{-I} with various oxidizing agents are also given in Sec. VII.

A. Re^{-I} Prepared from Perrhenic Acid with Amalgamated Zinc

1. Preparation of Re^{-I}

Reduction of perrhenic acid solutions in hydrochloric acid was done in the reductor shown in Figure 9. Both the reductor filled with zinc and the reservoir containing the rhenium solution could be repeatedly evacuated and rinsed with carbon dioxide by use of three-way horizontal stopcocks. The reductor could be surrounded by ice water.

The 20 mesh zinc used was amalgamated by stirring with 8% $Hg(NO_3)_2$ solution (containing a small amount of HNO_3 to prevent formation of mercury oxides (39)). Sufficient mercuric solution was used to furnish mercury for a 5% mercury-95% zinc product. The zinc was reamalgamated after 5 days of steady use. The reductor was usually three-fourths filled with the zinc. Solution was withdrawn from the reductor through a 1 mm. capillary stopcock which prevented the zinc from falling out of the reductor; twenty ml. of solution could be recovered to $\frac{1}{2}$-1 ml.

Factors in the operation of a Jones reductor have been studied by Stone and Hume (40). To prevent formation of zinc oxides, a 0.01 F hydrochloric acid solution was kept in the reductor when it was not in use.

Hydrochloric acid was used because Lundell and Knowles (35) reported high concentrations of Re^{-I} reduce sulfuric acid. Due to the possibility of forming Re^{IV} in the course of the investigation, it was also desirable to use hydrochloric acid to prevent precipitation of this state, Sec. V-D-1.

Most of the Re^{-I} solutions were analyzed by ceric sulfate. This was possible because the hydrogen ion concentration of the initially 4-6 F hydrochloric acid medium was reduced by the zinc after several minutes to 0.5 F typically. (The ceric sulfate itself was in 0.5 F sulfuric acid, Sec. I-B). Table XXII contains some ceric analyses, and it is seen that formation of Re^{-I} was largely, but not entirely, complete. Completely reduced Re^{-I} would consume 8 equivalents of ceric for reoxidation to Re^{VII}, ratios of 6-7 were usually found, Table XXII.

The fresh colorless solutions were kept in an atmosphere of carbon dioxide until addition of the Ce^{IV}. The same results were found in direct titrations as when excess Ce^{IV} was added and back titrated with Fe^{II}; however the back titration was preferable because of slow reaction near the end-point in the direct method, see Sec. V-D-2-a and Lingane (38).

The volume of the Re^{-I} was determined within 0.05 ml. for the 2 ml. samples by running the solution under CO_2 into graduated centrifuge tubes, checked against a 2 ml. pipette.

Analyses were also done with excess iodate (which formed ICl_2^- in the high chloride) determining the excess iodometrically as in Sec. IV-3-c. Comparison of the results in Table XXIII with those by ceric in Table XXII shows agreement. Reaction of the fresh Re^{-I} with excess iodine also gave the same results, Table XXIV.

Another indication that the solutions all had the same reduced state of (-I) even though the extent of formation varied somewhat was given by qualitative tests. All solutions gave a heavy black precipitate with cupric sulfate, which is shown in Sec. VII to have been copper. A black precipitate was also formed with mercuric nitrate (attributed to formation of mercury). Some indication was found of precipitates with lead chloride or bismuth sulfate solutions. The Re^{-I} solutions decolorized dilute permanganate, and gave a blue coloration with ammonium molybdate or ammonium vanadate.

Once the validity of using ceric sulfate to find the extent of reduction had been confirmed, this method was used

Table XXII

Analysis of Re^{-I} Solutions by Ceric Sulfate

Soln. No.	Rhenium Taken		Ce^{IV} Taken		Meq. of Reduced Rhenium Found	Meq. Re / Mm. Re
	Volume (ml.)	Millimols	Volume (ml.)	Meq.		
1 a,b)	2.0	0.0096	1.35	0.0615	0.0615	6.4
1 b)	2.0	0.0096	1.39	0.0642	0.0642	6.7
1 b)	2.00	0.0096	1.37	0.0635	0.0635	6.6
2 a,b)	2.0	0.0097	1.51	0.0696	0.0696	7.2
2 c,d)	2.1	0.0101	1.75	0.0810	0.0704	6.9
3 a,b)	2.0	0.0097	1.35	0.0625	0.0620	6.4
3 c,e)	2.3	0.0111	1.80	0.0831	0.0731	6.6
3 b)	2.0	0.0097	1.40	0.0646	0.0641	6.6
4 a,c, f)	2.0	0.0101	2.00	0.0924	0.0647	6.4
4 c)	2.0	0.0101	2.00	0.0924	0.0635	6.3

a) Solutions prepared as follows:
1) 30 ml. of 0.00480 $\underline{F}$ $HReO_4$ in 4 $\underline{F}$ HCl, reduced 3 min.
2) 20 ml. of 0.00483 $\underline{F}$ $HReO_4$ in 4 $\underline{F}$ HCl, reduced 4 min.
3) 26 ml. of 0.00483 $\underline{F}$ $HReO_4$ in 4 $\underline{F}$ HCl, reduced 3 min.
4) 40 ml. of 0.00504 $\underline{F}$ $HReO_4$ in 4 $\underline{F}$ HCl, reduced 4 min.

Table XXII (cont.)

b) Direct titration with ceric made.

c) Back titration made with Fe^{II}.

d) Added 2.25 ml. H_2O before titration.

e) Added 1.0 ml. H_2O before titration.

f) Added 2 ml. H_2O before titration.

Table XXIII

Analysis of Re^{-I} Solutions by Potassium Iodate

Soln. No.	Rhenium Taken		KIO_3 Taken		Meq. of Reduced Rhenium Found	Meq. Re / Mm. Re
	Volume (ml.)	Millimols	Volume (ml.)	Meq.		
1 a)	2.0	0.0096	1.00	0.0890	0.0712	7.4
1	2.0	0.0096	1.00	0.0890	0.0710	7.4
2 a)	2.0	0.0097	2.00	0.0890	0.0639	6.6
2 b)	2.0	0.0097	2.00	0.0890	0.0713	7.4
4 a)	2.0	0.0101	2.00	0.0890	0.0624	6.2
4	2.0	0.0101	2.00	0.0890	0.0603	6.0
5 a)	2.0	0.0096	1.00	0.0912	0.0315	3.3
5	2.0	0.0096	1.00	0.0912	0.0327	3.4
5	2.0	0.0096	1.00	0.0912	0.0327	3.4

a) Solutions prepared as follows:
1) 30 ml. of 0.00480 $\underline{F}$ $HReO_4$ in 4 $\underline{F}$ HCl, reduced 3 min.
2) 20 ml. of 0.00483 $\underline{F}$ $HReO_4$ in 4 $\underline{F}$ HCl, reduced 4 min.
4) 40 ml. of 0.00504 $\underline{F}$ $HReO_4$ in 4 $\underline{F}$ HCl, reduced 4 min.
5) 20 ml. of 0.00482 $\underline{F}$ $HReO_4$ in 5.4 $\underline{F}$ HCl, reduced 3 min.

b) 1½ hr. old solution, slightly yellow.

Table XXIV

Analysis of Re^{-I} Solutions by Iodine

Soln. No.	Rhenium Taken		I_2 Soln.		Meq. of Reduced Rhenium Found	Meq. Re / Mm. Re
	Volume (ml.)	Millimols	Volume Used (ml.)	Meq.		
2 a)	2.0	0.0097	1.0	0.0829	0.0599	6.2
2	2.0	0.0097	1.0	0.0829	0.0615	6.4
4 a)	2.0	0.0101	27	0.0890	0.0640	6.3
4	2.0	0.0101	27	0.0890	0.0628	6.2

a) Solutions prepared as follows:
2) 20 ml. of 0.00483 F $HReO_4$ in 4 F HCl, reduced 4 min.
4) 40 ml. of 0.00504 F $HReO_4$ in 4 F HCl, reduced 4 min.

to study the effect of varying the experimental conditions, conditions of the titrations being similar to those of Table XXII.

The effect of the time of reduction is shown in Table XXV. No specific effect is found within the limits of 1-10 minutes contact of the solution with the zinc. Such differences as were found may be attributable to a variable which was not susceptible to quantitative evaluation, the exact condition of the amalgam. Complete formation of Re^{-I} is seen for 0.00097 F solutions, but reduction is not complete for higher concentrations.

The volume of solution taken had no effect within the limits 10-40 milliliters, Table XXVI. The latter volume was used in the reductor filled with zinc so all the liquid was in contact with zinc.

Poor reduction resulted if the initial concentration of hydrochloric acid was less than 1 F, Table XXVII, Experiments 1, 2, 6, 7, 27. The other experiments show that change of the acidity from 4 to 6 or 8 formal had no great effect.

Formation of Re^{-I} was complete with initial concentration of perrhenic acid 0.001 F, but incomplete with higher concentrations, Table XXVIII. Brown solutions or precipitates resulted with the higher concentrations. No marked improvement was found with a 20% amalgam, Experiments 14-17.

Table XXV

Effect of Time of Reduction upon Formation of Re^{-I}

Expt. No.	Time Reduced (min.)	$HReO_4$ Soln. Vol. (ml.)	$HReO_4$ Soln. F Re	$HReO_4$ Soln. N HCl	Meq. Re / Mm. Re
1	5	10	0.00097	4	6.9
2	5	"	"	"	8.4
3	5	"	"	"	7.9
4	10	"	"	"	8.3
5	20	"	"	"	4.4
6	3	10	0.00242	2	4.6
7	3	"	"	"	3.5
8	5	"	"	"	5.4
9	5	"	"	"	5.4
10	2	10	0.00242	6	3.7
11	2	"	"	"	7.3
12	3	"	"	"	6.5
13	3	10	0.00483	4	4.6
14	10	"	"	"	4.6
15	11	"	"	"	4.6

Table XXV (cont.)

Expt. No.	Time Reduced (min.)	HReO$_4$ Soln. Vol. (ml.)	HReO$_4$ Soln. F Re	HReO$_4$ Soln. N HCl	Meq. Re / Mm. Re	
16	3	20	0.00482	5.4	3.3	
17	3	"	"	"	5.3	
18	5	"	"	"	5.0	
19	7	"	"	"	5.1	
20	$\frac{1}{2}$	20	0.00480	6	4.9	20% amalgam.
21	1	"	"	"	5.0	20% amalgam.

Table XXVI

Effect of Volume of Re Solution Taken upon Extent of Reduction

Expt. No.	Volume Reduced (ml.)	$\underline{F}$ Re	$\underline{N}$ HCl	Time Reduced (min.)	$\frac{\text{Meq. Re}}{\text{Mm. Re}}$
1	10	0.00483	4	11	4.6
2	10	"	"	10	4.6
3	10	"	"	3	4.6
4	20	"	"	4	7.2
5	20	"	"	"	6.9
6	26	"	"	3	6.4
7	26	"	"	"	6.6
8	26	"	"	"	6.6
9	30	0.00480	"	"	6.4
10	30	"	"	"	6.7
11	30	"	"	"	6.6
12	40	0.00504	"	4	6.4
13	40	"	"	"	6.3
14	5	0.0097	6	2	1.7
15	10	"	4	3	4.1
16	20	"	6	4	4.3
17	20	"	"	"	4.9
18	20	"	"	"	5.0

Later work, Sec. VII, suggested that the brown precipitate formed may be Re^{+I} or Re^{IV} formed by action of the Re^{-I} on unreduced Re^{VII}, rather than Re^{IV} formed as an intermediate stage in the reduction and precipitated because of removal of acid by the zinc.

The results in a few experiments were about as good if no ice was used around the reductor. Reductions were also tried with mercury saturated with zinc, but brown products were obtained and the oxidation state by ceric sulfate was usually (IV). Figure 10 shows that the light absorption of such products resembled rhenium dioxide in hydrochloric acid, Figure 6.

Efforts were made to determine the total concentration of rhenium in the reduced solutions by oxidizing all the rhenium to ReO_4^- either by a direct ceric titration or by hydrogen peroxide, and determining the ReO_4^- with chromous chloride as in Sec. V-B. Comparison of the data in Table XXIX with that for known ReO_4^- solutions in Table XVI of Sec. V-B gives an indication that some rhenium may have been lost by spray due to slight volatility of $HReO_4$ when the perrhenic acid was run into the reductor. Work in Sec. VII also gives some weight to this explanation of low Re^{-I} formation in some experiments.

Table XXVII

Influence of Acidity upon Formation of Re^{-I}

Expt. No.	$\underline{N}$ HCl	$\underline{F}$ Re	Volume Reduced (ml.)	Time Reduced (min.)	Meq. Re
1	1	0.00097	10	5	4.6
2	1	"	"	"	6.5
3	4	"	"	"	6.9
4	4	"	"	"	8.4
5	4	"	"	"	7.9
6	0.1	0.00242	10	2	2.2
7	0.5	"	"	"	1.6
8	2	"	"	5	5.4
9	2	"	"	"	5.4
10	2	"	"	3	4.6
11	2	"	"	"	3.5
12	6	"	"	"	6.5
13	6	"	"	2	3.7
14	6	"	"	"	7.3
15	8	"	"	5	5.5

Table XXVII (cont.)

Expt. No.	N HCl	F Re	Volume Reduced (ml.)	Time Reduced (min.)	Meq. Re / Mm. Re
16	4	0.00480	30	3	6.4
17	4	"	"	"	6.7
18	4	"	"	"	6.6
19	4	0.00483	26	"	6.4
20	4	"	"	"	6.6
21	4	"	"	"	6.6
22	4	0.00483	20	4	7.2
23	4	"	"	"	6.9
24	5.4	0.00482	20	3	3.3
25	5.4	"	"	"	5.3
26	5.4	"	"	5	5.0
27	0	0.0097	10	3	0.1
28	4	"	"	"	4.1
29	6	"	20	4	4.3
30	6	"	"	"	4.9
31	6	"	"	"	5.0
32	6	0.0097	5	2	1.7
33	8	"	"	"	4.0

Table XXVIII

Influence of Initial Concentration of Perrhenic Acid upon Formation of Re^{-I}

Expt. No.	Initial $\underline{F}$ $HReO_4$	Initial $\underline{N}$ HCl	Volume Reduced (ml.)	Time Reduced (min.)	$\frac{\text{Meq. Re}}{\text{Mm. Re}}$	Remarks
1	0.00097	4	10	5	6.9	
2	0.00097	"	"	"	8.4	
3	0.00097	"	"	"	7.9	
4	0.00097	"	"	10	8.3	
5	0.00483	"	"	3	4.6	
6	0.00483	"	"	10	4.6	
7	0.0097	"	"	3	4.1	
8	0.00242	6	10	2	3.7	
9	0.00242	"	"	"	7.3	
10	0.00242	"	"	3	6.5	
11	0.0097	"	20	4	4.3	
12	0.0097	"	"	"	4.9	
13	0.0097	"	"	"	5.0	
14	0.00480	6	20	$\frac{1}{2}$	4.9	20% amalgam.
15	0.00480	"	"	1	5.0	20% amalgam.
16	0.0242	"	"	2	2.6	20% amalgam.
17	0.0242	"	"	"	2.8	20% amalgam.

Table XXVIII (cont.)

Expt. No.	Initial $\underline{F}$ $HReO_4$	Initial $\underline{N}$ HCl	Volume Reduced (ml.)	Time Reduced (min.)	$\frac{\text{Meq. Re}}{\text{Mm. Re}}$
18	0.00482	5.4	20	3	3.3
19	0.00482	"	"	"	5.3
20	0.00482	"	"	5	5.2
21	0.0097	6	"	4	4.3
22	0.0097	"	"	"	4.9
23	0.0097	"	"	"	5.0

Table XXIX

Total Rhenium Analyses for Reduced Solutions by Reduction of Perrhenate by Chromous Chloride

Expt. No.	Method of Oxidation of Re^{-I} to ReO_4^-	Meq. Red. Agent Found	Millimols Rhenium		% Error based on Re^{IV} to Re^{VII}
			Taken	Found for Re^{IV} to Re^{VII}	
1	Direct ceric titration.	0.0216	0.0097	0.0072	-26
2	Direct ceric titration.	0.0226	0.0097	0.0075	-23
3	Heated one hr. with 0.2 ml. 30% H_2O_2.	0.0226	0.0097	0.0075	-23
4	Direct ceric titration.	0.0212	0.0097	0.0071	-27
5	Boiled ½ hr. with 0.5 ml. 30% H_2O_2 and 0.3 ml. 6 F H_2SO_4. Blank showed all H_2O_2 decomposed.	0.0243	0.0097	0.0081	-16
6	Direct ceric titration.	0.0304	0.0097	0.0101	+4
7	Direct ceric titration.	0.0236	0.0097	0.0079	-18
8	Direct ceric titration.	0.0232	0.0097	0.0077	-21

2. Light Absorption of Re^{-I}

Two volumes of colorless Re^{-I} solution were run into one volume of 12 F hydrochloric acid and the light absorption measured at room temperature against 4 F hydrochloric acid. Figure 11 shows low, non-characteristic absorption for three identical samples and for a blank of hydrochloric acid reduced similarly.

Increase in the light absorption at short wave-lengths was found after hours, Figures 12 and 13. Insufficient information is available to state whether this was due to reaction of Re^{-I} with H^+ or to other effects.

3. Test for Volatility of Re^{-I}

Re^{-I} was shown to be non-volatile from 6 or 8 F hydrochloric acid by evaporating solutions with a mechanical pump, condensing the vapors in a dry ice trap, and testing the condensate with ceric sulfate for reducing effect. The residue formed a brown semi-solid, and ceric sulfate showed a decrease in the reducing agent. Therefore the Re^{-I} was destroyed in concentrated solution for unknown reasons.

One experiment was done with 2 ml. of 0.0018 F Re^{-I} (60% complete reduction) in 6 F HCl, the other with 6 ml. of 0.0013 F Re^{-I} (80% complete) in 8 F HCl.

4. Possible Electronic Configurations for Re^{-I}

Addition of an electron to the rhenium atom, Z = 75, in which the shells from 1s to 4f are filled and with further electron distribution $5s^2 5p^6 5d^5 6s^2$ gives an atom isoelectronic with Os^0, Ir^I, Pt^{II}, or Au^{III}. A possible electron configuration would then be $5s^2 5p^6 5d^8$ in which the rhenium would be in an ion isoelectronic with (uncoordinated) Pt^{II} and would have two unpaired electrons. But Pauling (41) has pointed out that it would be expected that such an ion would form a square coplanar complex, probably with four water molecules, and be diamagnetic. Lingane (38) suggested that the rhenium could have configuration $5s^2 5p^6 6s^2 6p^6$.

It should be possible to gain information about these configurations by magnetic measurements provided the Re^{-I} were not dimerized, etc. Hence sample calculations were made to determine what concentration of Re^{-I} would be necessary to give a 10 mg. pull with the 8000 gauss magnet available, and a tube diameter 1.5 cm.

Taking as the criterion a 10 mg. pull for 2 electrons, a concentration of 0.06 F would be necessary, and configuration $5s^2 5p^6 5d^8$ could be established if it existed. The diamagnetic solvent correction would be (-) 60 mg. but would be nearly independent of small changes in the relative amounts of zinc chloride or hydrochloric acid introduced during the reduction. The highest concentration of Re^{-I} ever achieved was 0.005 F; brown precipitates formed in attempts to increase this concentration Sec. VI-A-1. Such a concentration would give a scarcely detectable effect, and if this configuration were ruled out, would yield little information as to the remaining diamagnetic possibilities.

