F. H. Brady - Thesis.

Subject: An attempt to investigate the reduction of Ruthenium Tetroxide by potentiometric methods.

Introduction: Brief historical review of RuO_4, its properties, especially its reduction;
(1) by various reagents, organic matter, etc.
(2) by HCl: work of Krauss, Remy, McConnell, et al.; efforts to establish the valence of Ru in RuO_4; Charonnat's establishment of quadrivalence of Ru in what was supposed to be $RuCl_3$.

Use of potentiometric methods in similar cases by Crowell, etc. Cf. J.Am.Chem.Soc. 54 (1932), 1324 (April); 51 (1929), 175, 1695.

Description of experimental work:
  Preparation of RuO_4 (equations for all reactions.
  Preliminary experiments, with curves. (Work with HCl solutions).
  Final work: preparation of a sufficient amount of solution of pure (washed) RuO_4 in water; estimation of content of RuO_4; reduction with HCl and potentiometric curves; (also, if necessary, same curves corrected for HCl); (curves in all cases to be based on ratio of RuO_4 to HCl molecules).
  Similar work with solution of OsO_4 in water, against HCl.
  Conclusions from experimental work.
Bibliography.

An Attempt to Investigate the Reduction of Ruthenium Tetroxide by Potentiometric Methods.

by

Frank H. Brady

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of Chemistry of Washington and Lee University
in partial fulfillment of the requirements for
the degree of Bachelor of Science in Chemistry.

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Introduction

An Attempt to Investigate the Reduction of Ruthenium Tetroxide by Potentiometric Methods.

Introduction: The silver grey metal, which is the rarest of the platinum group, was discovered in 1845 by Claus, who named it ruthenium which is the old name of Small Russia. Ruthenium is found in the platinum ores of the Ural Mountains, in Borneo, and in Oregon in a rare mineral known as lauerite(Ru_2S_3). In 1906 it was found in celestrial bodies. The melting point is 2400°C. The specific heat as determined by Bunsen is 0.0595.

Ruthenium combines with all four of the halogens. Of all the compounds of ruthenium that we know, the most interesting is the tetroxide, which appears as yellow crystals or dark red liquid or crystals. Much of the data in the literature of this particular compound seems contradictory. The solubility of ruthenium tetroxide in water as determined by Remy is 20.3 grams to a liter at 20°C., The solubility curve curve shows a sharp bend downward at 25°C., which corresponds to the melting point of RuO_4, the downward bend continues to 34°C. where the curve is reversed. It is generally conceded that at room temperature it is metastable but at high temperatures it is the stable compound. It will not change at room temperature if it is protected from light and moisture. There seems to be a slight difference of opinion of the stability of it in solution and these two sentences sum them up. Ephram (1)

''RuO_4 slowly decomposes with liberation of oxygen, especially in solutions''. Weiser (2) ''It dissolves slowly in water giving a solution that is fairly stable, provided some free chlorine or hypochlorite is present''.

In 1923 F. Kraus[3] published his article upon ruthenium tetroxide and brought to attention that there may be two kinds of RuO_4. He said, ''Contradictory statements in the literature are shown to be due to the existance of RuO_4 in two modifications: one labile, crystalizing in the well known yellow needles, m. p. 24.8°C. and soluble. The other is more stable, brown granular crystals, m. p. 27°C:, shows double refraction and is less soluble. At 40°C. it passes into a yellow vapor which condenses in the yellow form. The latter changes into the brown form when heated above its melting point.'' Kraus did some work upon the conductivity but got results which did not agree among themselves. In another part of Kraus's article this statement is found,''The ruthenium tetroxide in brown spheres can be dried with filter paper.''

This brings us bach to Claus's work upon RuO_4. We are familiar with the fact that dry RuO_4 will burn filter paper with a flame and with dilute alcohol will cause an explosion if no alkalai is present. Yet in Claus[4]s experiments with the tetroxide, we come across these statements:''If one pours a little water on it (RuO_4)

in a test tube and then dip it into hot water, the acid melts to large liquid drops and forms crystals when dipped into cold water; these drops can be dried completely between filter papers. As long as some moisture is present the paper will be blackened, however when the acid has become completely dry, we can rub it with filter paper as long as we wish, the acid neither blackening it or changing its yellow color; but if we breathe upon it, it will blacken the paper through reduction and is reduced to the black sesquioxide."

In chemical properties ruthenium tetroxide is similiar to osmium tetroxide although it is not as stable as the latter. Platimum metals do not form the tetroxide with the exception of these two. The remarkable thing is the volatility of these oxides. So far no one has been able to detect the prescence of an acid when either ruthenium or osmium tetroxide are dissolved in water. The theory suggested by Werner is that oxygen is co-ordinated to the central atom which seems plausable. The maximum co-ordination number is four as can be shown in the oxides of elements of different valency, for example, in the oxyacids $HClO_4$, H_2SO_4, H_3PO_4, But if either OsO_4 or RuO_4 were to act as an acid anhydride the maximum co-ordination number would have to be exceeded giving us H_2RuO_5 and H_2OsO_5. There are oxyacids in which this maximum number is exceeded as in the periodates of the formula M_5IO_6.

As was hinted previously there are no known salts of $^{=}RuO_5$ ion, but we do know salts of the perruthenates, thas is salts of the hypothetical oxyacid anhydride Ru_2O_7. Potassium perruthenate was first prepared by Deville and Debray$_5$. They obtained it by passing a current of chlorine into a moderately alkaline solution of K_2RuO_4, the orange red solution changing to a deep green. The green crystals were filtered off but they were contaminated with some KCl. The method of Debray and Joly$_6$ is better as it gives pure crystals. Fifty grams of RuO_4, melted under water, is slowly added to sixty grams KOH in 250 c.c. of water at 60°C. Oxygen is given off and the solution becomes green; crystals form upon the walls of the vessel. The green crystals of $KRuO_4$ are dried in vacuum. At 440°C. they decompose giving off oxygen. It is also $KRuO_4$ which is obtained when finely divided ruthenium is attacked by a mixture of KOH and KNO_3 in a silver crucible.

Analysis of potassium perruthenate

Composition		calculated	observed		
			a_1	b_1	b_2
Ru_2	202.8	49.61	50.00	50.05	50.05
O_7	112.0	27.40	??		
K_2O	94.0	22.99	22.44	22.98	22.36

a- Debray and Deville   b- Debray and Joly

$_1$- Obtained by action of Cl_2 on K_2RuO_4

$_2$- Obtained by action of KOH on RuO_4

The action of chlorine on K_2RuO_4 may be represented thus:

$2\ K_2RuO_4 + Cl_2 = 2KCl + 2KRuO_4.$

The action of KOH on RuO_4 may be represented by

$2\ RuO_4 + 2\ KOH = 2\ KRuO_4 + 2H_2O + O_2.$

The formation of the perruthenates is an action in which the ruthenium goes from a valence of VIII to VII. At ordinary temperatures RuO_4 forms the perruthenates which is metastable and gives off oxygen to form the ruthenate in which ruthenium has a valence of VI,for example,

$4\ KRuO_4 + 4\ KOH = 4\ K_2RuO_4 + 2H_2O + O_2$

Clauss in 1844 prepared two chlorides with potassium and gave them the formulas K_2RuCl_5 and K_2RuCl_6. Joly[7] showed that the supposed K_2RuCl_5 was a nitroso salt with the formula K_2RuCl_5NO. Remy[8] starting with what he thought was K_2RuCl_5 reduced it two units with the use of sodium amalgram. Therefore Remy concluded that he had univalent ruthenium in the blue solution. Kraus[9] studied the action of HCl on RuO_4 and using KI found that the ruthenium was reduced five units. It remained for Charronnat[10] to explain the results though his work was not accepted at first. He suggested that the true formula for the pentochloro salt is K_2RuCl_5OH because of the liberation of iodine from KI. Gall and Lehman[11] studied the reaction with KI with a view to using it analytically. They came to the conclusion that an equilibrium is established

$RuCl_3 + HI = RuCl_2 + HCl + I$

Howe[12] found in his experimental work using stannous chloride as a reducing agent that Ru in K_2RuCl_5 and K_2RuCl_6 were each reduced one unit. Since the ''aquo'' salt was formed in each case, he came to the conclusion that the valence of Ru in K_2RuCl_5 is always four.

Osmium

The most outstanding property of osmium is its ability to form the tetroxide, and its chemical behaivor is similiar to ruthenium tetroxide. This oxide may be formed when solutions of osmium are treated with oxidizing reagents, or when solutions containing compounds of osmium decompose under certain conditions. It is also produced when osmium is heated in an atmosphere of air or oxygen, and even at room temperature if an osmium sponge is allowed to remain in contact with air. " It has been said that the chemistry of osmium revolves about this oxide, since any work with this element is almost certain to involve at some stage the formation of the tetroxide" (Gilchrist)

The ready formation of the tetroxide is made use of in separating osmium from other platinum metals. The melting point of the tetroxide is 40° C. Von Wartenberg(15) found that it is stable up to 1500°C. Ruff (16) studied the vapor pressure at different temperatures with the following results:

Temperature °C.	95	115	125	135
Pressure mm. Hg	275	182	640.4	779

Osmium tetroxide is in the form of colorless transparent crystals at temperatures below its melting point. Ephram (17) says that the solubility of osmium tetroxide in water is 65 grams to each 1,000 grams of water at 20°C., but using carbon bisulphide the solubility is 2,500 grams to 1,000 grams of carbon bisulphide. He tells that because of this abnormal solubility it is not an electrolyte.

The aqueous solution will not redden litmus. It is difficult to see why a higher oxide should not have acidic properties when the lower oxide of the same metal, OsO_3, has this tendency.

Osmium is very interesting because it possesses remarkable catalytic properties. At the temperature of 40 C. it will cause hydrogen peroxide to break up into water and oxygen with explosive violence. It will catalysize the synthesis of ammonia at a pressure of 185 atmospheres and a temperature range of 800°C.- 1,000°C. It was also found that it could be used as a catalyst in the oxidation of certain organic compounds.

Osmium is a blue grey metal but when it is in the form of a powder it is blue black. It has the highest melting point of the platinum metals and it changes into the liquid at 2500°C. It has the greatest specific gravity of any element and it is 22.5.

Crowell and Kirschman (13) showed that octovalent osmium may be determined with an accuracy of 0.2% by direct potentiometric titration with hydrazine sulphate. Crowell (14) described potentiometric methods for the determination of bromine in hydrobromic acid solutions of octovalent and quadrivalent osmium. The reagent used is hydrazine sulphate. The accuracy obtained by this method is about 0.2%. Since the accuracy of potentiometric titrations with respect to osmium compounds is known, an attempt is made to apply the potentiometer to ruthenium tetroxide and osmium tetroxide using HCl as the reducing reagent.

Experimental Work

Preparation and Analysis of Solutions

The action of chlorine on alkaline sodium ruthenate solutions gave ruthenium tetroxide. The ruthenium tetroxide solutions were prepared by washing the tetroxide with distilled water to free it of traces of chlorine. In analyzing the solutions ten ml. samples were added to small beakers containing some HCl. The non-volatile chloride formed was evaporated in previously weighed silica boats. Placing the silica boats containing the dry ruthenium chloride in a reducing furnace a stream of hydrogen reduced it to metallic ruthenium.

An attempt was made to comfirm Remy's work on the solubility of ruthenium tetroxide in water. He determined the solubility by observing the density of the saturated solution. The method attempted, was to determine the exact amount of ruthenium in the saturated solution by weighing the metallic ruthenium which could be obtained from a definite amount of solution. The presence of organic acids present in the air interfered seriously with the evaporation of the ruthenium chloride in the silica boats. In the ordinary stock solutions the presence of organic vapor did not matter because the ruthenium chloride could be quickly evaporated in the silica boats. In the saturated solution more mass of ruthenium chloride solution had to be evaporated and before it could be done enough carbon was present to make the solution boil over with the steam.