The pertinent information in regard to the structure of Re^{-I} are in agreement with Pauling's suggestion though not necessarily requiring that structure. First, Re^{-I} is colorless, while all other observed rhenium compounds except ReO_4^- are colored; it is well known that presence of an unpaired electron often confers color. Second, the rate of oxidation of Re^{-I} by oxygen is slow, Sec. VII, which might be expected if the Re^{-I} were coordinated in a stable complex as with water molecules. Third, Re^{-I} is non-volatile, which would be immediately explained by Pauling's structure analogous to a hydrated Pt^{II}, but might also be explained if Re^{-I} were the anion of a strong acid. Finally, the Re^{-I} in hydrochloric acid appears to have the same behavior as Lundell and Knowles' (35) preparation in sulfuric acid, and as Tomicek and Tomicek's (36) Re^{-I} in H_2SO_4, HCl, and H_3PO_4. This suggests that either the Re^{-I} is coordinated with the same groups in all solutions, water in particular, or that it is not coordinated in any, or that its behavior is not changed greatly by different coordinating substances.

The lack of reaction of Re^{-I} with carbon monoxide, next section, cannot be given any significance at present. The experimental uncertainties in the CO experiment were relatively large, and partial reaction would have escaped detection.

The formation of Re^{+I}, isoelectronic with Pt^{IV}, by titration of Re^{-I} with $HReO_4$, Sec. VII, may be relevant in strengthening the analogy between the lower states of Re and the oxidation states of Pt.

Lingane's suggestion of $5s^2 5p^6 6s^2 6p^6$ is not in agreement with the filling up of 5d orbitals in the transition elements before filling 6p orbitals. No example can be given of a compound of the transition elements in which even one electron is present in a 6p orbital when a 5d orbital is also available. This structure would explain the lack of color of Re^{-I}, but would give no explanation for the slow reactivity of Re^{-I} with oxygen--indeed Lingane (38) originally proposed the structure because it might explain <u>high</u> reactivity of Re^{-I}. Lingane also stated that this structure would be analogous to a halide and the structure would not explain non-volatility of Re^{-I}. Equal reactivity in different media would be expected from Lingane's structure.

5. Effect of Carbon Monoxide upon Re^{-I}

The possible analogy with Pt^{II} mentioned above suggested attempts to prepare carbon monoxide complexes of Re^{-I}. Evacuated Re^{-I} solution was opened to carbon dioxide and the new pressure measured by a manometer in the system. No detectable reaction occurred when 6 ml. of 0.0030 $\underline{F}$ Re^{-I} in its 0.5 $\underline{F}$ HCl was shaken with 0.437 millimols of carbon monoxide, room temperature, 20 cm. of mercury pressure. No effect was found for 10 ml. of 0.0052 $\underline{F}$ Re^{-I} in 4 $\underline{F}$ hydrochloric acid under similar conditions. The experimental uncertainties were such that formation of $Re^{-I}CO$ might have escaped detection, but any more highly complexed compound would have been observed.

6. Summary of the Chemistry of Re^{-I}

Re^{-I} was formed completely if 0.001 $\underline{F}$ $HReO_4$ in 4-6 $\underline{F}$ hydrochloric acid was contacted with 5% amalgamated zinc for several minutes under carbon dioxide. Incomplete reduction was obtained with 0.005 or 0.01 $\underline{F}$ $HReO_4$. The effect of other variables was shown small.

Fresh solutions could be determined with excess ceric, iodate, or iodine. They reduced various oxidants to lower valences. The light absorption of the colorless solutions increased somewhat with time. No volatility of Re^{-I} was found from 6 to 8 F hydrochloric acid, and carbon monoxide had no effect.

B. Other Attempts to Prepare Re^{-I}

In Sec. VI-A-1 it was mentioned that liquid amalgams were less satisfactory than solid. Work described in the present section showed no reduction by chemical means of $HReO_4$ or Re under various conditions, except for potassium vapor and liquid on K_2ReCl_6 which gave Re metal, and K_2ReCl_6 reduced in the Jones reductor, which may have formed some Re^{-I}. Electrolytic reduction of $HReO_4$ under various conditions gave only Re^{IV}.

1. Reduction with Amalgamated Zinc

a. Perrhenate in Sodium Hydroxide

Perrhenate in 1 F sodium hydroxide was left in the Jones reductor, but the solution had no reducing agent, Expt. 1, Table XXX.

b. K_2ReCl_6 in Hydrochloric Acid

After potassium rhenichloride in hydrochloric acid was run from the Jones reductor, the solution still contained some $ReCl_6^=$ (CsCl test) but titration with ceric sulfate showed the presence of a reducing substance, Expts. 2 and 3. It gave no effect with $CuSO_4$ in 1.7 $\underline{F}$ H^+ but the Cu^{II} test may be invalid for Re^{-I} in high acid. It appeared to be unaffected by iodine. It is not clear whether some Re^{-I} had formed, or whether the $Re^{IV}Cl_6^=$ was merely converted to a reactive and weakly colored form as that of Sec. V-E.

2. Reduction of K_2ReCl_6 by Potassium

Potassium vapor at approximately 1.5 mm. Hg vapor pressure gave a metallic black solid with K_2ReCl_6; similar observations were made with liquid potassium, Expts. 4 and 5, Table XXX. The solid was not a rhenium oxide because of the absence of air; it dissolved in H_2O_2 and was therefore rhenium metal. No reducing agent was formed in this experiment.

3. Other Chemical Attempts

a. Hydrogen with Rhenium in Sodium Hydroxide or in Hydrochloric Acid

Rhenium in NaOH or in HCl was unaffected by hydrogen, solutions at room temperature, Expts. 6 and 7, Table XXX.

Table XXX

Chemical Attempts to Prepare Re^{-I}

Expt. No.	Experimental Procedure	Observations
1	20 ml. of 0.005 F $HReO_4$ in 1 F NaOH left in reductor 5 min. under nitrogen.	No effect on Cu^{II}, Hg^{II}, Ce^{IV}, KIO_3.
2	20 ml. of 0.0050 F K_2ReCl_6 in 4 F HCl in reductor 4 min.	0.0125 N to Ce^{IV}. 1.7 N in H^+. Considerable yellow ppt. with CsCl. No effect on Cu^{II}.
3	16 ml. of 0.0050 F K_2ReCl_6 in 4 F HCl in reductor 4 min.	0.0137 N to Ce^{IV}. 3 N in H^+. Considerable ppt. with CsCl. No reaction with iodine.
4	0.56 g. K distilled, vapor at 330-350°C in contact with 100 mg. K_2ReCl_6, 4 hrs.	Black solid formed, yellow K_2ReCl_6 also present. Black solid insol. in 6 F HCl, no reducing agent in 6 F HCl by cerium (IV)
5	50 mg. K doubly distilled onto 20 mg. K_2ReCl_6, kept at 250°C 25 min.	Black metallic solid formed, unreacted K_2ReCl_6 also present. Black solid insol. in 6 or 12 F HCl, readily sol. in H_2O_2.

Table XXX (cont.)

Expt. No.	Experimental Procedure	Observations
6	H_2 bubbled thru 10.5 mg. Re powder in 2 ml. 6 F NaOH 1 hr., room temp.	No visible change. No reducing agent in soln., by cerium (IV).
7	H_2 bubbled thru 10 mg. Re powder and 2 ml. 6 F HCl for 40 min., room temp.	No reducing agent in soln. by cerium (IV).
8	0.01 F $HReO_4$ in 4 F HCl shaken with Hg.	No effect on Cu^{II}. Slight effect on $KMnO_4$ or $(NH_4)_2MoO_4$ due to suspended Hg.

b. Mercury with Perrhenate

Practically no reducing agent was given by mercury with perrhenate, Expt. 8, Table XXX.

4. Electrolytic Attempts

a. Electrolysis with a Rhenium Plated Cathode

Re^{-I} was not formed when finely divided rhenium was electrolyzed under hydrogen in sodium hydroxide solution, Expt. 1, Table XXXI. The rhenium was deposited on platinum by electrolysis (35).

b. Electrolysis of Perrhenate at Platinum

Electrolysis of perrhenate at platinum gave yellow-green solutions whose light absorption resembled active Re^{IV}, Expt. 2, Table XXXI.

c. Electrolysis of Perrhenate at Silver

Since the hydrogen overvoltage is greater on silver than for other common inert electrodes (42), electrolysis of perrhenate was tried at silver cathodes but gave only products resembling Re^{IV}, Expts. 3-5, Table XXXI.

d. Electrolysis of Perrhenate under Carbon Monoxide

Since Re^{-I} is not affected by carbon monoxide, Sec.

Table XXXI

Electrolytic Attempts to Prepare Re^{-I}

Expt. No.	Experimental Procedure	Observations
1	Electrodeposited 12 mg. Re from $HReO_4$ in 1 F H_2SO_4 onto Pt wire. Made Re on Pt cathode, Pt anode in 6 F NaOH, electrolyzed 17 hrs., 80 milliamps, 2 volts, alundum diaphragm, stream of H_2 over Re on Pt.	O_2 at anode, H_2 at cathode. No reducing agent in cathode soln. by Ce^{IV}.
2	Electrolyzed 5 ml. of 0.01 F $HReO_4$ in 4 F HCl at 3.5 cm^2 Pt foil, Ag anode, sintered glass diaphragm. Rotated Pt cathode, electrolysis 1½ hrs., 21 milliamps, 2 volts.	Yellow-green soln. with light absorption similar to ReO_2 in
3	Electrolyzed 3 ml. of 0.01 F $HReO_4$ in 4 F HCl at 7.4 cm^2 Ag sheet, Ag anode, sintered glass diaphragm. Rotated Ag cathode electrolysis 13 hrs., 64 milliamps, 2 volts.	H_2 at cathode. Yellow-brown soln. with light absorption similar to ReO_2
4	Same as 3 but 5 milliamps, 1.5 volts, electrolysis 1½ hrs.	Green, then yellow solution, absorption similar to ReO_2 in HCl.
5	Same as 3 except in 9.8 F HCl electrolysis several minutes.	Yellow solution.
6	Electrolyzed 4 ml. of 0.01 F $HReO_4$ in 4 F HCl at 7.4 cm^2 Ag sheet, Ag anode, sintered glass diaphragm. Rotated Ag cathode, electrolysis 1½ hrs., 18 milliamps, 0.5 volts, stream of CO over Ag cathode in $HReO_4$ soln.	Yellow solution, only little reducing agent by Ce^{IV}.

VI-5, it would be expected that CO would not favor electrolytic production of Re^{-I}. Indeed, the same yellow products were obtained upon electrolyzing ReO_4^- in the presence of CO as in its absence, Expt. 6, Table XXXI.

5. Summary of Other Attempts to Prepare Re^{-I}

Electrolytic and chemical attempts to prepare Re^{-I} either had no effect or formed yellow products resembling Re^{IV}, with the exception of reduction of K_2ReCl_6 by potassium, which formed rhenium metal, and reduction of K_2ReCl_6 in the Jones reductor, which formed a reactive product of unknown composition.

VII. THE CHEMISTRY OF RHENIUM (+I)

In this section evidence is given for the formation of Re^{+I} by titration of Re^{-I} with $HReO_4$ or $CuSO_4$.

Lundell and Knowles (35) found indications that Re^{+I} was formed when a dilute Re^{-I} solution in 0.9 F sulfuric acid stood 30-60 minutes at 50 °C, because by permanganate titration the yellow solution gave average valence +1.0 instead of -1.0 as for the original Re^{-I}. Tests showed formation of a volatile sulfur compound, so they attributed the change to oxidation of the Re^{-I} by the sulfuric acid. The average valence remained +1.0 when the solution was heated at 72 °C and titrated in the course of 30 minutes, but the Re^{+I} was destroyed by prolonged digestion.

These authors found a marked increase in potential when permanganate was added in a potentiometric titration of Re^{-I} to give average valence +1. During this titration the yellow color formed, and disappeared on further addition of MnO_4^-. In a few cases a slight tendency for a break in potential at zero valency was observed, but no breaks other than these occurred until the amount of permanganate required for complete oxidation to ReO_4^- had been added.

From polarographic studies of the products formed and by amperometric titration of Re^{-I} solutions, Lingane (38) concluded that the Re^{-I} was oxidized to the +2 state, then to the +3, +5, and +7 states. He confirmed an average valence of +1 for partly oxidized solutions in warm sulfuric acid, but found that this solution was a mixture of Re^{-I} and higher states such as Re^{III}, Re^{IV}, or Re^{V} in proportions equivalent to an average oxidation state of +1.

Tomicek and Tomicek (36) found no intermediate potential break in a potentiometric titration of Re^{-I} with ceric sulfate.

Young and Irvine (42) reported the preparation of Re^{I} as $Re_2O \cdot H_2O$ by reduction of very dilute perrhenic acid solutions in 0.2 $\underline{N}$ hydrochloric acid by zinc in the absence of air.

W. and I. Noddack (12) described a reduced solution which they believed contained Re^{I}, prepared by reduction of rhenium trichloride, $ReCl_3$, by zinc or sodium amalgam in strong hydrochloric or sulfuric acid.

In the present work, light absorption showed the formation of two states of rhenium between (-I) and (+VII) when Re^{-I} was exposed to air. These brown substances were formed consecutively. The same two states formed when perrhenic acid, $HReO_4$, was added to Re^{-I}, and the observed light absorption for mixtures of Re^{-I} and Re^{VII} could best be explained on the basis of formation of Re^{I} and Re^{IV}. Re^{-I} did not react with inert $Re^{IV}Cl_6^{=}$. Copper metal was produced in titration of Re^{-I} with $CuSO_4$ in just the amount expected on the basis of

$$Re^{-I} + Cu^{II} = Re^{+I} + Cu^{0}. \qquad (21)$$

Further addition of Cu^{II} oxidizes the rhenium beyond the Re^{I} stage to Re^{IV} and Re^{VII}, and gives Cu^{I}. In a potentiometric titration of Re^{-I} with $CuSO_4$, a yellow intermediate was formed and removed by addition of Cu^{II} but no potential break was observed till the finish. Potentiometric titration of Re^{-I} with Fe^{III} or Ce^{IV} also showed no breaks till oxidation to Re^{VII}.

1. Oxidation of Re^{-I} by Oxygen

The light absorption measured for a Re^{-I} solution exposed to air various lengths of time is shown in Figures 14 and 15. It is seen that a substance with maximum absorption at 610 millimicrons first formed, then disappeared as a substance with maximum at 690 mμ formed. This second product underwent some oxidation after further exposure to air, Figure 15. In the next section it is shown that the same substances result when Re^{-I} is titrated by Re^{VII}, and there they are attributed to formation of Re^{+I} followed by Re^{+IV}.

The same observations are seen in Figure 16 for another Re^{-I} solution exposed to air.

Oxygen was bubbled through Re^{-I} and the analysis with ceric sulfate after oxidation compared with that before. Table XXXII gives some indication that at about 25% oxidation of the Re^{-I}, i.e. at Re^{+I} stage, a substance is formed which is more difficult to oxidize, since after 30 minutes the now yellow-brown solution suffered less change than had the original Re^{-I} in 5 minutes oxidation.

2. Preparation of Re^{I} from Re^{-I} with Re^{VII}

Upon mixing perrhenic acid, $HReO_4$, with Re^{-I} the same

Table XXXII

Effect of Oxygen upon Re^{-I}

Expt. No.	Volume Rhenium Solution (ml.)	Meq. Ce^{IV} Consumed before Oxidation	Time O_2 bubbled thru Re Solution (min.)	Meq. Ce^{IV} Consumed after Oxidation	% Decrease in reducing agent (Re^{-I}) present
1	2.0	0.041_4	5	0.0328	21
2	2.0	0.048_8	5	0.0370	24
3	2.0	0.067_5	5	0.0526	22
4	2.0	0.067_5	30	0.0465	31

two colored substances formed which were observed for Re^{-I} exposed to air. Mixtures of $HReO_4$ and Re^{-I} of average valence +1 formed a yellow-brown substance with maximum at 610 mμ. Mixtures of $HReO_4$ and Re^{-I} with average valence +2 or +3 contained both this substance and another with maximum at 690 mμ, while with average valence +4 or larger only the substance absorbing at 690 mμ could be detected.

Figures 17-20 record the course of the reaction as followed by light absorption when various ratios of $HReO_4$ in relatively concentrated solution (to leave volumes unchanged) were added to similar Re^{-I} solutions under carbon dioxide in capped cells. These figures show that the substance first formed, absorbing at 610 mμ, disappears as the substance absorbing at 690 mμ is formed when more $HReO_4$ is used. These two species are the same as formed by oxygen with Re^{-I}, comparison with Figures 14-16. Since oxygen first formed the substance absorbing at 610 mμ (and it was the first product also with $HReO_4$), it is a lower state than the substance absorbing at 690 mμ.

The absorption became constant after about 15 hours indicating completion of the reactions. Re^{-I} alone had much lower absorption even after 40 hours, Figures 12 and 13 and Sec. VI-A-2.

From the studies with oxygen, it is known that the rhenium of the Re^{-I} can be converted into the two colored states. The reason for assuming that the rhenium from the $HReO_4$ also goes into these colored states is that the absorption observed with mixtures of Re^{-I} and $HReO_4$ was higher than when the same concentration of Re^{-I} was exposed to oxygen. The highest optical density values observed for a 0.0013 F Re^{-I} solution exposed to air are 0.105 at 610 $m\mu$, Figure 15, or 0.14 at 610 $m\mu$, Figure 16. For $HReO_4$ added to Re^{-I} to give an average valence of +1, the value was 0.175, Figure 17. Hence the amount of rhenium in this colored state might be of the order of 25-50% greater for the solution in which $HReO_4$ was added to Re^{-I} compared to the Re^{-I} solution exposed to air, indicating that rhenium from the $HReO_4$ also went into this colored state. This would be compatible with an increase of 33% expected on the basis of

$$3\ Re^{-I} + Re^{VII} = 4\ Re^{+I}, \qquad (22)$$

but would not be in good agreement with 60% expected for

$$5\ Re^{-I} + 3\ Re^{VII} = 8\ Re^{II}. \qquad (23)$$

Comparison of the large maximum at 690 $m\mu$ for a mixture of average valence +4.5, Figure 20, with the curves for Re^{-I} exposed to oxygen, Figures 15 and 16, proves that all the rhenium in the $HReO_4$ was converted into the yellow-green substance absorbing at 690 mμ in the +4.5 mixture.

The highest maximum at 690 mμ observed for a Re^{-I} solution exposed to air was 0.125 for the solution of Figure 16. The maximum for a mixture of average valence +4.5 was 0.35, Figure 20, 2.8 times as large. Assumption of a reaction

$$3\ Re^{-I} + 5\ Re^{VII} = 8\ Re^{IV} \qquad (24)$$

would give a ratio 8/3 = 2.7.

By these considerations and because some of the substance absorbing at 690 mμ was present for a mixture of average valence +2 but absent for +1, the lower state absorbing at 610 mμ is Re^{+I}. Since the absorption for a mixture of average valence +4.5 was greater at 690 mμ than for a mixture of average valence +3.2, comparison of Figures 19 and 20, the substance absorbing at 690 mμ is not Re^{III} but so far could be Re^{IV} or Re^{V}.

To show that the substance absorbing at 690 mμ was Re^{IV}, the formal apparent extinction coefficients were considered. We have for the optical density in a mixture of two absorbing species (1) and (2), and extinction coefficients ϵ_1, and ϵ_2,

$$d = d_1 + d_2 = \epsilon_1 c_1 + \epsilon_2 c_2 \qquad (25)$$

since the path length was always 1 cm., Sec. II. Using formal concentrations, the extinction coefficients are formal coefficients. The apparent formal extinction coefficient for the mixture is defined to be

$$\epsilon_A = \frac{d}{c_1 + c_2} = \frac{d_1 + d_2}{c_1 + c_2} = \frac{\epsilon_1 c_1 + \epsilon_2 c_2}{c_1 + c_2} . \qquad (26)$$

From the definition of the apparent formal extinction coefficient, the following properties follow in the case that the extinction coefficient of the second species ϵ_2 is greater than that of the first species ϵ_1, $\epsilon_2 > \epsilon_1$: (1) the apparent extinction coefficient ϵ_A is less than (or equal to if $c_1 = 0$) ϵ_2; (2) ϵ_A is greater than (or equal to) ϵ_1; and most important in the present application, (3) if the percent of the more absorbing species, $\frac{100 c_2}{c_1 + c_2}$, is greater in a second solution (') than in a first solution, the apparent coefficient is larger for this second solution with the higher relative amount of the more absorbing species, $\epsilon_A' > \epsilon_A$.