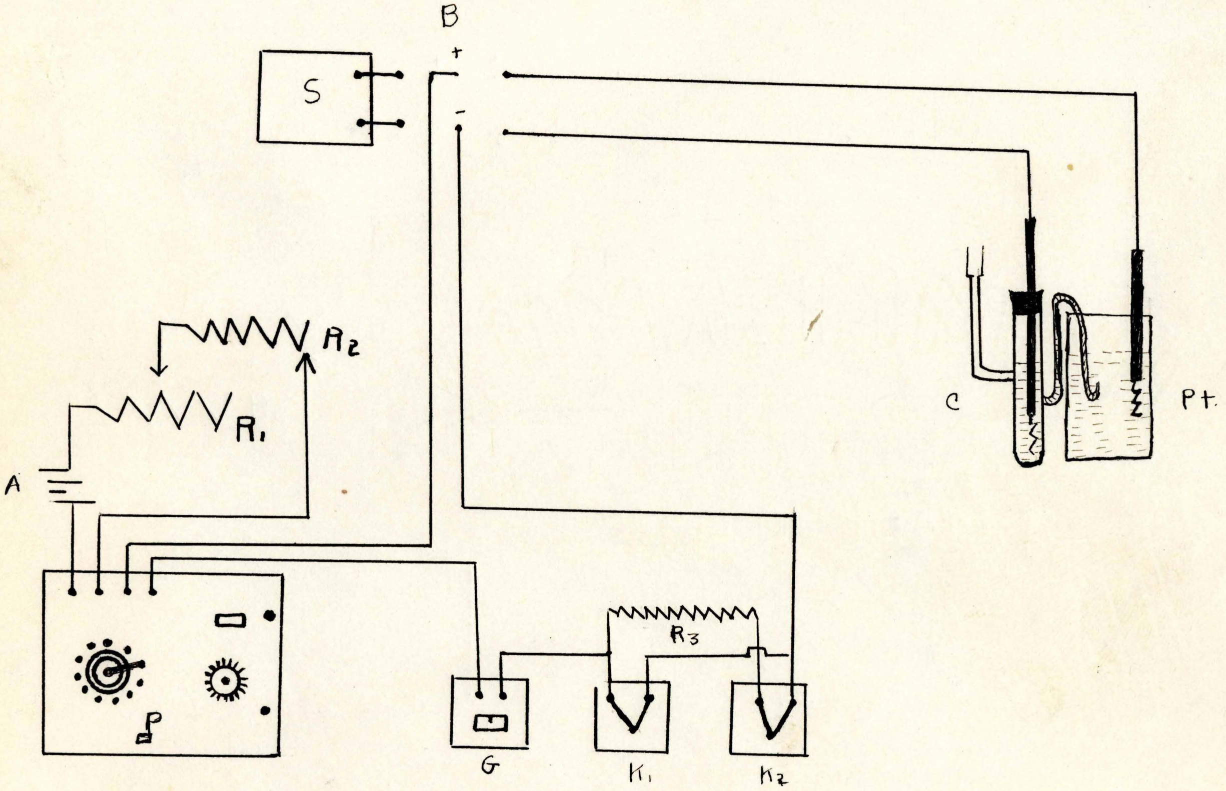
The osmium tetroxide solution was prepared by dissolving the osmium tetroxide in water. Osmium tetroxide was furnished by J. T. Baker Co.

Experimental Work

Potentiometric Work

Figure I

The Apparatus used to determine the electromotive force of the Ruthenium and Osmium tetraoxide solutions.



A- Edison storage cell (approximate 3 volts)

B- Double pole, double throw knife switch

C- Tenth normal calomel electrode

S- Standard cell emf 1.0189

G- Lees and Northrup galvameter

P- L. and N. student potentiometer

R1- Variable resistance (1250 ohms)

R2- Variable resistance (50 ohms)

R3- fixed resistance (1,000 ohms)

Pt- platinum electrodes

In order to have some experience with potentiometric work it was necessary to carry out titrations with substances whose titrations curves are known. The preliminary experiments consisted in titrating tenth normal solutions of potassium dichromate and potassium permanganate with Mohr's salt solutions.

The following procedures were used. Twenty cubic centimeters of 0.1 normal potassium dichromate and an equal amount of dilute sulphuric acid were placed in the beaker in which the titrations were made. The volume was made equal to 100 cubic centimeters by the addition of distilled water. The Mohr's salt solution was titrated from a burette into the solution containing the chromate salt. Twenty cubic centimeters of 0.1 normal potassium permanganate was placed in the beaker and an equal amount of 6 normal sulphuric acid added. The volume of the solution was made equal to 100 cubic centimaters by the addition of 60 cubic centimeters of distilled water. Like in the preceding experiments the Mohr's salt solution was titrated into the permanganate solution from a burette.

Summary of the Potassium Dichromate - Mohr's Salt Titrations.

When a solution of Mohr's salt is titrated into an acid solution of potassium dichromate, the voltage rises steadily but gradually. It begins to fall slowly after about 4/5 of the amount for complete reduction is added. At the point of equivalence there is a sharp drop in potential. The sharp drop in potential occurred as follows:

A		B		C	
voltage	ml.	voltage	ml.	voltage	ml.
0.7727	22.39	0.7600	22.79	0.7600	22.81
0.5221	22.80	0.4457	22.03	0.4175	23.00
0.2506	0.41	0.3143	0.23	0.3425	0.19

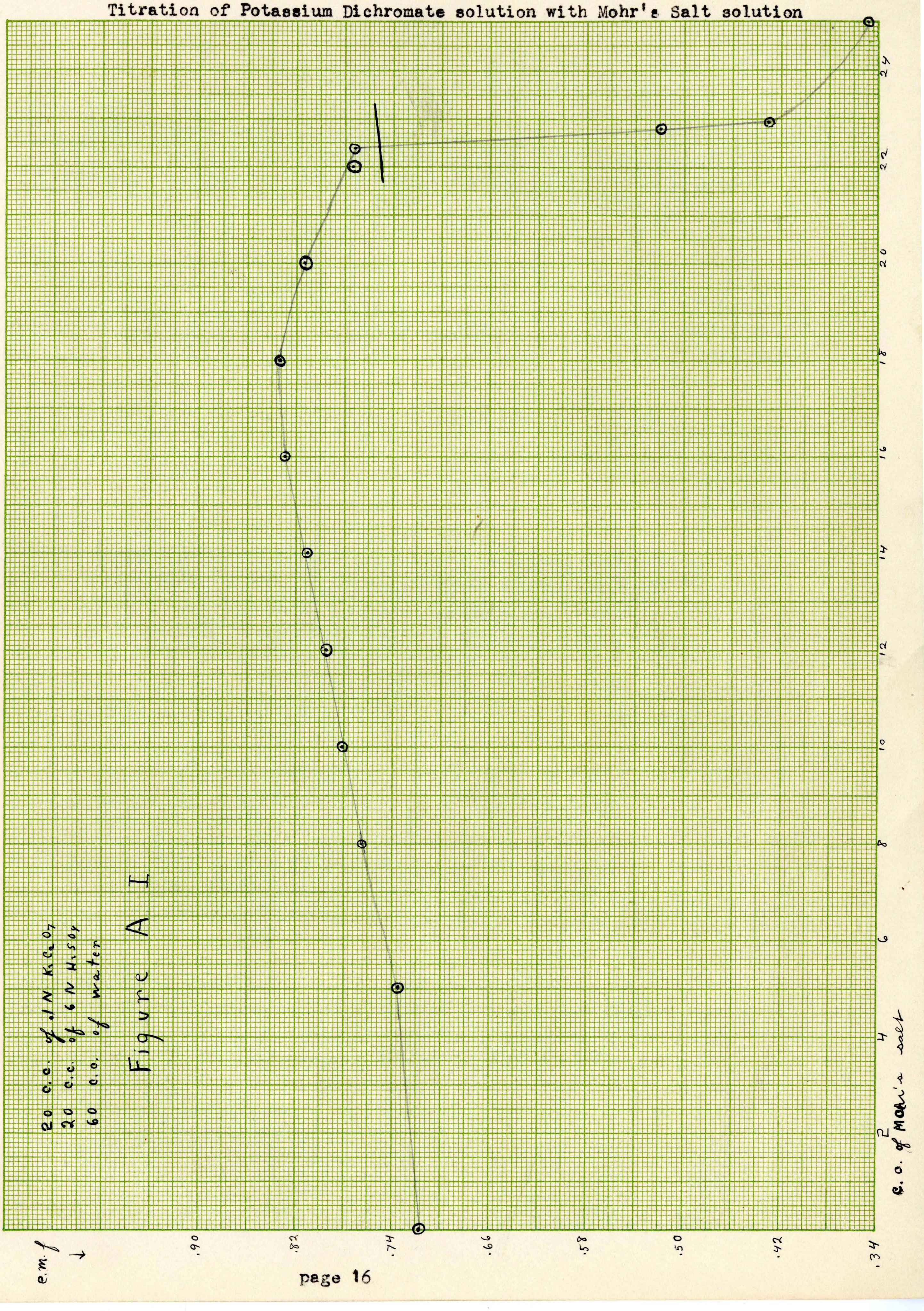
20 c.c. of .1 N K^2Cr^207

20 c.c. of 6 N sulphuric acid

60 c.c. of water

I		II		III	
e.m.f.	c.c. Mohr's salt	e.m.f.	c.c.	e.m.f.	c.c.
0.7190	0.0	0.7176	0.0	0.7188	0.0
0.7376	5.03	0.7267	2.04	0.7274	2.01
0.7645	8.02	0.7376	4.02	0.7375	4.02
0.7812	10.03	0.7582	6.01	0.7555	5.96
0.7950	12.02	0.7714	8.02	0.7698	8.01
0.8108	14.0	0.7850	10.01	0.7800	9.95
0.8300	16.01	0.7905	12.0	0.7873	12.01
0.8349	18.0	0.8086	14.0	0.8023	14.03
0.8165	20.02	0.8145	15.98	0.8134	16.05
0.7746	22.01	0.8160	18.0	0.8205	18.01
0.7727	22.39	0.8102	20.01	0.8162	20.01
0.5221	22.80	0.7705	22.0	0.7702	22.01
0.4310	25.01	0.7600	22.79	0.7600	22.81
		0.4457	23.02	0.4175	23.0
		0.3531	25.0	0.3495	25.0