The substance absorbing at 690 mμ, which cannot be Re^{III} but may be Re^{IV} or else Re^{V}, has a greater coefficient at this wave-length than has Re^{+I}, Figure 16, and the solution with average valence +4.5 has more of this absorbing component than the +3.2 solution since the valence of the substance absorbing at 690 mμ is greater than +3, therefore Property 3 above may be applied. Table XXXIII contains the apparent coefficients calculated for these two solutions assuming (1) the high state is Re^{V}, and (2) it is Re^{IV}. Figure 21 shows that the high state cannot be Re^{V} because the apparent coefficient for the +4.5 mixture comes out lower than for the +3.2 mixture, while it should come out higher since the +4.5 solution has a relatively greater amount of the highly absorbing component. The coefficients were also plotted assuming the highest state was Re^{IV}; under this assumption some $HReO_4$ was unreacted, lowering the concentration and increasing ϵ_A, $\epsilon_A \sim 1/c$. Figure 22 shows that the extinction coefficients are in the right order at 690 mμ if the high state is Re^{IV}. The Re^{IV} resembles ReO_2 in HCl, Figure 6.

Apparent coefficients were calculated for all the other solutions of Figures 17-20, Table XXXIV. Figure 23 shows that these coefficients are in the correct order at the maxima and minima with the assignment of the states Re^{+I} and Re^{+IV}.

Other solutions were prepared with amounts of $HReO_4$ and Re^{-I} to give average valences from 4 to 6, and their apparent extinction coefficients agreed with Figure 22 if it was assumed that none of the $HReO_4$ reacted beyond forming Re^{IV}.

Table XXXIII

Formal Extinction Coefficients for Mixtures of Re^{-I} and Re^{VII}

Extinction coefficients have been calculated for a mixture of average valence +4.5 under the assumption that none of the rhenium reacted beyond the amount to give an average valence 3, and the same assumptions in other calculations for +4 and +4.5. Calculated extinction coefficients for a mixture with average valence +3.2 are also given.

Average valence	3.2	4.5	4.5	4.5
Assumed valence	3.2	3.0	4.0	4.5
Age (hr.)	40	40		
Re^{-I} (mm.)	0.0039	0.0039	0.0039	0.0039
ReO_4^- (mm.)	0.0043	0.0086	0.0086	0.0086
Volume (ml.)	3.10	3.20	3.20	3.20
Assumed conc.	0.00264	0.00246	0.00325	0.00390

Wave-length (mμ)	$\frac{d}{0.00264}$	$\frac{d}{0.00246}$	$\frac{d}{0.00325}$	$\frac{d}{0.00390}$
320		810 +	615 +	510 +
400	760 +	670	524	435
425	760 +	341	258	215
450	306	153	115	96
475	219	116	88	73
500	129	73	55	46
525	84	50	38	32
550	56	39	29	24
575	49	38	29	24
590	55	42	32	27
600	60	46	34	29
610	65	51	38	32
625	66	57	43	36
640	69	71	54	45
660	82	102	78	65
680	102	139	105	87
700	106	146	110	92
720	93	122	92	77
750	68	83	62	52
800	47	51	38	32
850	39	41	31	26
900	38	38	29	24
950	40	41	31	26
1000	33	39	29	24

with the Re^{-I}, thus confirming Re^{IV}.

The solution with average valence +2 of Figure 18 was prepared by adding more $HReO_4$ to a 40 hour old +1 mixture. However, a solution of average valence +2 prepared from fresh reactants had both the Re^{IV} and the low valent state, verifying that the low state is not Re^{II}, but Re^{I}. Two other +1 mixtures also agreed with that of Figure 17.

Addition of more perrhenate to a 40 hour old +4.5 mixture gave no change, as expected. Addition of perrhenate to an old Re^{-I} solution in amount to give average valence +1 gave, not a Re^{I} curve as Figure 17, but a Re^{IV} curve as in Figure 20 with considerably lower concentration of Re^{IV}. This apparent change in old Re^{-I} solutions may agree with observed changes in the light absorption of old Re^{-I}, Sec. VI-A-2. Addition of perrhenate to old +3.2 mixture gave no detectable change; the explanation is not known.

From these results, it appears as though apparent incomplete formation of Re^{-I}, Sec. VI-A-1, cannot be explained by assuming the presence of unreduced $HReO_4$ as it would be expected that this would form appreciable amounts of colored products with the Re^{-I}, contrary to observation, Figures 12 and 13 and Sec. VI-A-2. Hence assuming losses of rhenium from the system would be a preferable explanation for incomplete formation. On the other hand, the knowledge that

Table XXXIV

Formal Extinction Coefficients for Mixtures of Re^{-I} and Re^{VII}

The observed optical densities after reaction was complete (40 hours in most cases) for mixtures of Re^{-I} and Re^{VII} were divided by the total formal concentration of rhenium to calculate extinction coefficients.

Average valence	-1.0	1.0	1.9	3.2	4.5
Age (hr.)	41	40	62	40	40
Re^{-I} (mm.)	0.0039	0.0039	0.0039	0.0039	0.0039
ReO_4^- (mm.)	0	0.0013	0.0022	0.0043	0.0086
Volume (ml.)	3.00	3.03	3.05	3.10	3.20
$\underline{F}$ Re	0.0013	0.00172	0.0020_1	0.00264	0.00390

Wave-length (mμ)	$\frac{d}{0.0013}$	$\frac{d}{0.00172}$	$\frac{d}{0.00201}$	$\frac{d}{0.00264}$	$\frac{d}{0.00390}$
320	1540+				510+
350	1020		1000+		
375	502		1000+		
390	394		1000+		
400	333	1160+	1000+	760+	435
425	159	1160+	1000+	760+	215
450	89	506	502	306	96
475	69	361	358	219	73
500	53	216	210	129	46
525	47	145	138	84	32
550	42	99	89	56	24
575	39	85	76	49	24
590	39	93	85	55	27
600	39	98	91	60	29
610	38	101	96	65	32
625	37	94	92	66	36
640	37	85	86	69	45
660	37	77	82	82	65
680	38	77	88	102	87
700	42	78	89	106	92
720	35	76	82	93	77
750	35	69	67	68	52
800	36	58	57	47	32
850	40	56	52	39	26
900	40	57	51	38	24
950	42	58	52	40	26
1000	42	43	39	33	24

$HReO_4$ reacts with Re^{-I} may explain why brown solutions or precipitates formed in attempts to prepare high concentrations of Re^{-I} from $HReO_4$. There is more evidence in support of this explanation of the precipitates than to support the assumption that Re^{IV} formed as an intermediate in the reduction of $HReO_4$ and was then precipitated due to low concentration of hydrochloric acid present.

3. Effect of $K_2Re^{IV}Cl_6$ upon Re^{-I}

The light absorption of a mixture of 0.00208 F K_2ReCl_6 and 0.00106 F Re^{-I} in 6 F hydrochloric acid was sufficiently close to the sum of the separate absorptions of the components to permit the statement that not more than 10-15% of the rhenichloride could have entered into reaction within an hour or two.

4. Preparation of Re^{+I} from Re^{-I} with Cupric Sulfate

Re^{-I} in 5 F chloride was titrated by Cu^{II}. An external test was made with starch-iodide, thus determining whether Cu^{I} was present (white precipitate of CuI) or whether Cu^{II} was present (white precipitate and formation of iodine). It was found that the first addition of cupric gave a black metallic precipitate and a brown solution which contained neither Cu^{II} nor Cu^{I}. Therefore copper metal had been formed, and the rhenium went to a colored higher oxidation state. Further addition of Cu^{II} formed Cu^{I}, which remained in solution due to the high chloride present.

In Experiment 1 of Table XXXV, the metallic precipitate was centrifuged, dried, weighed, and found to give ammonia or ferrocyanide tests for copper. The ferrocyanide precipitate was dried in an oven and found to weigh 14.9 mg. It is known that the product formed is $Cu_2Fe(CN)_6$ (43), but there is some difficulty in washing and drying such a precipitate, so the observed 14.9 mg. is satisfactory agreement with 11.9 mg. expected from the amount of copper metal observed. This near agreement shows that very little if any rhenium metal could have formed, also indicated by the fact that the strong color of the reaction mixture of Re^{-I} and Cu^{II} showed much rhenium still in colored forms.

The 4.3 mg. of copper was 0.068 mm., while 0.067 mm. of Re^{-I} had been present calculated from a ceric sulfate titration; the amount of copper agrees with

$$Re^{-I} + Cu^{II} = Re^{+I} + Cu^{0}. \qquad (21)$$

This reaction also explains the strong intermediate color similar to Re^{+I}.

Table XXXV

Effect of Cupric Sulfate upon Re^{-I}

Expt. No.	Experimental Procedure	Observations	Conclusions
1a	Slowly added 3.4 ml. of 0.070_0 F $CuSO_4$ to 23 ml. of 0.0029 F Re^{-I} in 5.4 formal chloride, 0.8 N H^+.	Metallic black ppt. formed, intense brown color in soln.	Some of the Re^{-I} was oxidized to a colored form.
1b	Centrifuged metallic ppt. Dried, weighed. Added nitric acid.	Weighed 4.3 ±0.3 milligrams. Slight blue.	Probably Cu.
1c	Added excess ammonia.	Intense blue.	Black ppt. was copper.
1d	Neutralized, added potassium ferrocyanide.	Red-brown ppt.	$Cu_2Fe(CN)_6$.
1e	Centrifuged red-brown ppt. Washed with acetone. Dried overnight at 125 °C. Weighed.	Weighed 14.9 mg.	Fair agreement with 11.5 mg. Cu_2FeCN_6 expected.
1f	Analyzed brown-yellow rhenium solution by adding KI, titrating I_2 formed.	Found 0.031 meq. I_2 for 23 ml.	0.139 mm. of the copper added was Cu^I.

An attempt had been made to add Cu^{II} to the Re^{-I} just to the first excess of Cu^{II}, however addition of KI indicated some Cu^{II} because a little iodine formed along with a heavy white CuI precipitate. The Cu^{II} added was 0.238 millimols, of this 0.068 mm. went to copper metal, 0.031 mm. was found by titration of the iodine, and by difference 0.139 mm. was Cu^{I}. Assuming all the 0.031 mm. Cu^{II} resulted from air oxidation of Cu^{I}, the Re^{I} was largely oxidized to Re^{IV} by Cu^{II}, also indicated by the large CuI precipitate observed.

In a similar experiment, 30 ml. of 0.0029 F Re^{-I} in 5.4 F chloride was treated with 1.8 ml. of 0.070 F $CuSO_4$ adding the Cu^{II} slowly. The copper formed weighed 6.2 ± 0.3 milligrams, or was 0.098 millimols, a ratio of 1.1 to the 0.086 millimols of Re^{-I} compared to 1.0 expected for Reaction 21.

No indication of oxidation of Cu^{0} by Cu^{II} was given unless considerable excess Cu^{II} was added. If the Re^{-I} was titrated slowly, the amount of Cu^{II} used was about that for oxidation to Re^{IV}. With rapid addition, not much Cu^{0} but rather Cu^{I} formed, and excess gave oxidation of some of the Re^{IV} to Re^{VII}, as expected from Sec. V-D-2-d.

5. Potentiometric Titrations of Re^{-I}

Solutions of Re^{-I} were titrated by Ce^{IV}, measuring the potential with a platinum indicator electrode against a saturated calomel reference electrode. The observed potential, corrected to the hydrogen electrode by subtraction of 246 millivolts for the calomel electrode, remained practically constant at +50 millivolts until an amount of Ce^{IV} corresponding to complete oxidation to ReO_4^- had been added. The potential (vs. hydrogen electrode) then fell to about -1500 millivolts for the solutions in 5.4 F chloride and 1.5 N H^+. A check titration of ferrous sulfate was made by ceric sulfate, and all the observed values of potential came out 150-170 millivolts more negative than the values expected. The observed potential 1% past the end-point was -1.53 volts instead of -1.32 volts expected from the formal potentials for the ferrous-ferric and the ceric-cerous couples, Swift (45); this titration was done in 0.2 F H_2SO_4. Because of this discrepancy, no attempt will be made to interpret the results on the Re solutions.

The Re^{-I} had been exposed to air during the 15 minutes of the titration, but the results ran only 10-15% lower than direct titration of a fresh solution. Although the potential remained nearly constant till the last addition of the Ce^{IV}, a brown intermediate formed and disappeared.

In similar experiments on the titration of Re^{-I} with ferric sulfate, it was found by external tests that the reduction product was ferrous, no iron metal was observed.

No potential break from the value +50 millivolts was obtained till complete oxidation to ReO_4^-. Titrations were also performed with cupric sulfate, forming copper metal initially as in Sec. VII-4. Because of the complex reactions of rhenium with cupric, and the unknown air oxidation of the Cu^I formed in later stages, all that can be stated is that considerable oxidation of the Re^{-I} occurred and that the potential remained the same till the end of the titration.

6. Summary of the Chemistry of Re^{+I}

Light absorption measurements showed that Re^{-I} is oxidized by perrhenate, ReO_4^-, to Re^{+I} and that further addition of $Re^{VII}O_4^-$ gave Re^{IV}. The Re^{+I} was stable in 4 F hydrochloric acid in capped cells; because of low rates, formation of Re^I or Re^{IV} required 15 hours. Oxygen also formed Re^I and Re^{IV} in steps from Re^{-I}, giving Re^{VII} as final product. The absorption spectrum of the Re^{IV} prepared from Re^{-I} with Re^{VII} resembled that of rhenium dioxide in hydrochloric acid. Potassium rhenichloride and Re^{-I} were found not to react.

In a slow titration of Re^{-I} by cupric sulfate, copper was formed in just the amount expected from

$$Re^{-I} + Cu^{II} = Re^{+I} + Cu^0. \qquad (21)$$

The rhenium solution also acquired a yellow-brown color similar to that of Re^{+I}. Further addition of Cu^{II} oxidized the Re^{I} to Re^{IV} and formed cuprous chloride, complexed in the hydrochloric acid present.

Potentiometric titrations of Re^{-I} by ceric sulfate or ferric sulfate showed no potential break till complete oxidation to $Re^{VII}O_4^-$. Similarly, no intermediate break was observed with cupric sulfate.

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Supplementary Data for Table VIII

Solution Number	Age of Solution	Volume Re Soln in 4 F HCl (ml.)	$Ce(SO_4)_2$ Soln. Volume (ml.)	$Ce(SO_4)_2$ Soln. Meq.	F HCl after mixing Re and Ce^{IV} Solutions
1	45 min.	0.50	0.30	0.0139	2.5
2	2½ hr.	0.50	0.80	0.0370	1.5
3	2 hr.	0.50	0.80	0.0370	1.5
3	2½ hr.	0.50	0.80	0.0370	1.5
4	50 min.	0.50	0.80	0.0370	1.5
1	50 min.	0.50	0.30	0.0139	2.5
2	4 hr.	0.50	0.80	0.0370	1.5

Supplementary Data for Table IX

Solution Number	Age of Solution	Volume of Re^{V} Soln. in 4 $\underline{F}$ HCl (ml.)	Volume $I_2 + H_2O$ (ml.)	Meq. I_2 present	$\underline{F}$ HCl after mixing solutions
1	30 min.	0.50	10	0.0178	0.2
1	55 min.	0.50	10	0.0268	0.2
1	60 min.	0.50	10	0.0356	0.2
2	730 min.	1.00	2.54	0.0445	1.16

Supplementary Data for Table X

Solution Number	Age of Solution	Volume Re Soln. in 4 F HCl (ml.)	Volume KIO_3+ H_2O (ml.)	Meq. KIO_3 Added	F HCl after mixing Re and KIO_3 solutions
2	2½ hr.	0.50	0.80	0.0335	1.4
3	2 hr.	0.60	1.10	0.0490	1.5
5	735 min.	1.00	2.54	0.0445	1.13

Supplementary Data for Table XIII

Solution Number	Age of Solution	Volume Re Soln. in 4 F HCl (ml.)	$Ce(SO_4)_2$ Soln.		F HCl after mixing Re and Ce^{IV} solutions
			Volume (ml.)	Meq.	
1	22 hr.	0.50	0.80	0.0370	1.5
2	66 hr.	1.00	1.00	0.0462	2.0
3	$64\frac{1}{2}$ hr.	1.00	1.00	0.0462	2.0
5	$64\frac{1}{2}$ hr.	1.00	1.00	0.0462	2.0
1	22 hr.	0.50	0.80	0.0370	1.5
1	24 hr.	0.40	0.80	0.0370	1.3
1'	$6\frac{1}{4}$ hr.	0.50	0.80	0.0370	1.5
3	$64\frac{1}{2}$ hr.	1.00	1.00	0.0462	2.0
3	113 hr.	0.50	1.00	0.0462	2.0
5	113 hr.	0.50	0.50	0.0231	2.0

Supplementary Data for Table XIV

Solution Number	Age of Solution	Volume Re Soln. in 4 $\underline{F}$ HCl (ml.)	Volume I_2 + H_2O (ml.)	Meq. I_2 Present	$\underline{F}$ HCl after mixing Re and I_2 Solutions
1	22 hr.	0.522	16	0.0355	0.1
1	24 hr.	0.30	16	0.0355	0.07
1	24 hr.	0.40	16	0.0379	0.1
1'	6 hr.	0.50	16	0.0356	0.1
5	64½ hr.	1.00	5	0.0445	0.7
5	113 hr.	0.40	10	0.0111	0.2
1	22 hr.	0.50	16	0.0355	0.1

Table XVI

Reaction of Chromous Chloride with Perrhenic Acid

Supplementary Data

Expt. No.	$HReO_4$ in HCl Vol. (ml.)	 F $HReO_4$	Vol. Cr Soln. (ml.)	Time with O_2 (min.)	Vol. Ce^{IV} 0.0462 N	Remarks
1	0.50	0.0100	1.25	2	0.50	Bubbled air.
2	1.00	0.0100	2.0	2	1.08	Bubbled air.
3	2.00	0.00483	5.0	1	0.59	
4	2.00	0.00483	5.0	1	0.59	
5	2.00	0.00483	5.0	1	1.00	
6	2.00	0.00483	3.0	1	0.59	
7	2.00	0.00483	3.0	1	0.80	
8	2.00	0.00483	5.0	1	0.61	Added 25 ml. H_2O.
9	2.00	0.00483	3.0	1	0.65	
10	1.00	0.0252	5.0	1	2.00	
11	1.00	0.0252	5.0	1	1.62	$KReO_4$ Soln. in H_2O.
12	1.00	0.0252	5.0	1	1.50	"
13	1.00	0.0252	5.0	1	1.80	"
14	1.00	0.0252	5.0	1	1.65	" Added 1 ml. 6 N HCl.
15	1.00	0.0252	5.0	1	1.47	" $KReO_4$ Soln. in H_2O.
16	0.50	0.0480	5.0	1	1.43	
17	0.50	0.0480	5.0	1	1.42	
18	0.50	0.0480	5.0	1	1.44	