Titration of Potassium Dichromate solution with Mohr's Salt solution

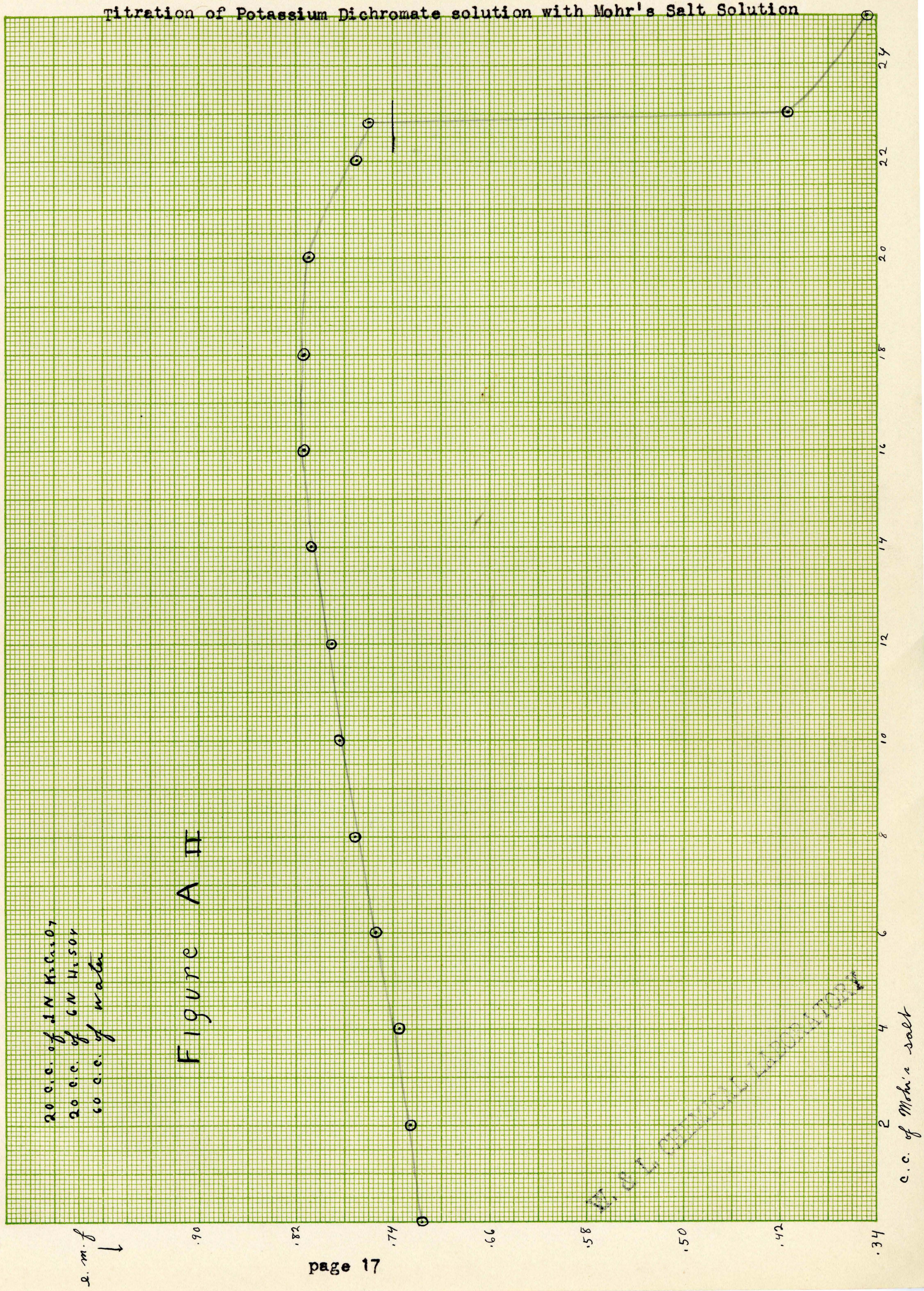


20 c.c. of .1 N $K_2Cr_2O_7$
20 c.c. of 6 N H_2SO_4
60 c.c. of water

Figure A I

I

Titration of Potassium Dichromate solution with Mohr's Salt Solution

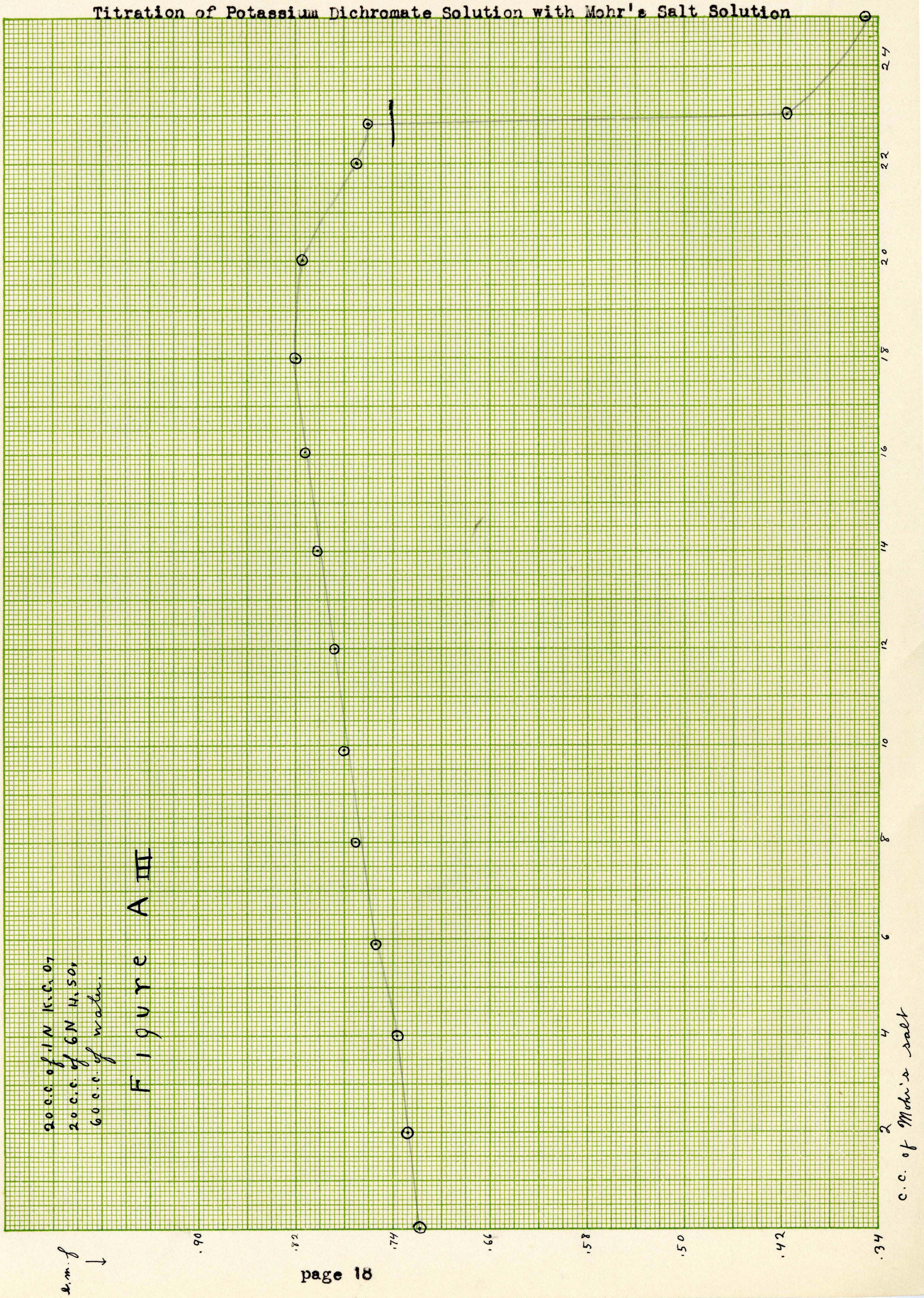


II

Figure A II

20 c.c. of 1N $K_2Cr_2O_7$
20 c.c. of 6N H_2SO_4
60 c.c. of water

Titration of Potassium Dichromate Solution with Mohr's Salt Solution



20 c.c. of .1 N $K_2Cr_2O_7$
20 c.c. of 6N H_2SO_4
60 c.c. of water.

Figure A III

III

Summary of the Potassium Permanganate- Mohr's Salt Titrations.

When an acid solution of potassium permanganate is titrated with Mohr's salt solution, the voltage rises, then falls a little, then remains practically constant until it reaches the point of equilivalence. At this point the drop in potential is more marked than that obtained with potassium dichromate. The sharp drop in potential occurred as follows:

A		B		C	
voltage	ml.	voltage	ml.	voltage	ml.
0.9731	22.30	0.9349	22.21	0.9655	22.20
0.4305	22.41	0.4293	22.42	0.4412	22.50
0.5426	0.11	0.5056	0.21	0.5243	0.30

20 c.c. of $K^2Mn^2O^8$ (.1N.)