Supplementary Data for Table XVIII

Soln. No.	Age of Soln. (min.)	Volume Re Soln. used (ml.)	Total Volume Re + Ox. Agent + H_2O + HCl (ml.)	F HCl in mixture Ox. Agent + Re Soln.
1	21	5.00	10.7	2.8
1	6	5.00	7.0	5.1
1	25	5.00	7.0	4.7
2	8	5.00	10.7	2.8
2	1	5.00	6.5	5.1
2	6	5.00	6.5	5.1
3	6	5.00	7.0	3.6
3	16	5.00	7.1	3.6
3	1	5.00	6.0	4.3
3	10	5.00	7.3	3.5
3	20	5.00	7.5	3.4

Supplementary Data for Table XX

Expt. No.	Volume of Rhenium Soln. Used (ml.)	Total Volume Re with I_2 (ml.)	$\underline{F}$ HCl in $\overline{M}$ixture of Re with I_2
1	0.30	5.7	0.23
2	0.20	5.5	0.22
3	0.20	5.5	0.22
4	0.50	6	0.47
5	0.50	15.7	0.40
6	0.80	11.2	0.29
7	5.00	11	2.2
8	5.00	11	2.3

Supplementary Data to Table XXI

Expt. No.	Volume Re Soln. (ml.)	Total Volume Reaction Mixture of Re + Fe^{III} (ml.)	F HCl in Reaction Mixture of Re + Fe^{III}	F HCl in Solution of Re, Re^{III} and KI before Titration of I_2
1	0.50	0.595	4.7	
2	0.50	0.62	4.5	0.2
3	5.00	5.75	3.9	1.5
4	2.00	2.35	3.8	0.6
5	5.00	5.80	5.2	2.0
6	5.00	6.00	5.0	2.0
7	5.00	5.75	5.2	2.0
8	5.00	5.75	5.2	2.0
9	5.00	6.50	4.6	2.0

Figure 1. Absorption for Various Ratios of $SnCl_2$(meq.):$HReO_4$(mm

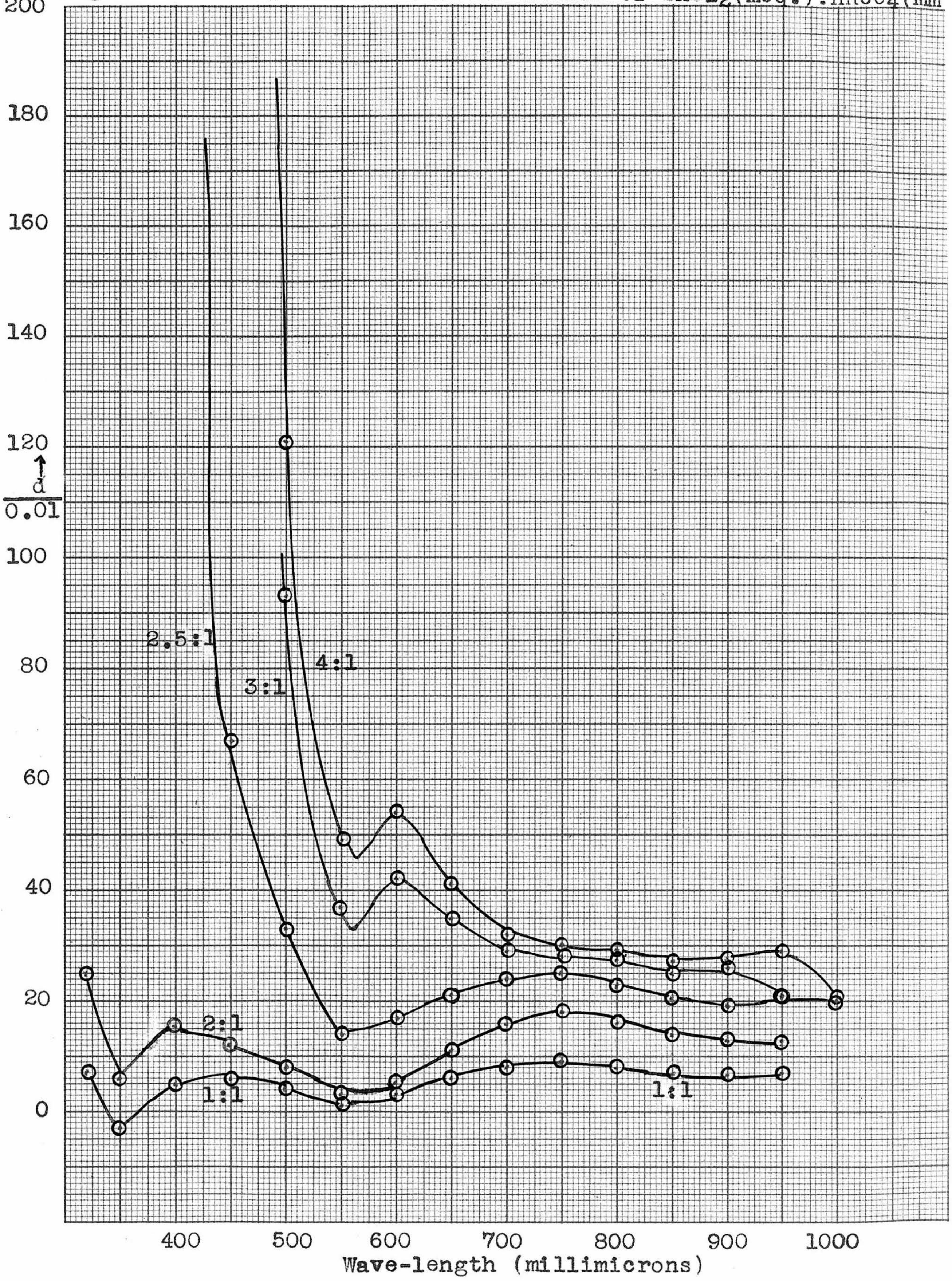


Figure 2. Absorption Curve for Re(V) in 4 F HCl

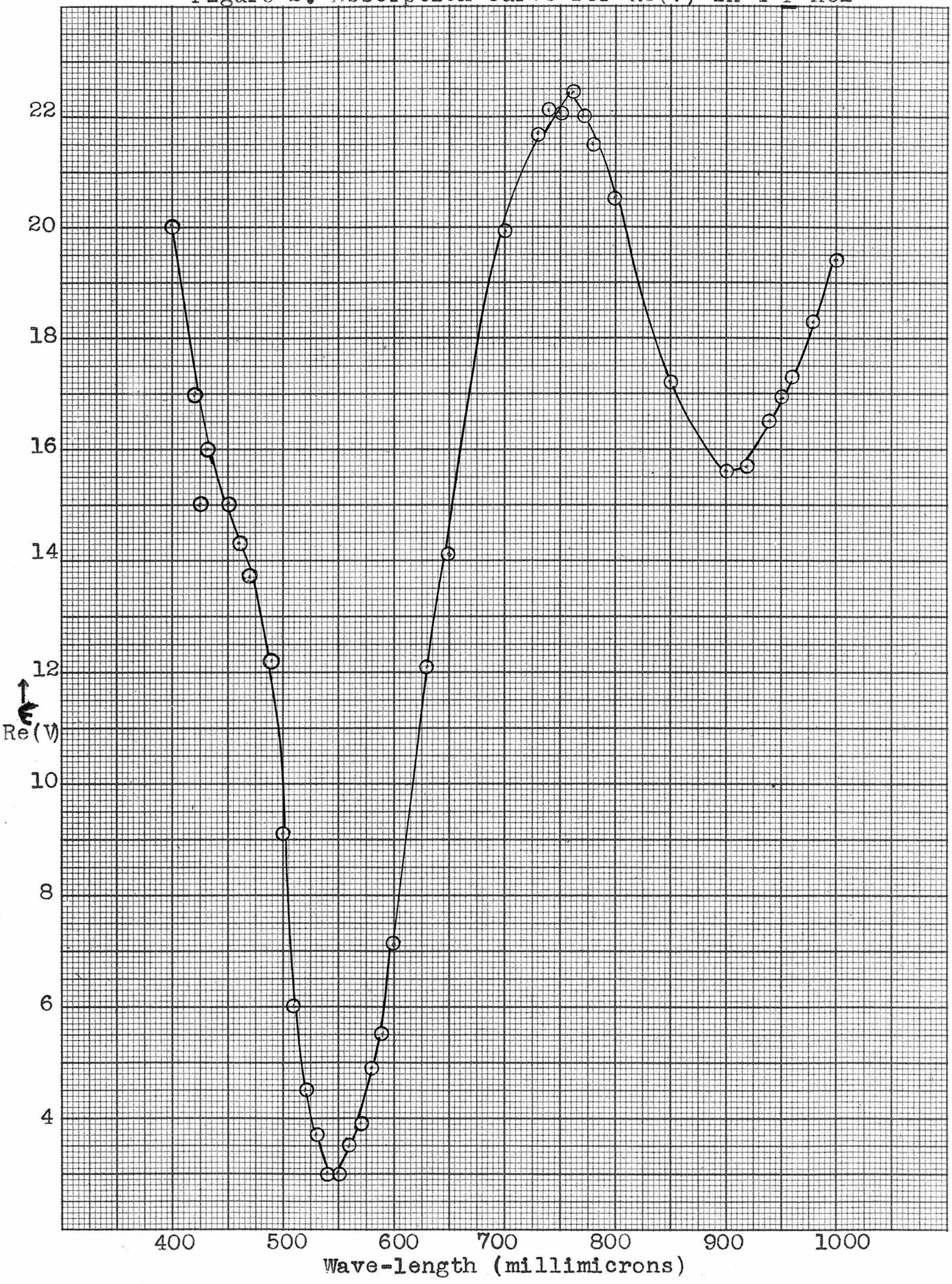


Figure 3. Absorption for Various Ratios of $SnCl_2$(meq.):$HReO_4$(mm.)

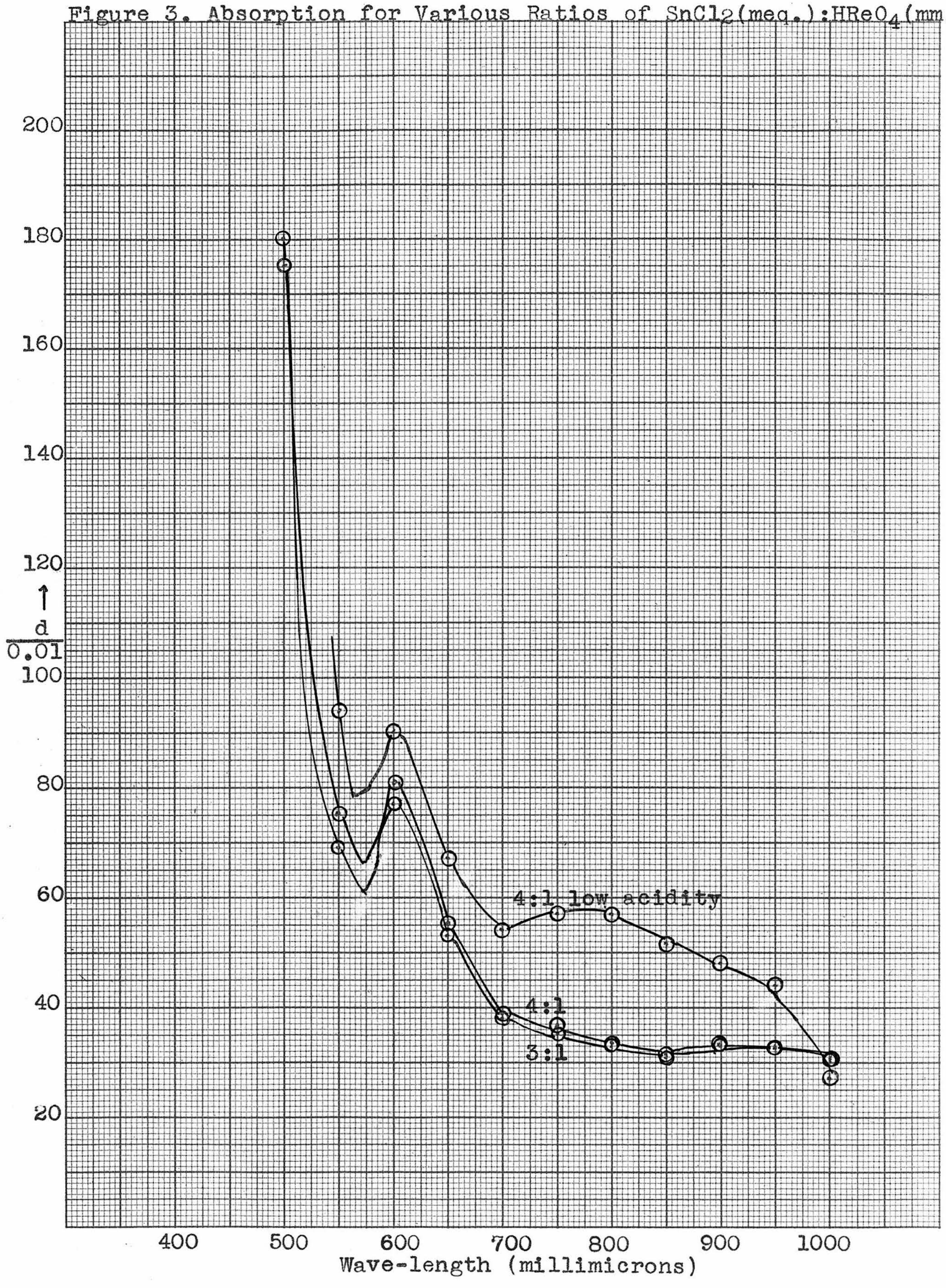


Figure 4. Absorption Curves for Re(V) and Re(IV) in 4 F HCl

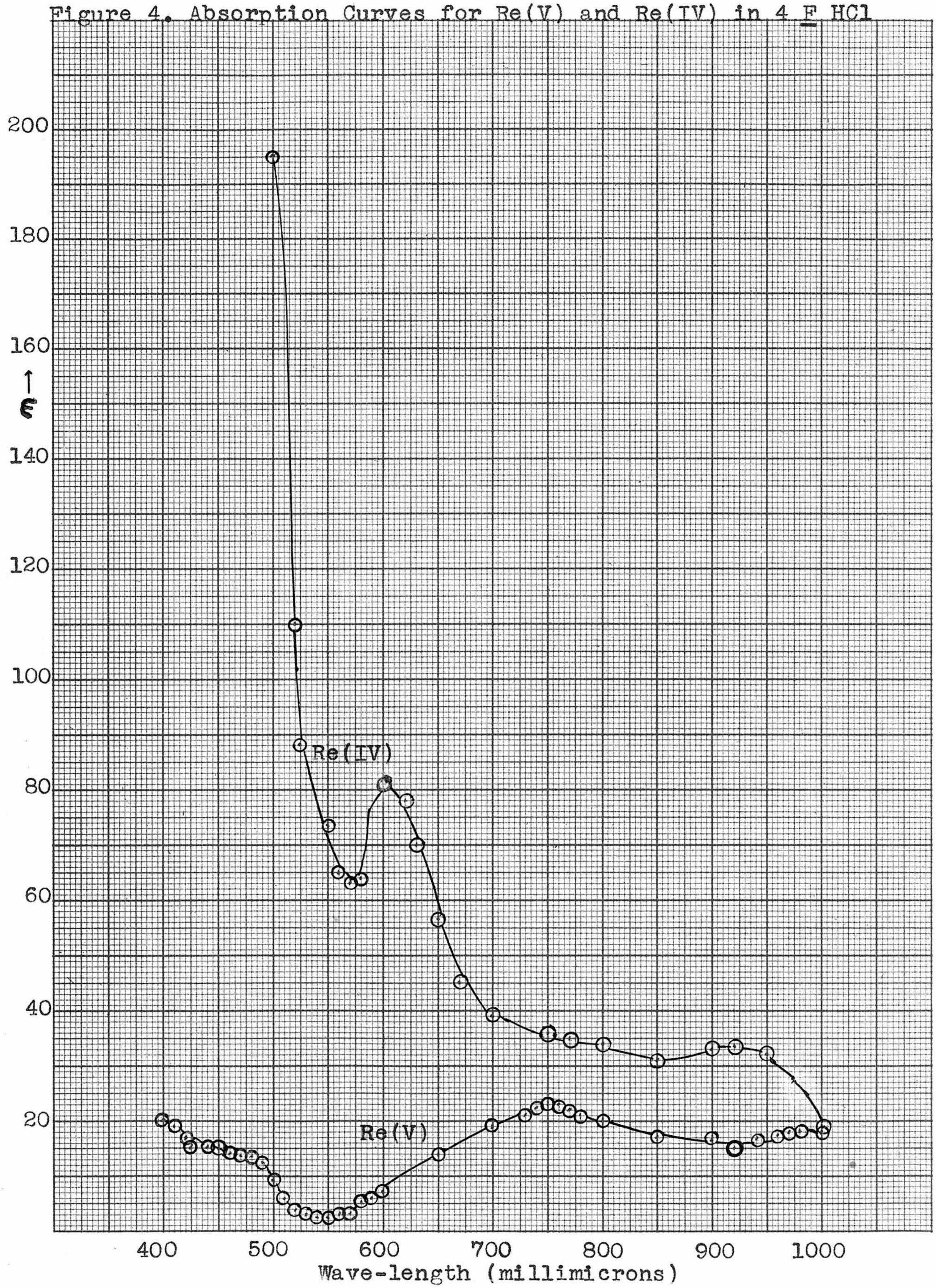


Figure 5. Light Absorption of Potassium Rhenichloride

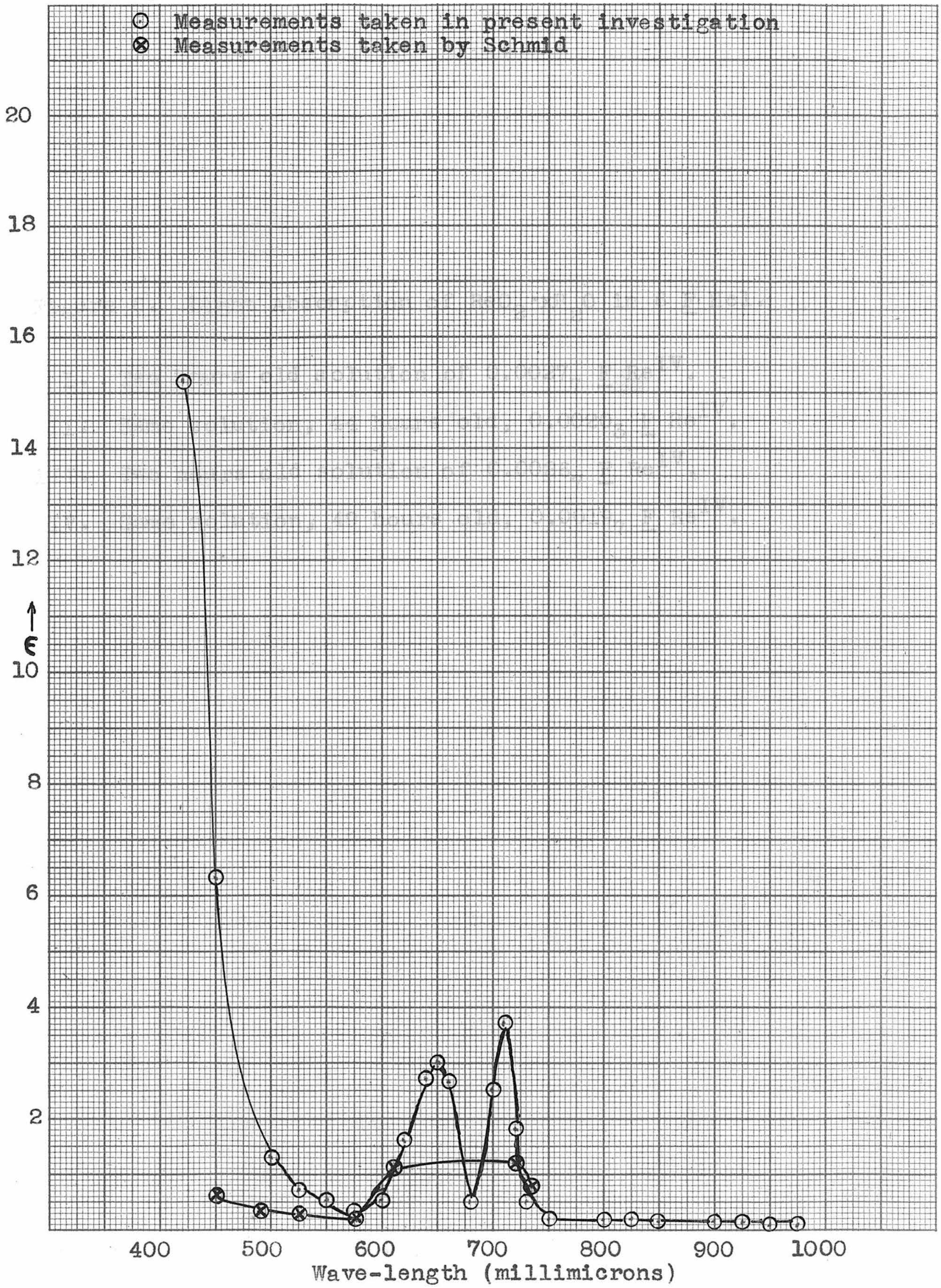


Figure 6. Light Absorption of $ReO_2 \cdot xH_2O$ in 6 F Hcl.

I. Two hours old solution of 0.0027_7 F Re^{IV}.

II. Same solution, 44 hours old, 0.0020_3 F Re^{IV}.

III. Two hours old solution of 0.0026_7 F Re^{IV}.

IV. Same solution, 49 hours old, 0.0019_7 F Re^{IV}.

Figure 6. Light Absorption of $ReO_2 \cdot xH_2O$ in 6 F HCl

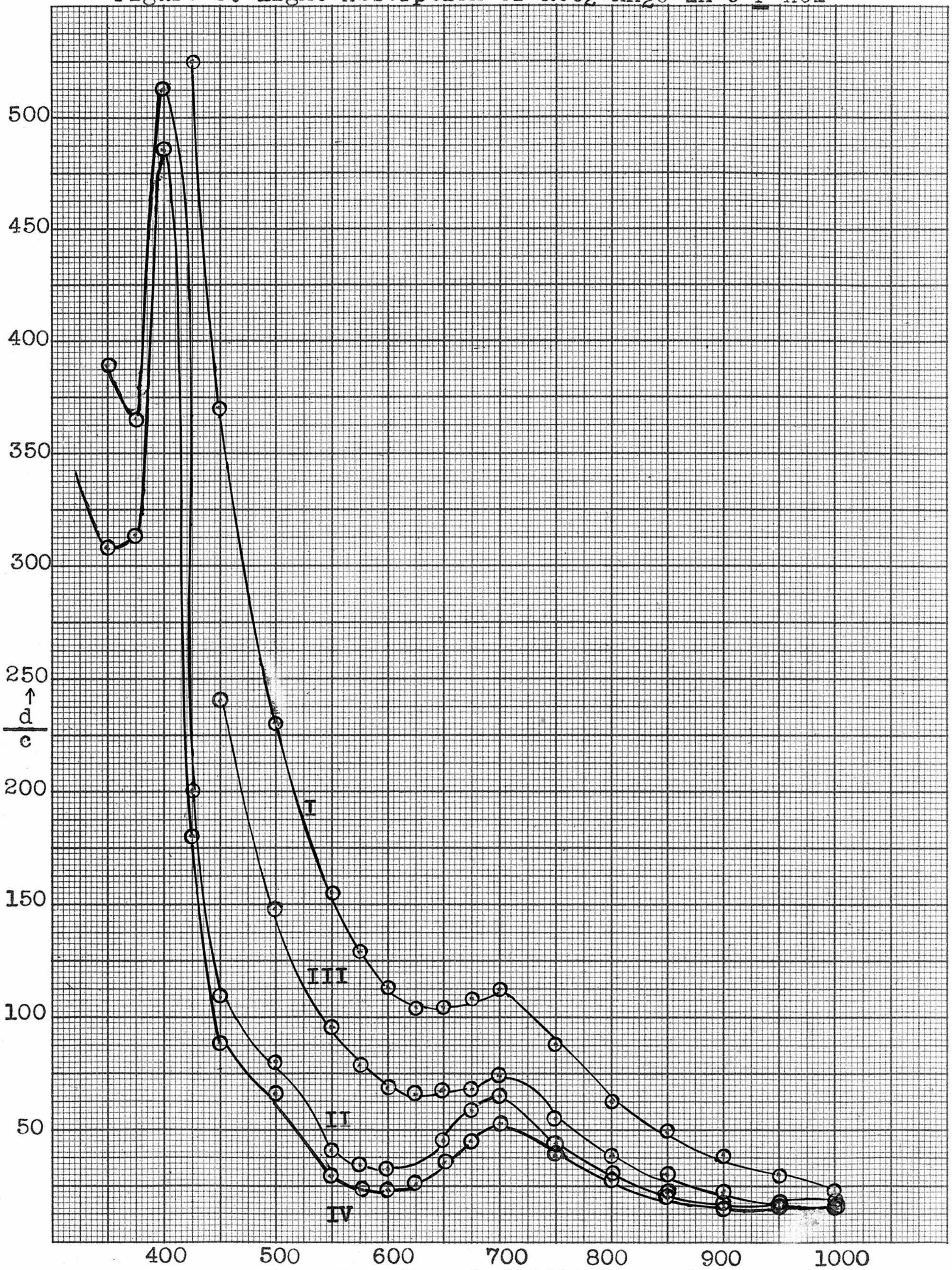


Figure 7. Absorption of $ReCl_6^{=}$ Prepared from $ReO_2 \cdot xH_2O$

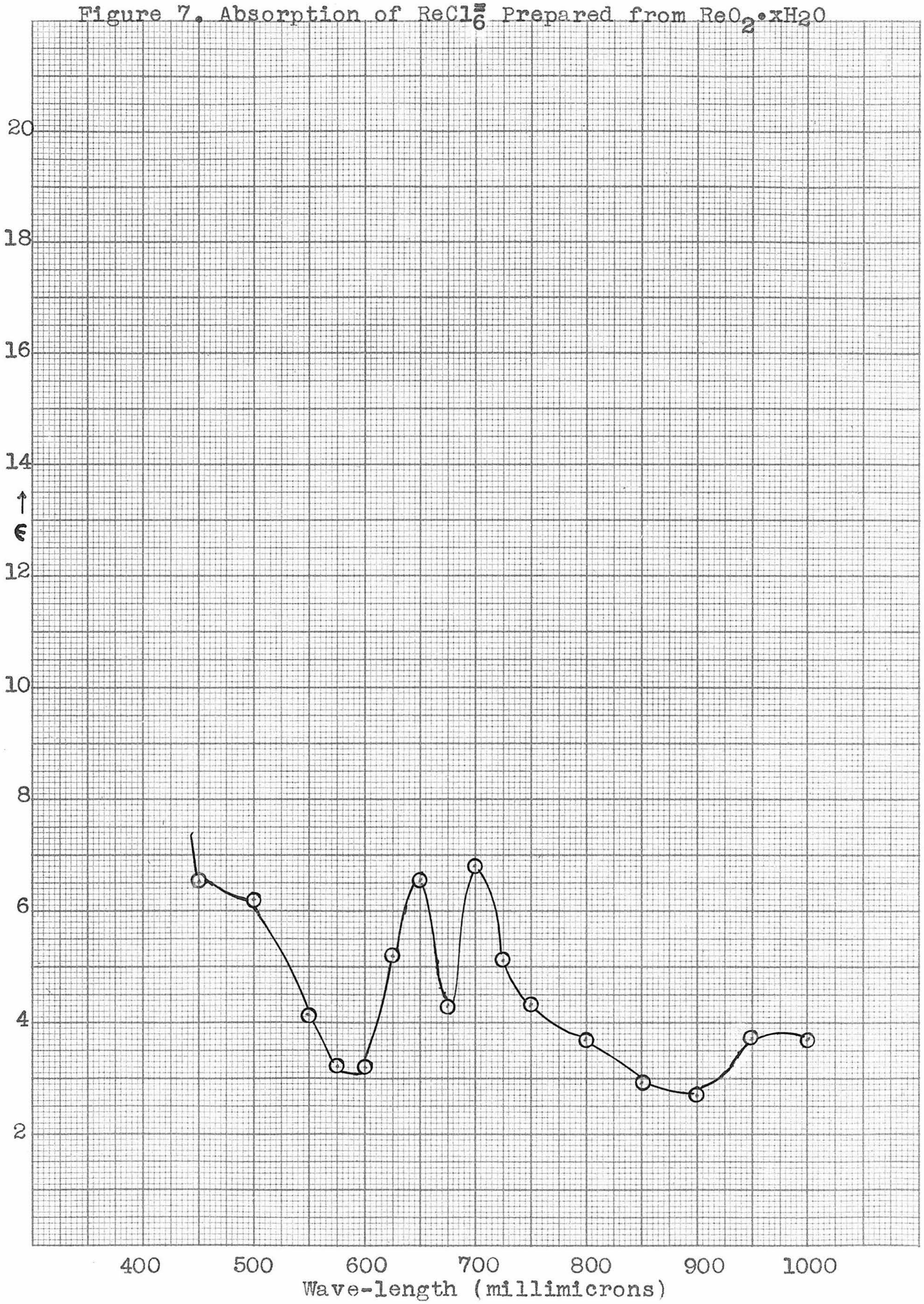


Figure 8. Absorption of Re(IV) from Perrhenate and Cold Iodide

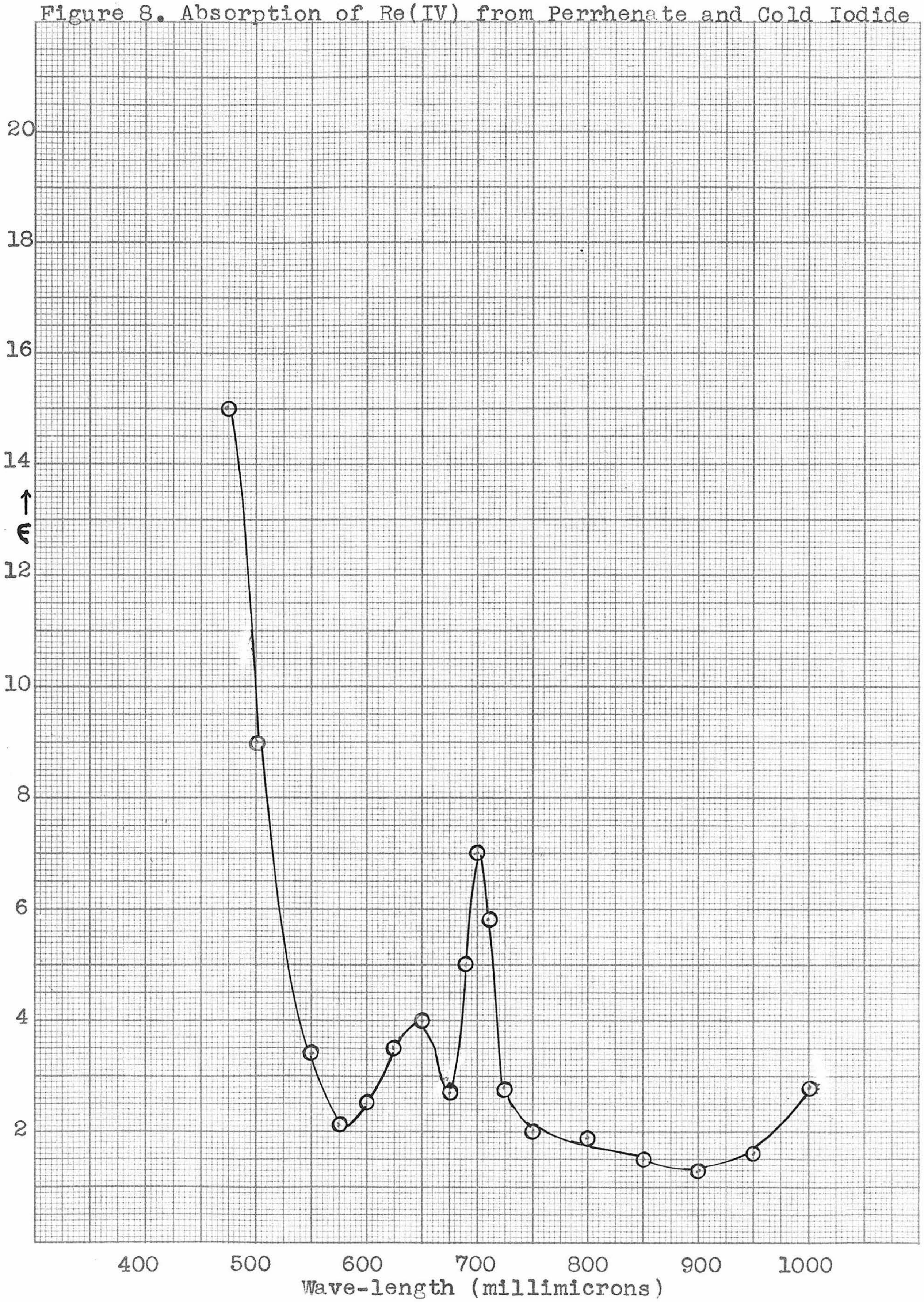


FIG. 9 JONES REDUCTOR

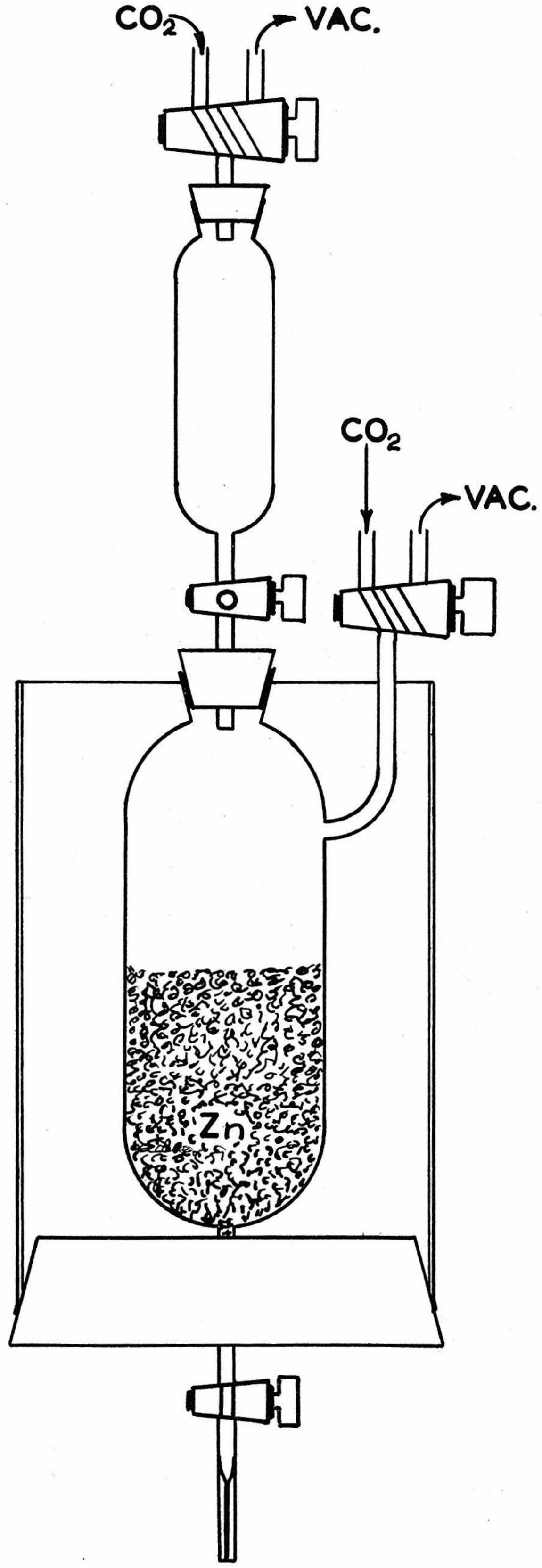


Figure 10. Light Absorption of 0.024 F $HReO_4$ in 6 F HCl reduced by liquid amalgam of zinc