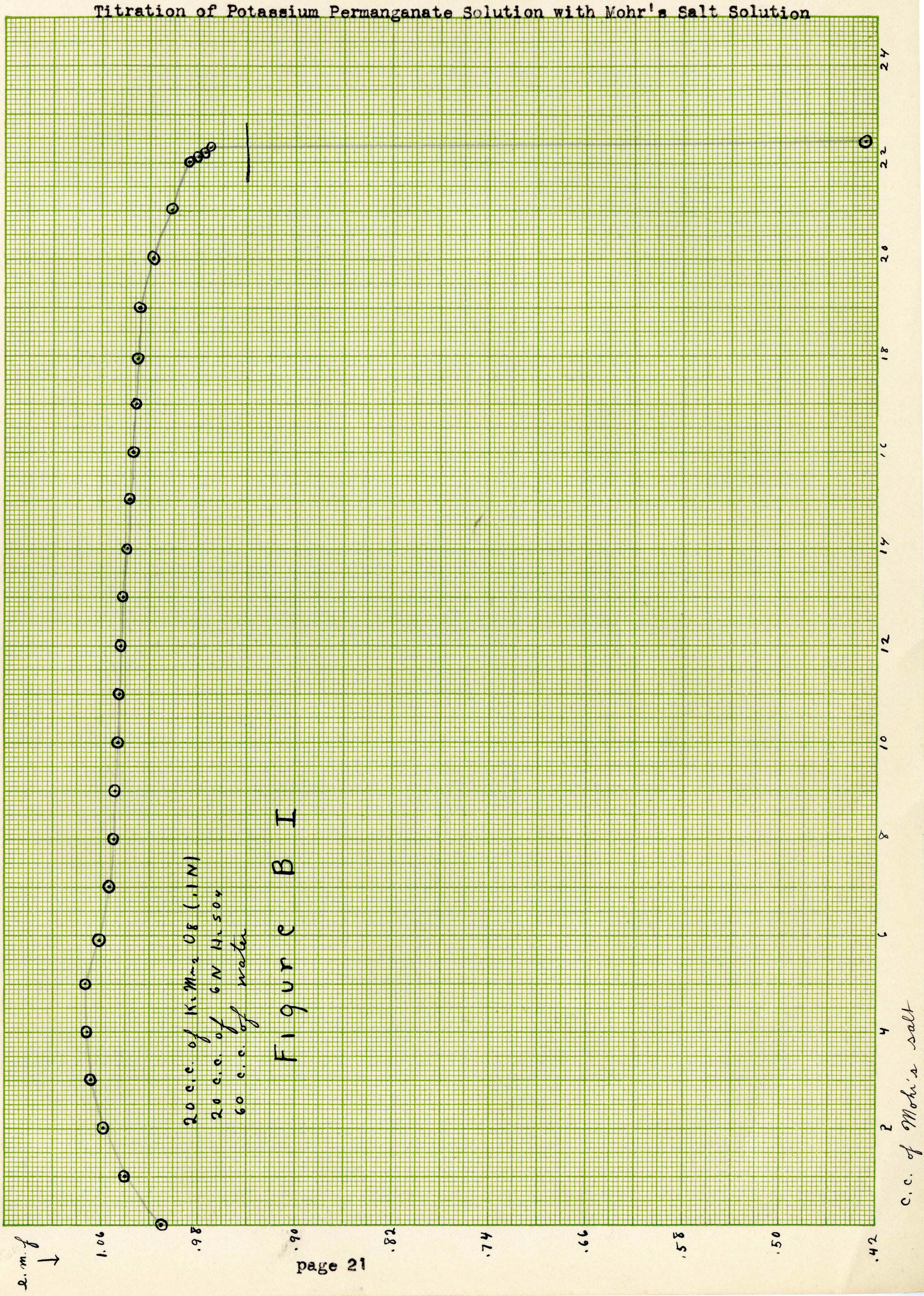
Table B

20 c.c. of dilute sulphuric acid

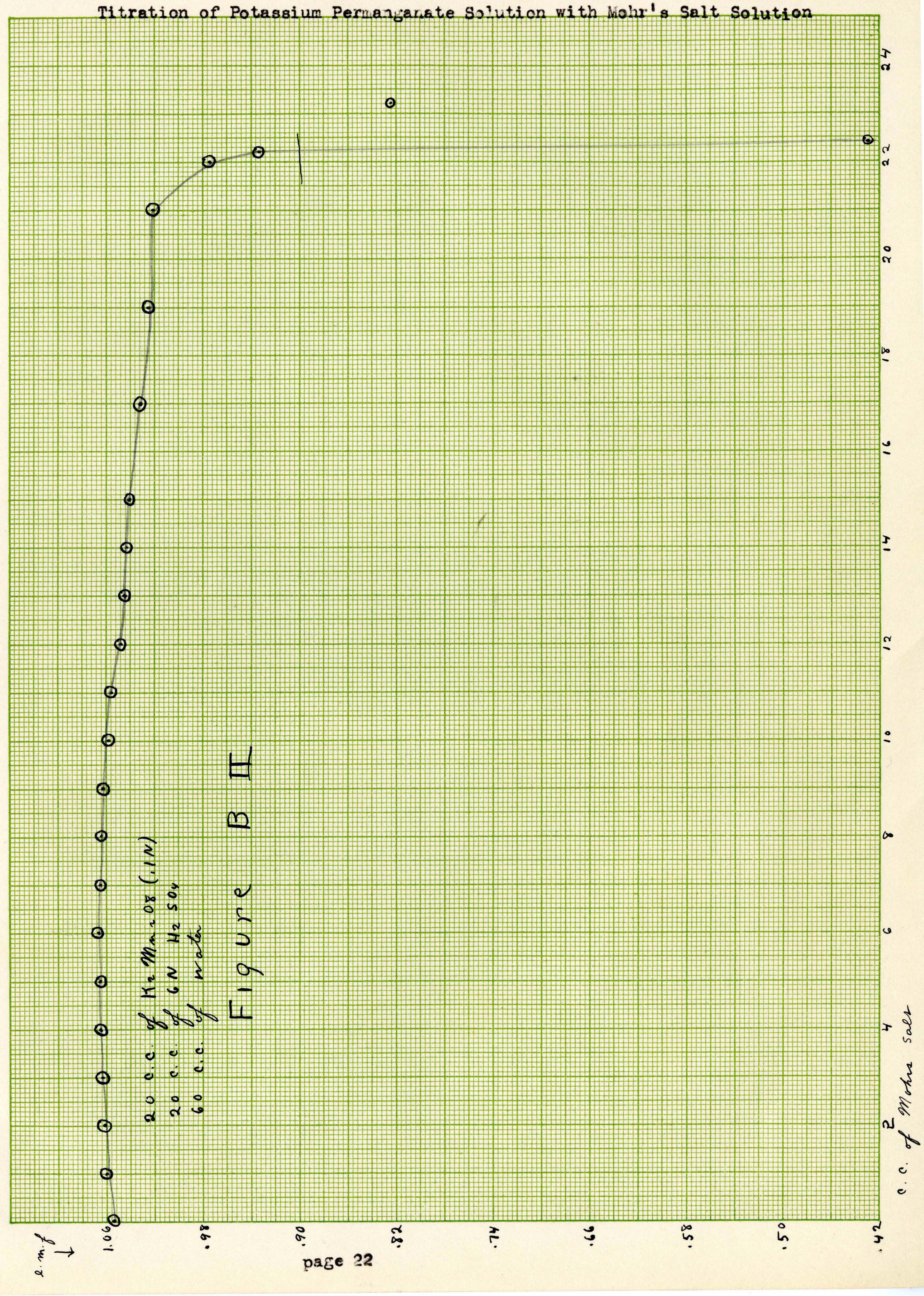
60 c.c. of water

I		II		III	
e.m.f.	c.c. Mohr's salt ~~HCl~~	e.m.f.	c.c. Mohr's salt ~~HCl~~	e.m.f.	c.c. Mohr's salt ~~HCl~~
1.0095	0.0	1.0558	0.0	1.0444	0.0
1.0385	1.01	1.0605	1.03	1.0592	0.97
1.0582	2.0	1.0622	2.01	1.0716	1.98
1.0692	3.01	1.0644	2.98	1.0720	3.01
1.0737	4.03	1.0660	4.01	1.0760	4.03
1.0746	5.01	1.0672	5.0	1.0775	5.03
1.0616	5.96	1.0678	5.99	1.0777	5.99
1.0553	7.0	1.0672	7.0	1.0749	6.98
1.0512	7.98	1.0652	8.03	1.0725	7.97
1.0494	9.01	1.0628	8.98	1.0710	9.0
1.9475	9.99	1.0588	9.99	1.0558	11.02
1.0455	11.0	1.0570	11.03	1.0432	13.03
1.0440	11.99	1.0470	11.98	1.0342	15.03
1.0416	13.02	1.0455	13.09	1.0318	16.96
1.0398	14.0	1.0420	14.02	1.0293	18.08
1.0378	15.02	1.0405	15.01	1.0285	19.04
1.0358	15.99	1.0336	17.0	1.0005	21.11
1.0332	17.01	1.0242	19.99	0.9752	22.10
1.0310	17.97	1.0017	21.02	0.9655	22.20
1.0282	19.04	0.9765	22.03	→ 0.4412	22.50 ←
1.0176	20.03	0.9349	22.21	0.3355	25.01
1.0018	21.0	→ 0.4293	22.42 ←		
0.9837	22.01	0.3400	24.95		
0.9796	22.12				
0.9762	22.21				
→ 0.9731	22.30 ←				
0.4305	22.41				

Titration of Potassium Permanganate Solution with Mohr's Salt Solution



Titration of Potassium Permanganate Solution with Mohr's Salt Solution

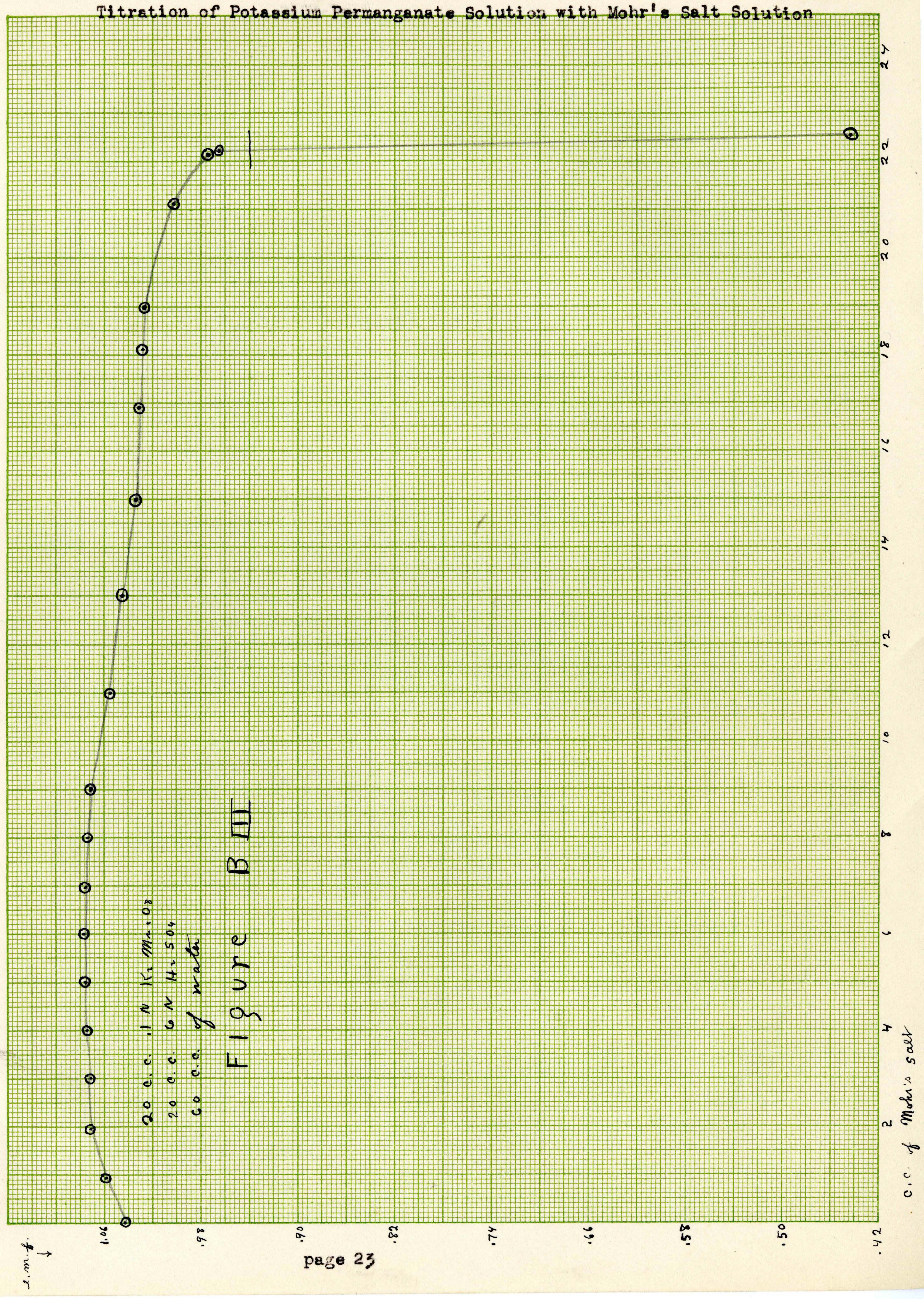


20 c.c. of $K_2Mn_2O_8$ (.1N)
20 c.c. of 6N H_2SO_4
60 c.c. of water

Figure B II

II

Titration of Potassium Permanganate Solution with Mohr's Salt Solution



III

The next experiments were to ascertain the effect of HCl and NaCl on the potential of distilled water. The HCl and NaCl were titrated into 50 cubic centimeters of water from a burette and the change in potential recorded. Afetr this HCl was titrated from a burette into 25 cubic centimeters of water with 25 ml. of NaCl solution.