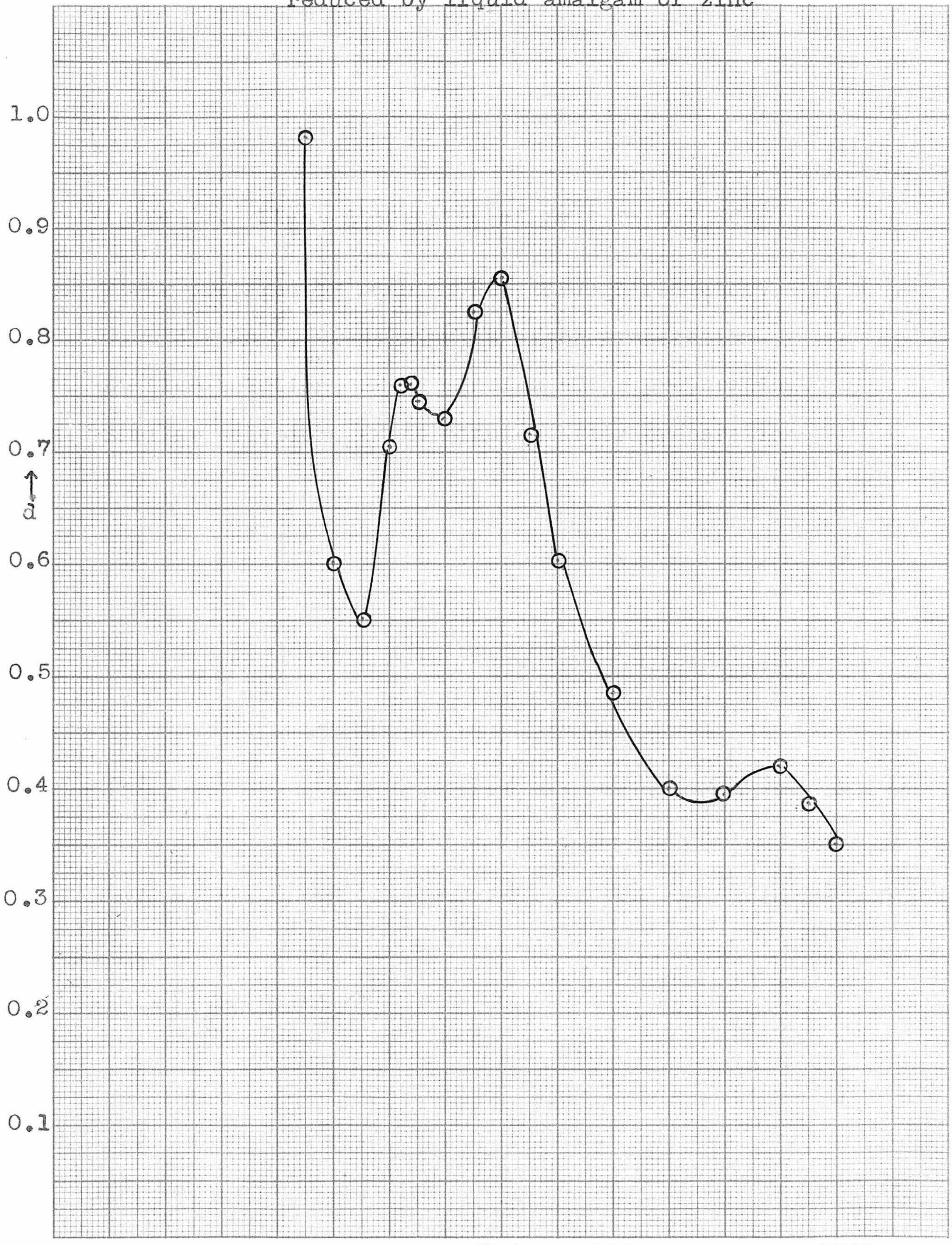


Figure 11. Light Absorption of Re^{-I} in 4 $\underline{F}$ HCl

B. Blank prepared by running HCl through reductor.

I. 0.0013 $\underline{F}$ Re^{-I}, 22-44 minutes after preparation.

II. Similar solution, 22-44 minutes after preparation.

III. Similar solution, 22-44 minutes after preparation.

Figure 11. Light Absorption of Re(-I) in 4 F HCl

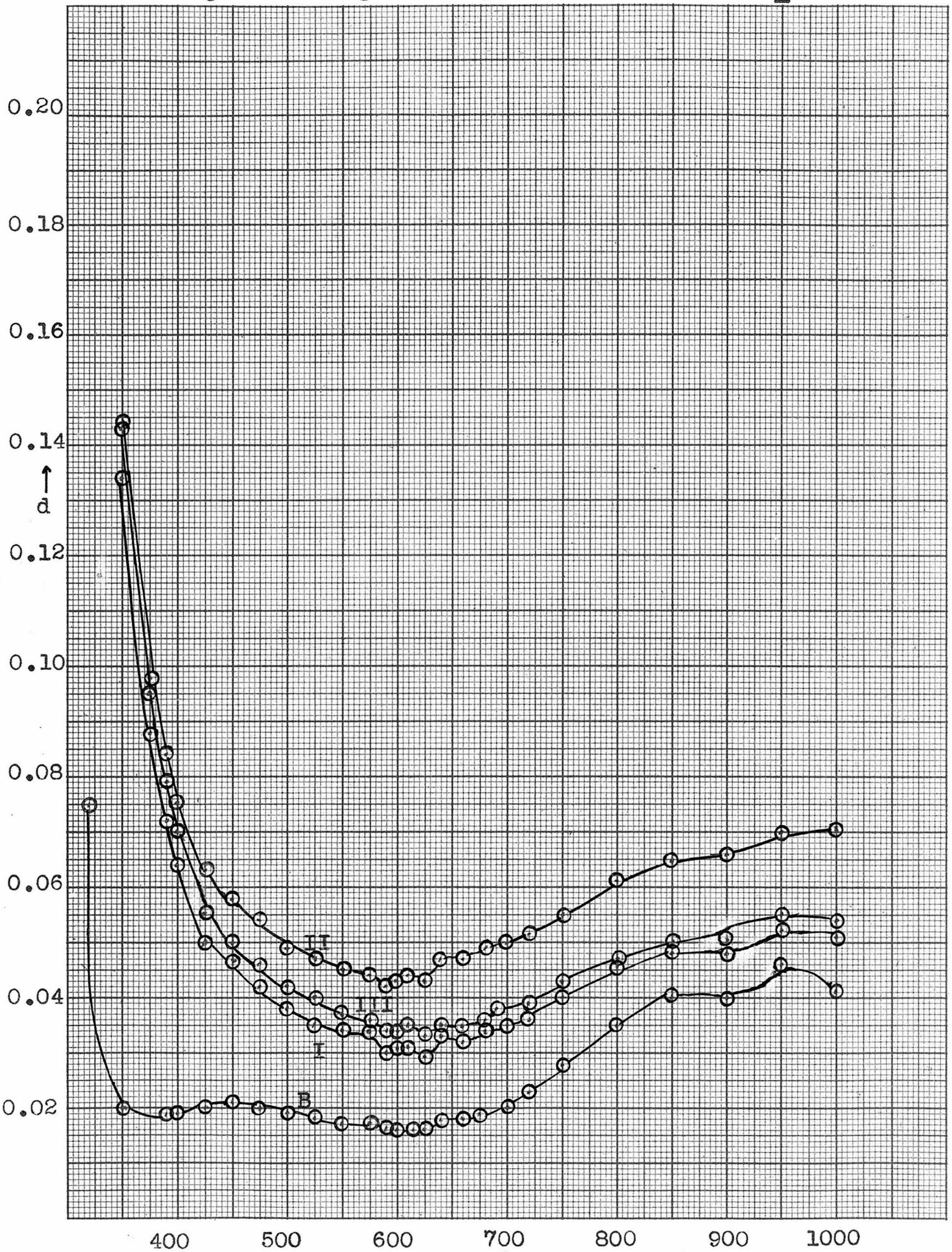


Figure 12. Effect of Time upon 0.0012_7 F Re(-I) in 4 F HCl

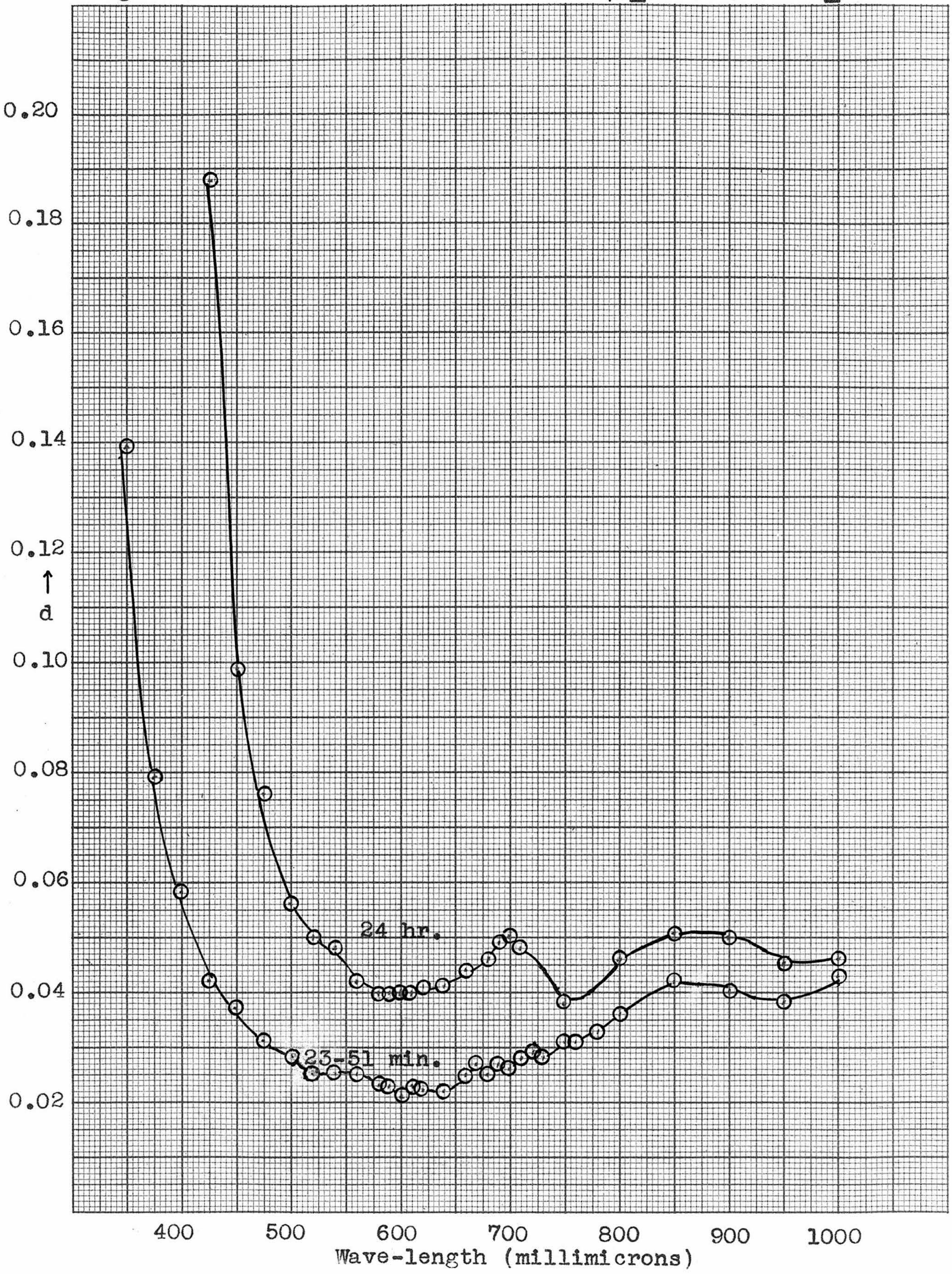


Figure 13. Effect of Time upon 0.0013 F Re(-I) in 4 F HCl

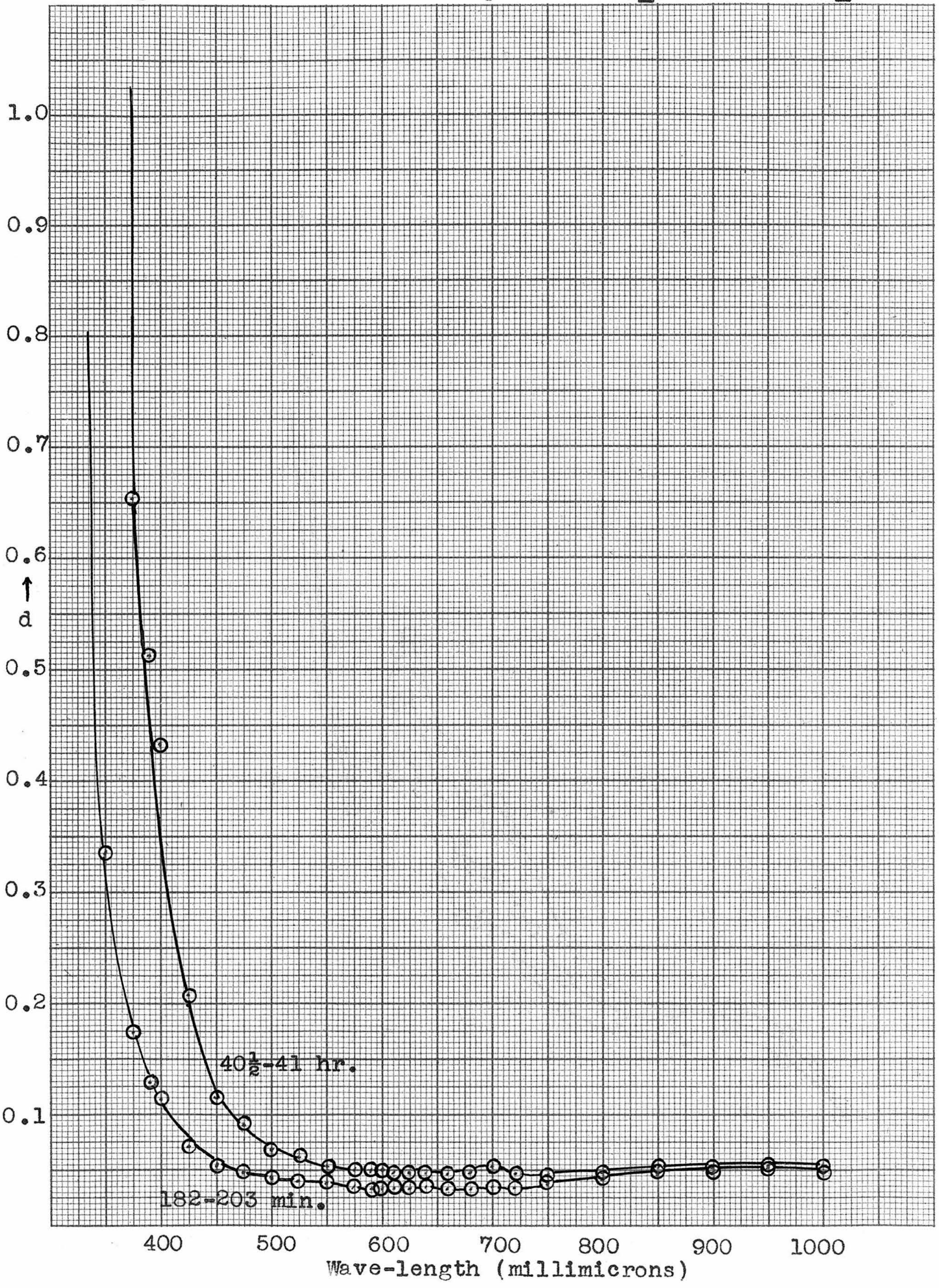


Figure 14. Light Absorption of 0.0012$_7$ F Re(-I) in 4 F HCl Exposed to Air for Time Given

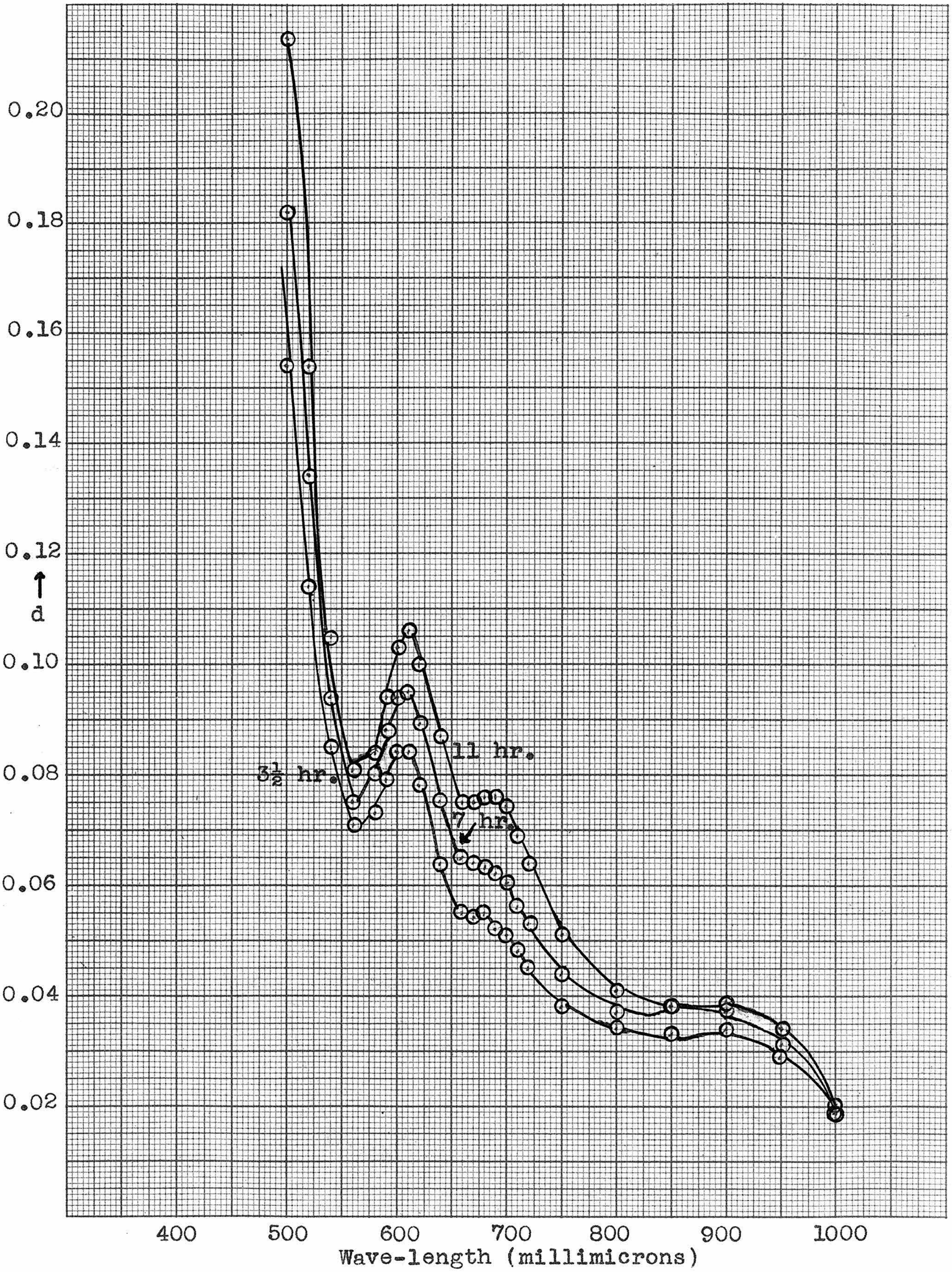


Figure 15. Light Absorption of 0.0012$_7$ F Re(-I) in 4 F HCl Exposed to Air for Time Given

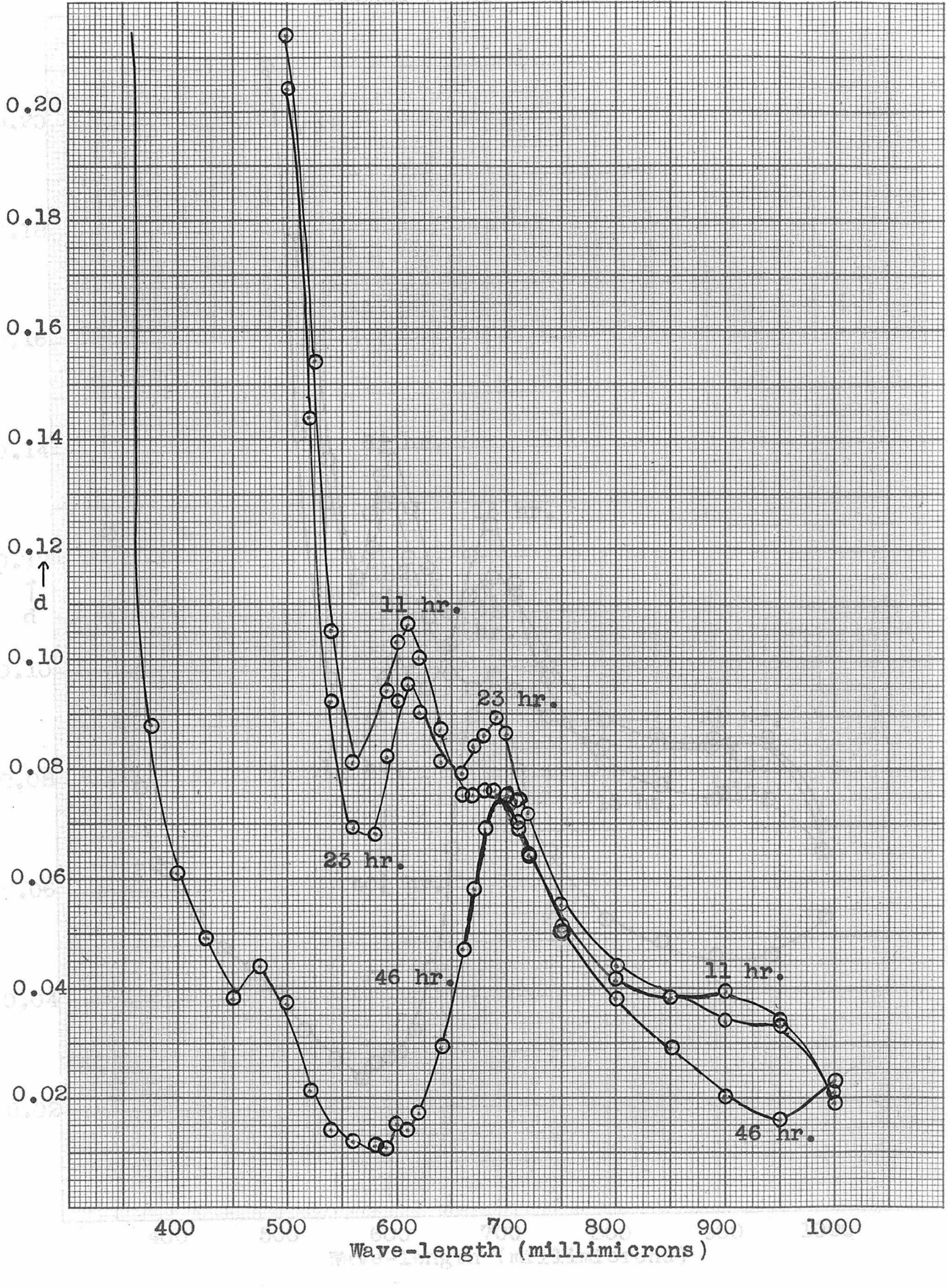


Figure 16. Light Absorption of 0.0013 F Re(-I) in 4 F HCl Exposed to Air for Time Given

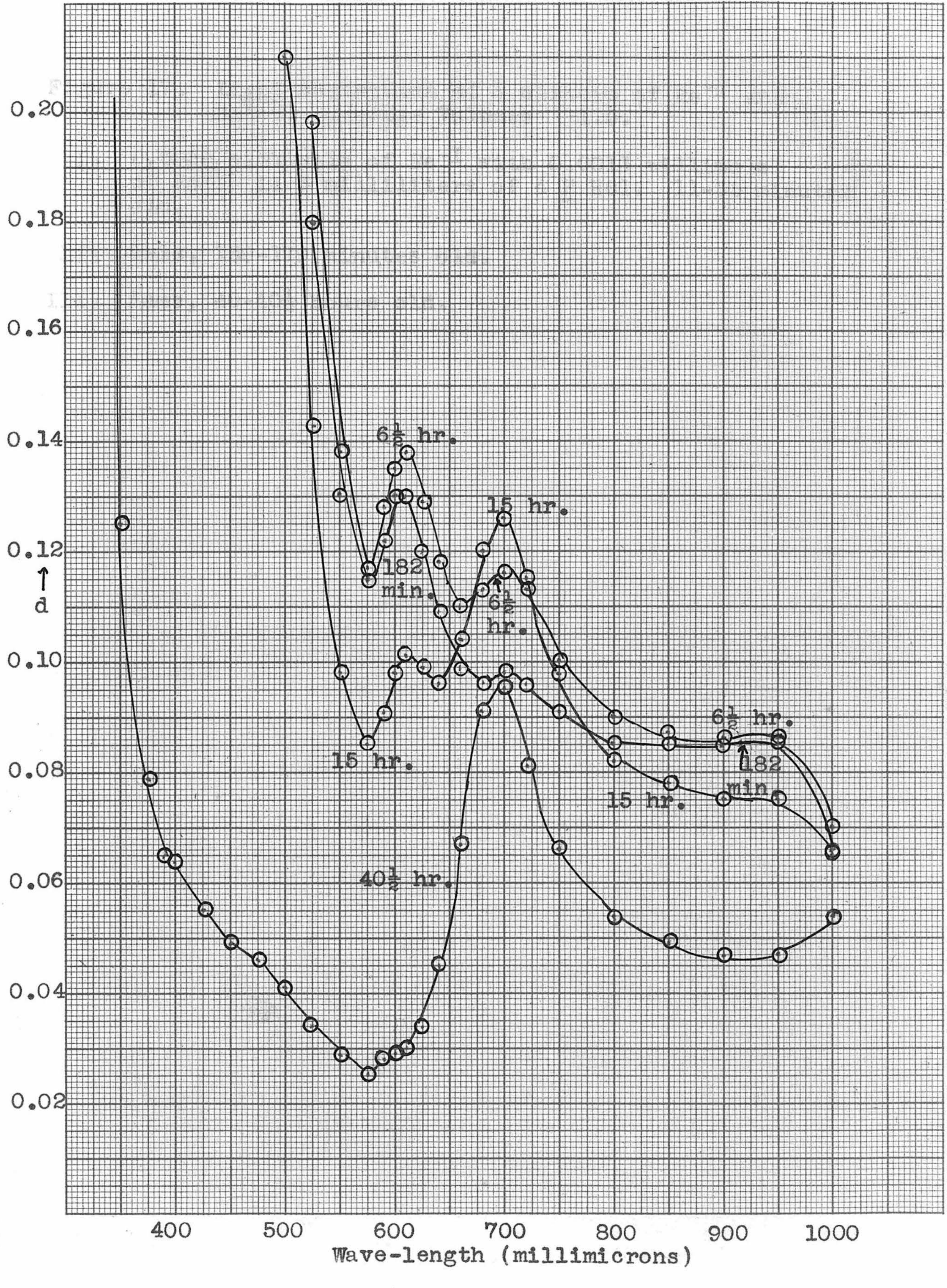


Figure 17. Light Absorption of a Mixture of Re^{-I} and Re^{VII}. Average Valence +1.0.

I. 0.0039 millimols of Re^{-I} with 0.0013 millimols of Re^{VII} in 3 milliliters of 4 F HCl. 11-35 minutes old.

II. Same, 159-179 minutes old.

III. Same, 40-40½ hours old.

Figure 17. Light Absorption of a Mixture of Re(-I) and Re(VII)
Average Valence +1.0

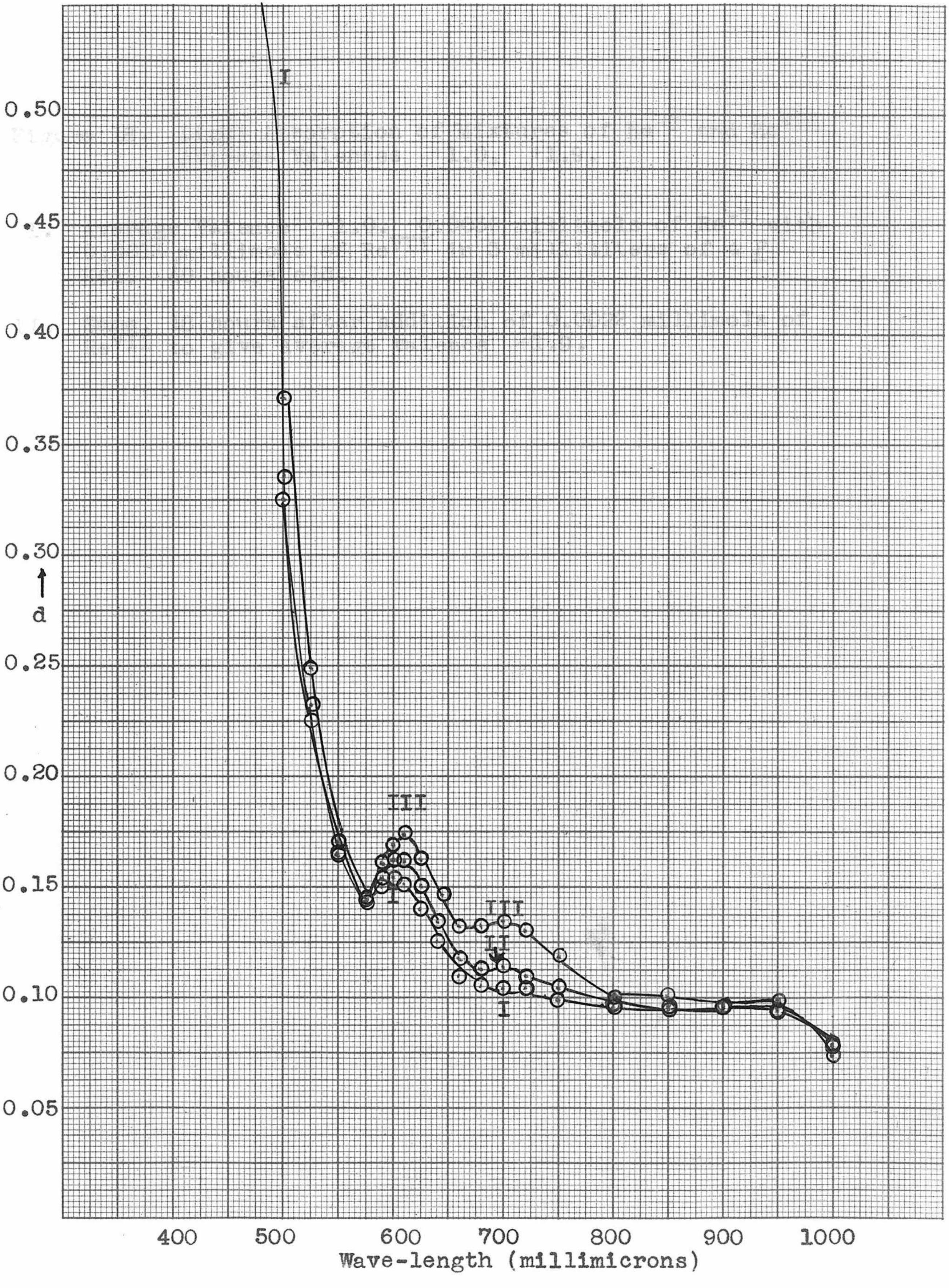


Figure 18. Light Absorption of Mixtures of Re^{-I} and Re^{VII}. Average Valences +1.0, +1.9.

I. Average Valence +1.0. 0.0039 millimols of Re^{-I} with 0.0013 millimols of Re^{VII} in 3 milliliters of 4 F HCl. 40 hours old.

II. Same, 18 hours after addition of 0.0022 millimols of Re^{VII} to give average valence +1.9.

Figure 18. Light Absorption of Mixtures of Re(-I) and Re(VII)
Average Valences +1.0,+1.9

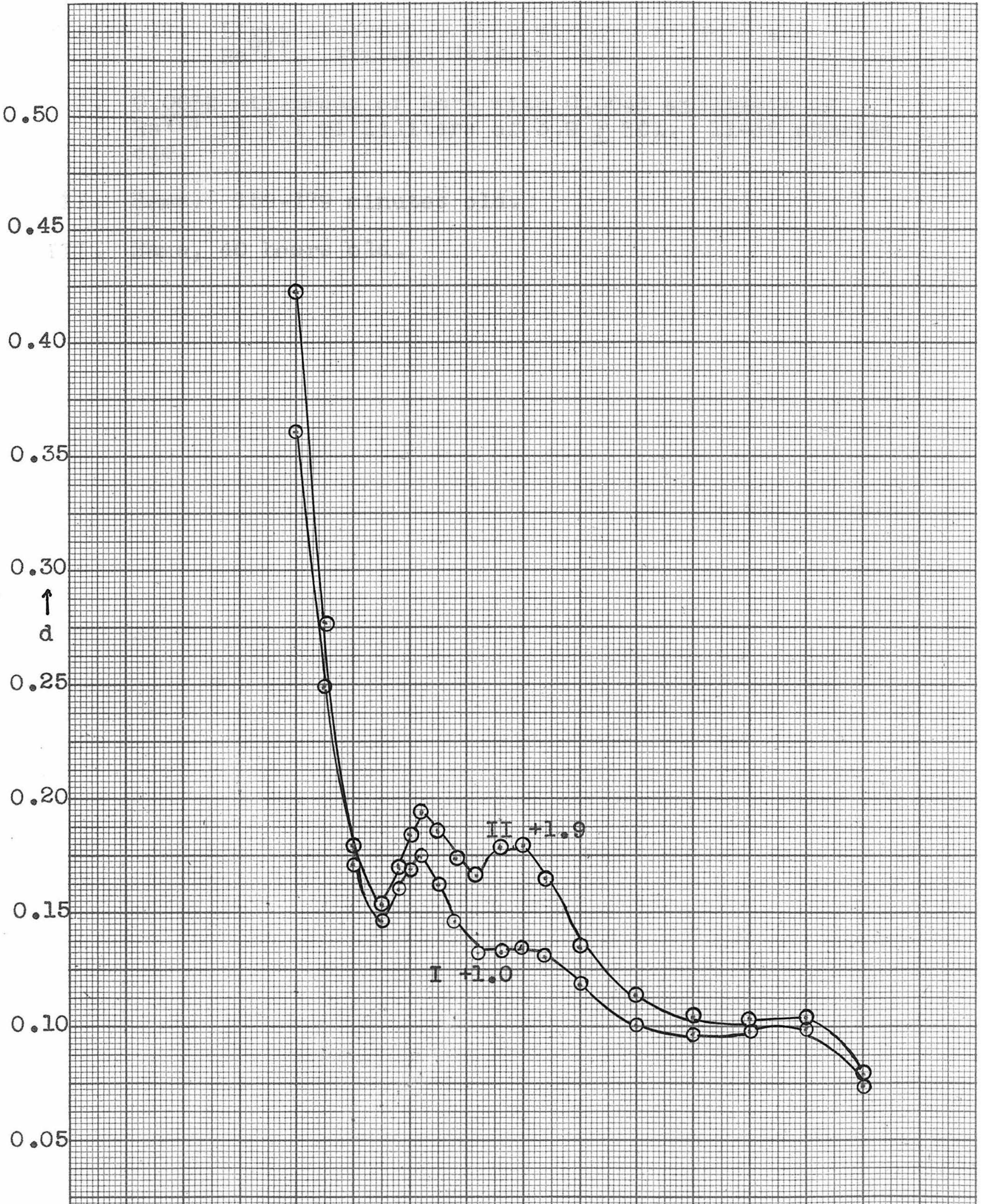


Figure 19. Light Absorption of a Mixture of Re^{-I} and Re^{VII}. Average Valence +3.2

I. 0.0039 millimols of Re^{-I} with 0.0043 millimols of Re^{VII} in 3.1 milliliters of 3.9 F HCl. 11-35 minutes old.

II. Same. 159-179 minutes old.

III. Same, 40 hours old.

Figure 19. Light Absorption of a Mixture of Re(-I) and Re(VII) Average Valence +3.2

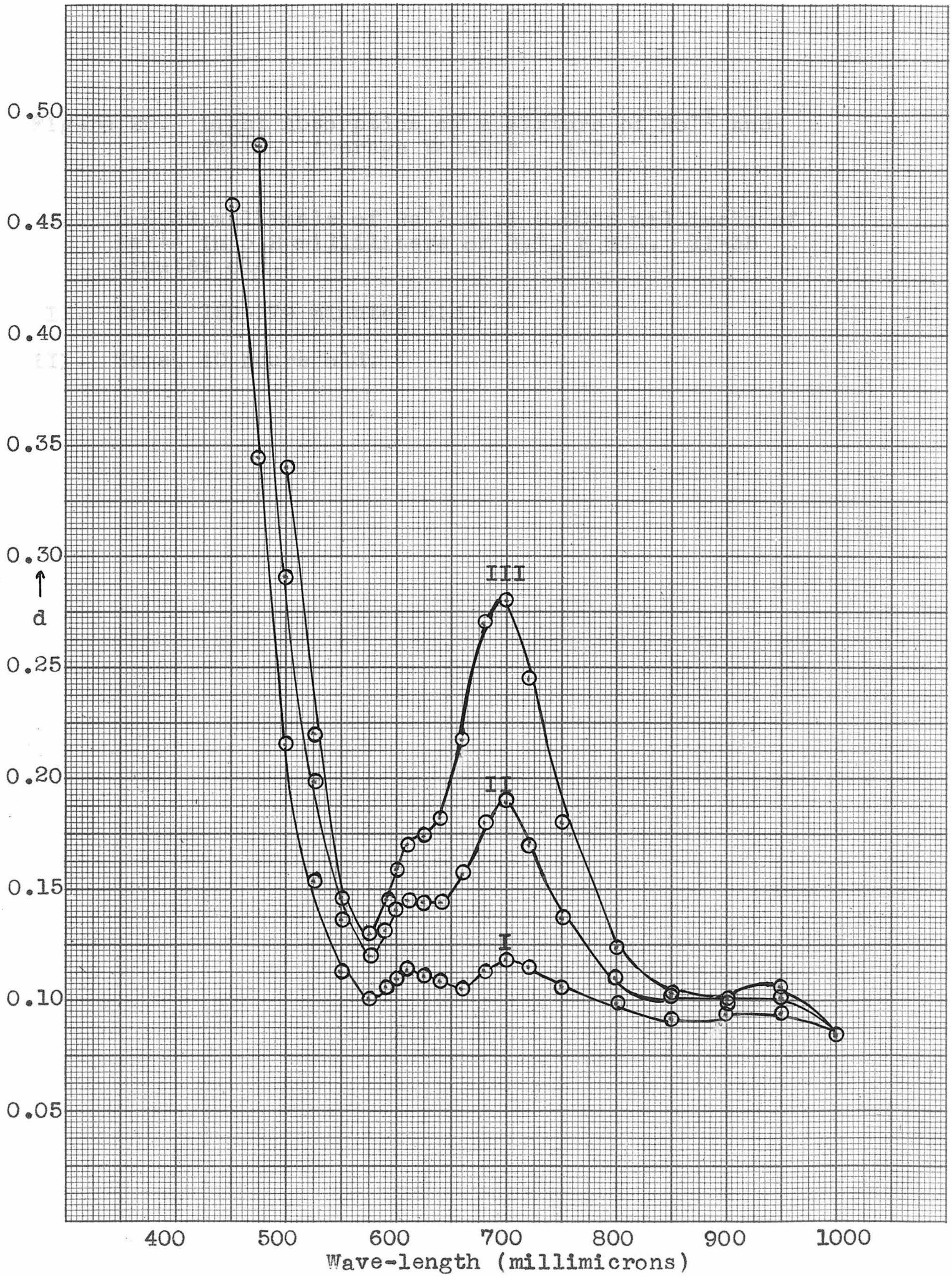


Figure 20. Light Absorption of a Mixture of Re^{-I} and Re^{VII}. Average Valence +4.5.

I. 0.0039 millimols of Re^{-I} with 0.0086 millimols of Re^{VII} in 3.2 milliliters of 3.7_5 F HCl. 11-35 minutes old.

II. Same, 159-179 minutes old.

III. Same, 40 hours old.

Figure 20. Light Absorption of a Mixture of Re(-I) and Re(VII)
Average Valence +4.5

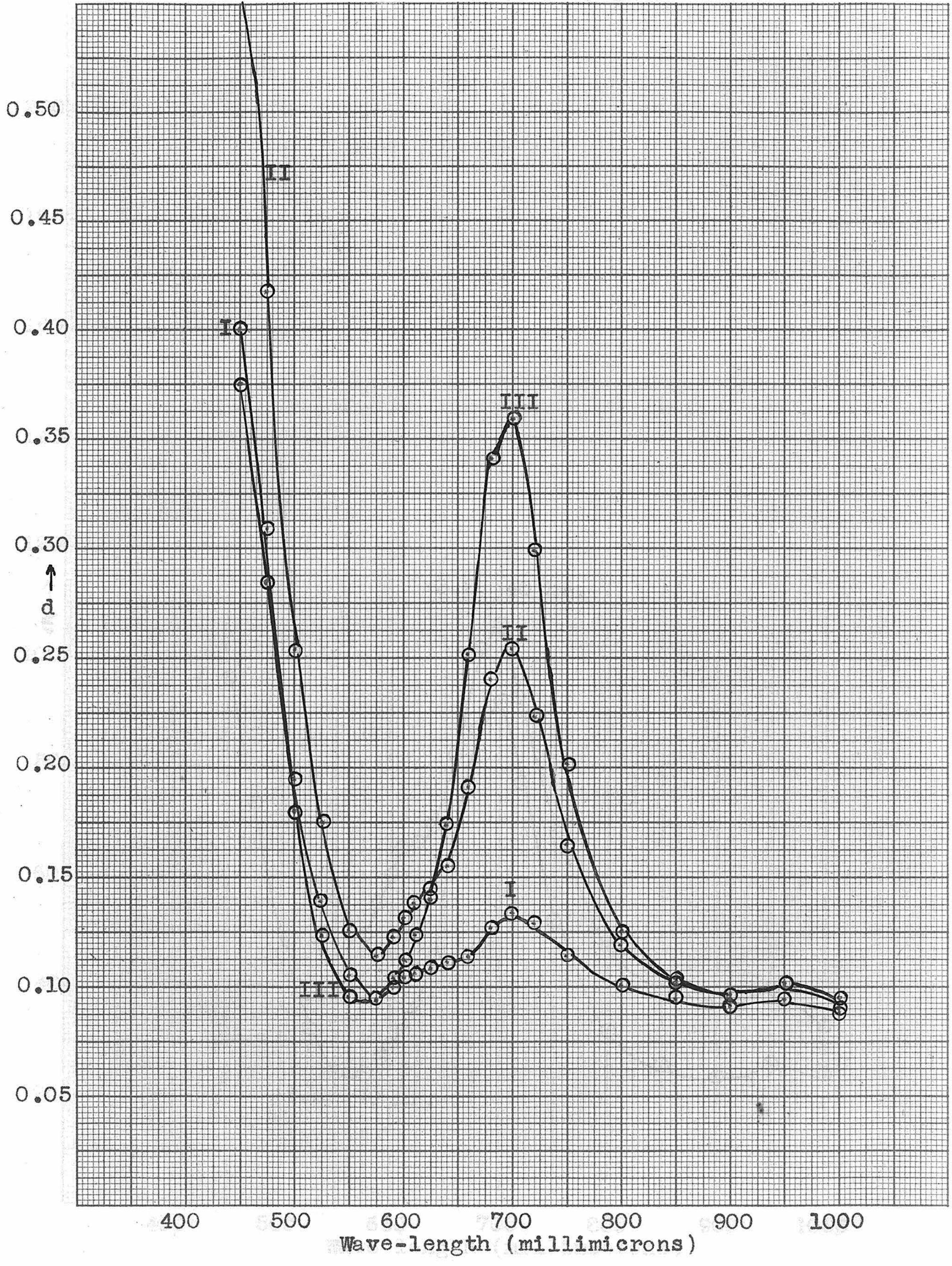


Figure 21. Apparent Extinction Coefficients of Mixtures of Re(-I) and Re(VII) assuming Re(V) as Highest Oxidation State

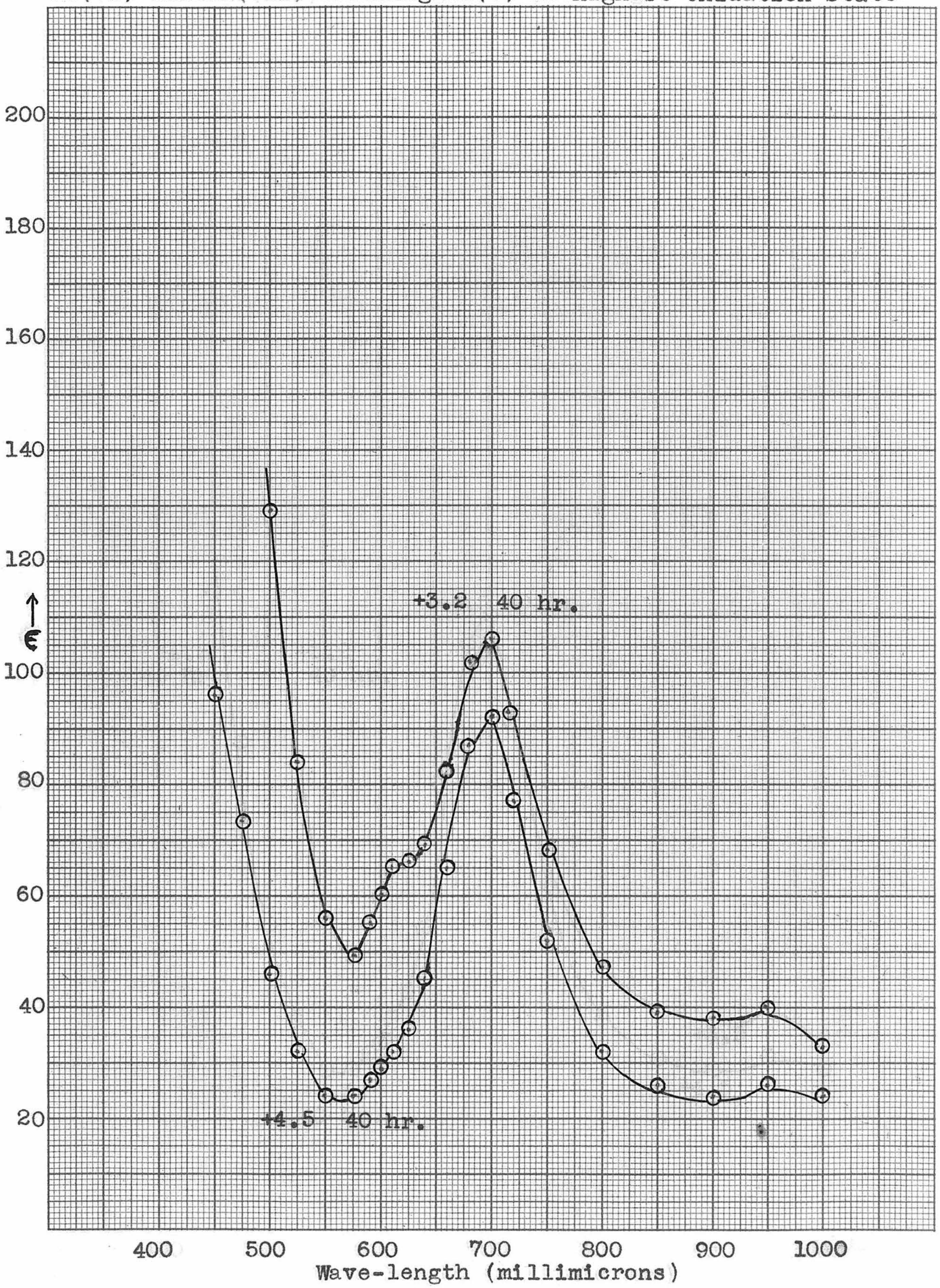


Figure 22. Apparent Extinction Coefficients of Mixtures of Re(-I) and Re(VII) assuming Re(IV) as Highest Oxidation State

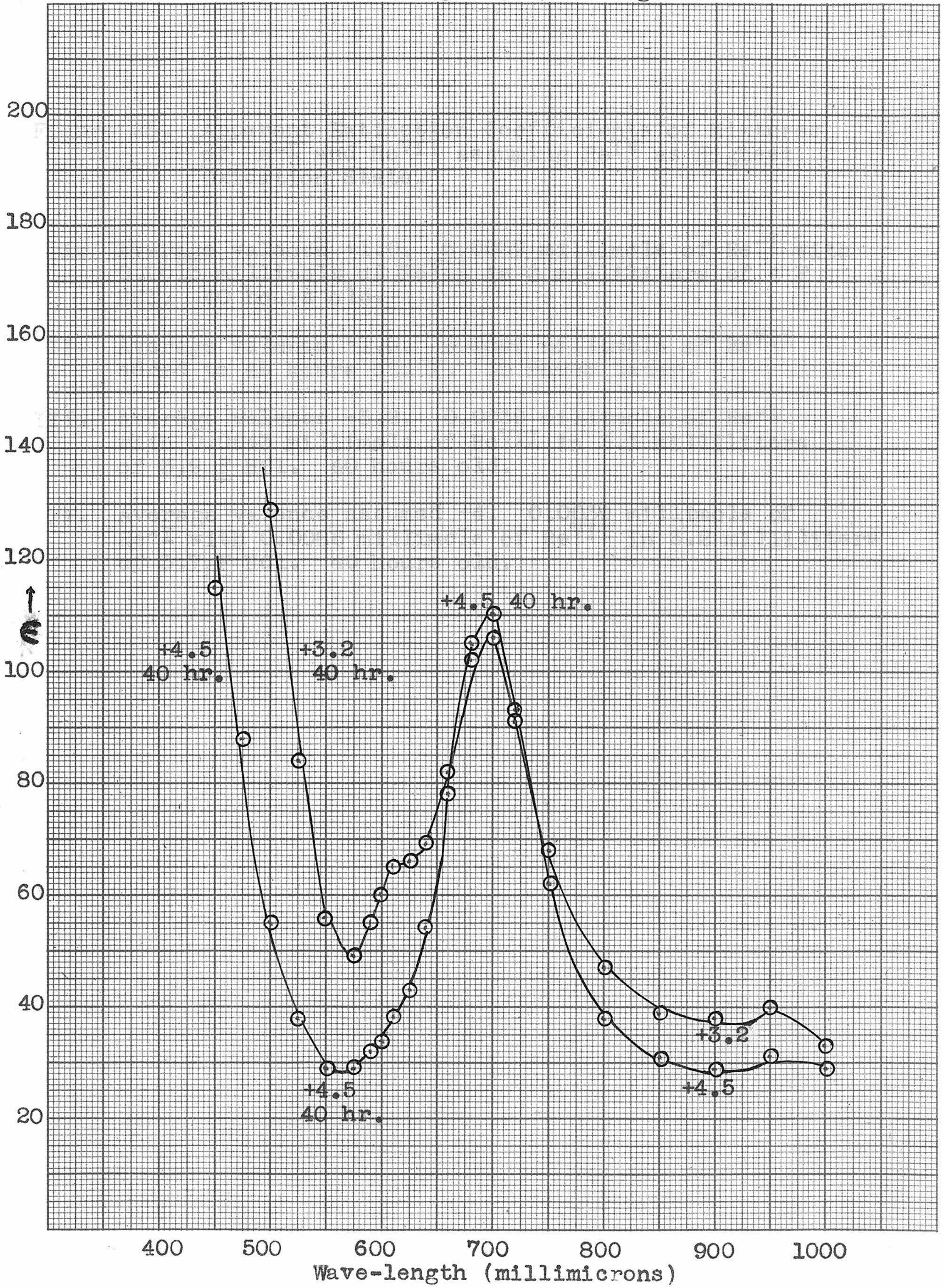


Figure 23. Apparent Extinction Coefficients of Mixtures of Re^{-I} and Re^{VII} assuming Re^{IV} as Highest Oxidation State.

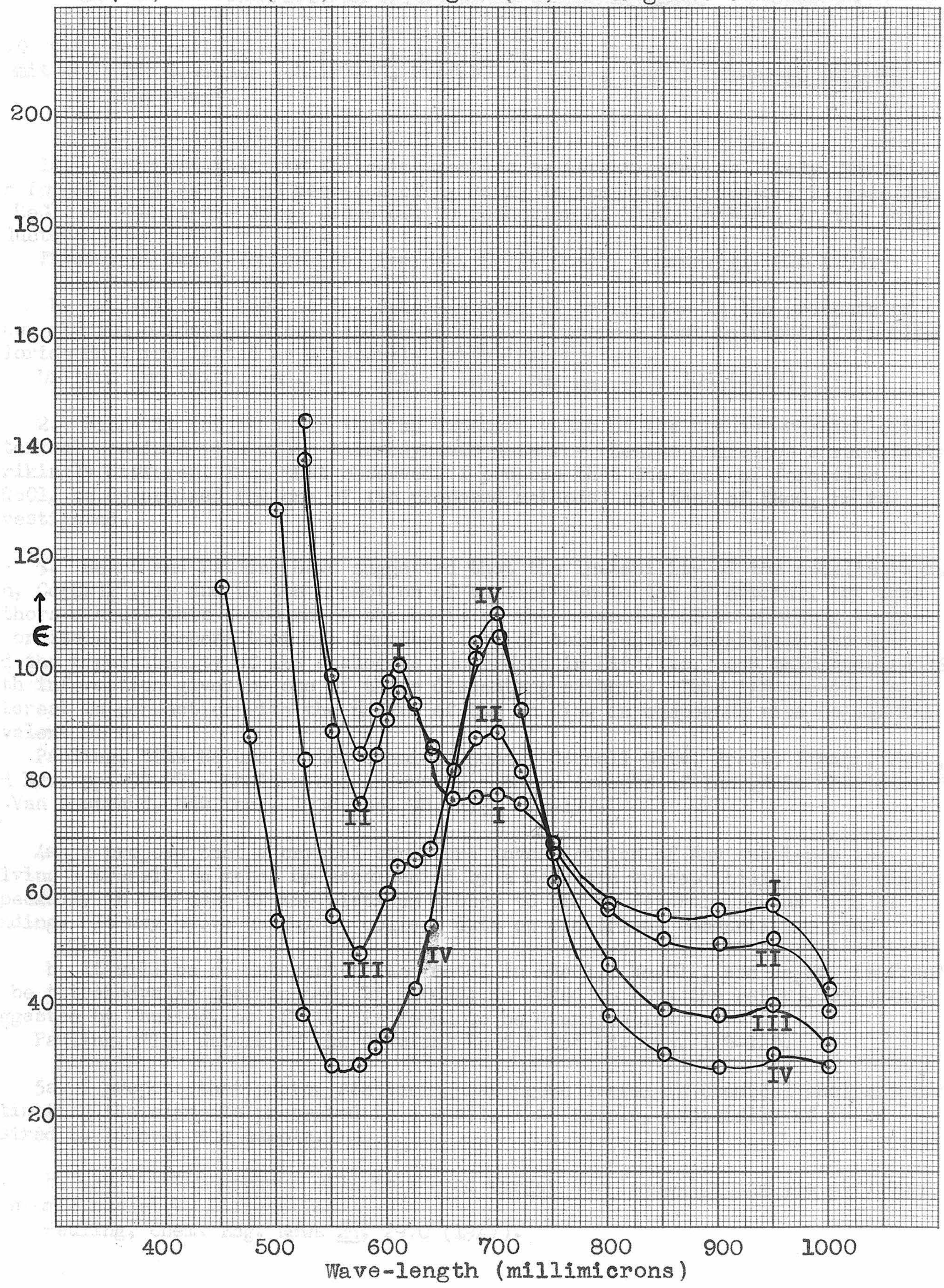
I. Average valence +1.0. 0.0039 millimols of Re^{-I} with 0.0013 millimols of Re^{VII} in 3 milliliters of 4 F HCl. 40 hours old.

II. Average valence +1.9. 0.0009 millimols of Re^{VII} added to 40 hours old I. 18 hours later.

III. Average valence +3.2. 0.0039 millimols of Re^{-I} with 0.0043 millimols of Re^{VII} in 3.1 milliliters of 3.9 F HCl. 40 hours old.

IV. Average valence assumed +4. 0.0039 millimols of Re^{-I} with 0.0086 millimols of Re^{VII} in 3.2 milliliters of 3.7_5F HCl. 40 hours old.

Figure 23. Apparent Extinction Coefficients of Mixtures of Re(-I) and Re(VII) assuming Re(IV) as Highest Oxidation State



Propositions submitted by Eugene K. Maun.

Ph.D. Oral Examination, May 4, 1949, 1:00 P.M., Crellin Conference Room.
Committee: Dr. Davidson (chairman), Professors Bates, Fowler, Niemann, Pauling, and Swift.

1a. I propose that the following methods be investigated as likely favorable for formation of Re^{-I}: 1) reaction of K_2ReCl_6 in the Jones reductor, 2) reaction of $ReCl_3$ in HCl in the Jones reductor, 3) reduction of $HReO_4$ in H_3PO_4 in the Jones reductor.

Thesis, p. 166. Tomicek and Tomicek, Coll. Czech. Commun. 11, 626 (1939).

b. A difficult task is the determination of perrhenate in the presence of other rhenium oxidation states and metal ions. I propose that tetraphenylarsonium chloride be investigated as a possible useful precipitant.

Willard and Smith, Ind. Eng. Chem., Anal. Ed. 11, 186, 305 (1939).

2. Since it can be shown that an expected value of the rhenium-rhenichloride potential combined with other thermodynamic data for rhenium indicates a reactivity strikingly different from that observed, I propose that the heat of formation of K_2ReCl_6 be determined (by one of two proposed methods) and that of $KReO_4$ be reinvestigated.

3. Hoard and Pauling have suggested that the instability of the cobaltocyanide ion, $Co(CN)_6^{-4}$, is due to the promotion of an electron to the 4d orbital, but some authors discuss this compound on the basis of the promotion of an electron to the 5s orbital. I propose that the improbability of this latter suggestion for Co^{II} and the impossibility of its analogous occurrence in Ni^{II}(l.c.) can be demonstrated with information given by one of these dissenting authors. This information is of interest in connection with the nature of the bonding in compounds with octahedral covalent Ni^{II}.

Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N.Y., 2nd Ed., pp. 95-97. Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand, New York, 1938, pp. 98, 173, 176-177.

4a. I propose that a crystal structure investigation of any substance involving a transition metal be accompanied by a magnetic susceptibility measurement, especially in the case of the platinum group, to aid in determining the type of bonding. It may prove useful to collect data on electrical conductivity too.

b. It will be of interest if the metal in $KReCl_4$, Re_2Cl_6, and Re_2Br_6 is found to be tetrahedrally coordinated, if $Ni(CN)_2$ is found to have the $Pd(CN)_2$ structure suggested by Pauling, or if PtO_3 is found to be diamagnetic.

Pauling, "The Nature of the Chemical Bond," 2nd Ed., pp. 119-120.

5a. I propose that proton scattering may prove useful in chemical analysis for estimating the elements presented in a small, thin sample, especially if it is desired to recover the sample.

b. The lithium nucleus will be a good target for investigating the structure of atomic nuclei by diffraction.

Pauling, Chem. Eng. News 25, 2970 (1947).

6a. Jensen's report on his investigation of the structure of $(NH_4)_2SbBr_6$. Rb_2SbBr_6, (and Rb_2SbCl_6), does not mention the presence of the two octahedral complex ions $SbBr_6^-$ and $SbBr_6^{-3}$, and his interpretation of the structure he reports assumes the presence of resonating electrons. I propose that efforts be made to grow single crystals of one of these compounds, such as K_2SbBr_6, and that the structure be investigated using intensity data taken from rotation photographs.

Jensen, Z. anorg. allgem. Chem. 232, 193 (1937); 252, 317 (1944).

b. It will be of interest to study the factors determining the bonding of Co^{II} complexes since this ion has representatives in each of the following classes: tetrahedrally coordinated, square coordinated, octahedrally cordinated with essentially ionic bonds, and octahedrally coordinated with essentially covalent bonds.

7. The virial coefficient for helium can be expressed as a Laplace transform of a function of the potential.

8a. I propose the following approximate scheme of potentials for the oxidation states of rhenium in 4 $\underline{F}$ hydrochloric acid:

$$\begin{aligned}
Re^{V} &= HReO_4 + 2\,e^- && E_1 \quad -0.5 \text{ v.}\\
Re^{IV} &= Re^{V} + e^- && E_2 \quad -0.55 \text{ v.}\\
Re^{I} &= Re^{IV} + 3\,e^- && E_3 \quad 0.2 \text{ v.}\\
Re^{-I} &= Re^{I} + 2\,e^- && E_4 \quad 0.3 \text{ v.}\\
Re^{-I} &= Re^{0} + e^- && E_5 \quad 0.3 \text{ v.}
\end{aligned}$$

b. Despite frequent researches, the nature of the red color formed by the action of stannous chloride and potassium thiocyanate on perrhenate (the Geilmann reaction) is still not clear. I propose a set of spectrophotometric experiments to elucidate this problem.

9a. Non-reactivity of aqueous Re^{-I} with carbon monoxide as observed in the present research is consistent with the structure proposed by Pauling.

Pauling, Chem. Eng. News 25, 2970 (1947). Thesis, p. 165.

b. I propose that conflicting statements in the literature of the lower valence states of rhenium can be reconciled if it is assumed that Re^{III}, like Re^{IV}, exists in an active and an inert form.

Geilmann and Wrigge, Z. anorg. allgem. Chem. 214, 253 (1933). Manchot and Düsing, Lieb. Ann. 509, 228 (1934). Biltz, Geilmann, and Wrigge, Lieb. Ann. 511, 301 (1934). W. and I. Noddack, Z. anorg. allgem. Chem. 215, 174 (1933).

10a. I propose that instead of waiting until noted scientists are dead, their papers should be collected during their lifetime as they appear and kept available in libraries.

b. A problem which has puzzled innumerable chemists is whether to pour sulfuric acid into water or vice versa. This can be treated as follows:

Water into Acid is Waaah, Acid into Water is Aaah!

* * *