Summary

When 0.1 normal HCl is added to distilled water, there seems to be a sudden rise in potential as the HCl is added reaching its maximum at the point where the hydrogen ion concentration is 0.004. When this concentration is exceeded the potential drops slowly until the hydrogen ion concentration is 0.042. After this concentration is passed the potential becomes constant. The same phenomenon is observed when 0.1 normal NaCl is added to distilled water. The maximum point is reached when the sodium and chloride ions in the solution are 0.0004 molar. After this the potential becomes constant at 0.04. However if 0.1 normal HCl is added to 50 ml. of 0.05 normal NaCl, there is a sudden rise of potential with each addition of HCl up to one ml. After this the potential assumes a constant value.

50 c.c. of water and led 0.0995 N. HCl into it. Table C

I		II	
e.m.f.	c.c. HCl	e.m.f	c.c. HCl
0.2590	0.0	0.2550	0.0
0.4150	1.0	0.3690	0.5
0.4170	2.0	0.4010	1.0
0.4160	3.0	0.4030	2.0
0.4153	4.05	0.4020	3.0
0.4135	5.0	0.3990	4.0
0.4090	6.0	0.3960	5.0
0.4050	7.0	0.3910	6.05
0.4010	8.0	0.3855	7.0
0.3960	9.0	0.3830	8.0
0.3890	10.1	0.3820	9.0
0.3850	11.0	0.3810	10.1
0.3820	12.1	0.3800	11.0
0.3790	13.0	0.3790	12.0
0.3725	14.0	0.3785	15.0
0.3720	15.1	0.3780	18.0
0.3708	18.0	0.3775	20.0
0.3695	20.0	0.3775	23.1
0.3695	22.0	0.3775	25.0
0.3690	25.0		

Change of Potential on Addition of HCl to Distilled Water

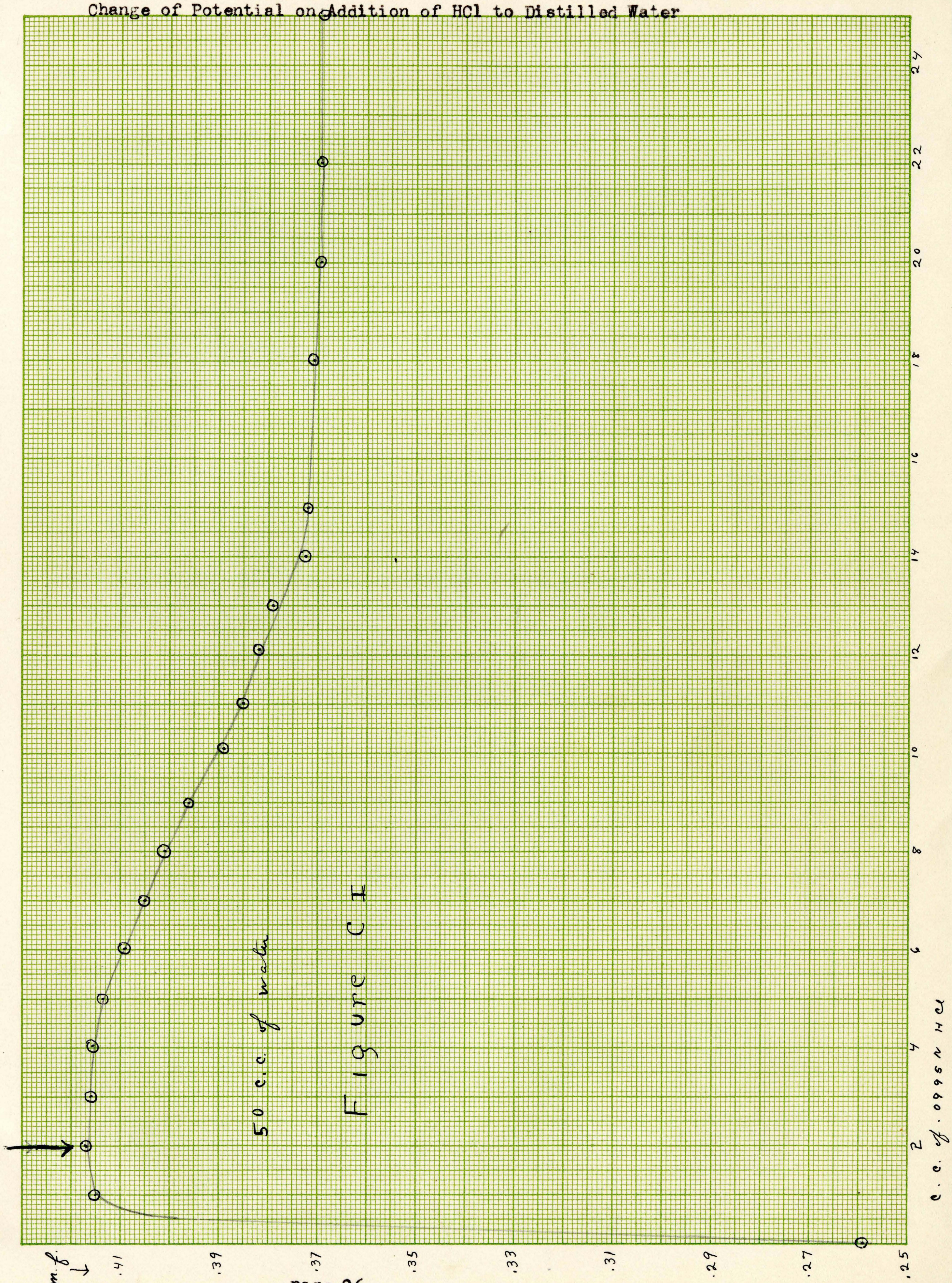


Figure C I

Change of Potential on Addition of HCl to Distilled Water

II

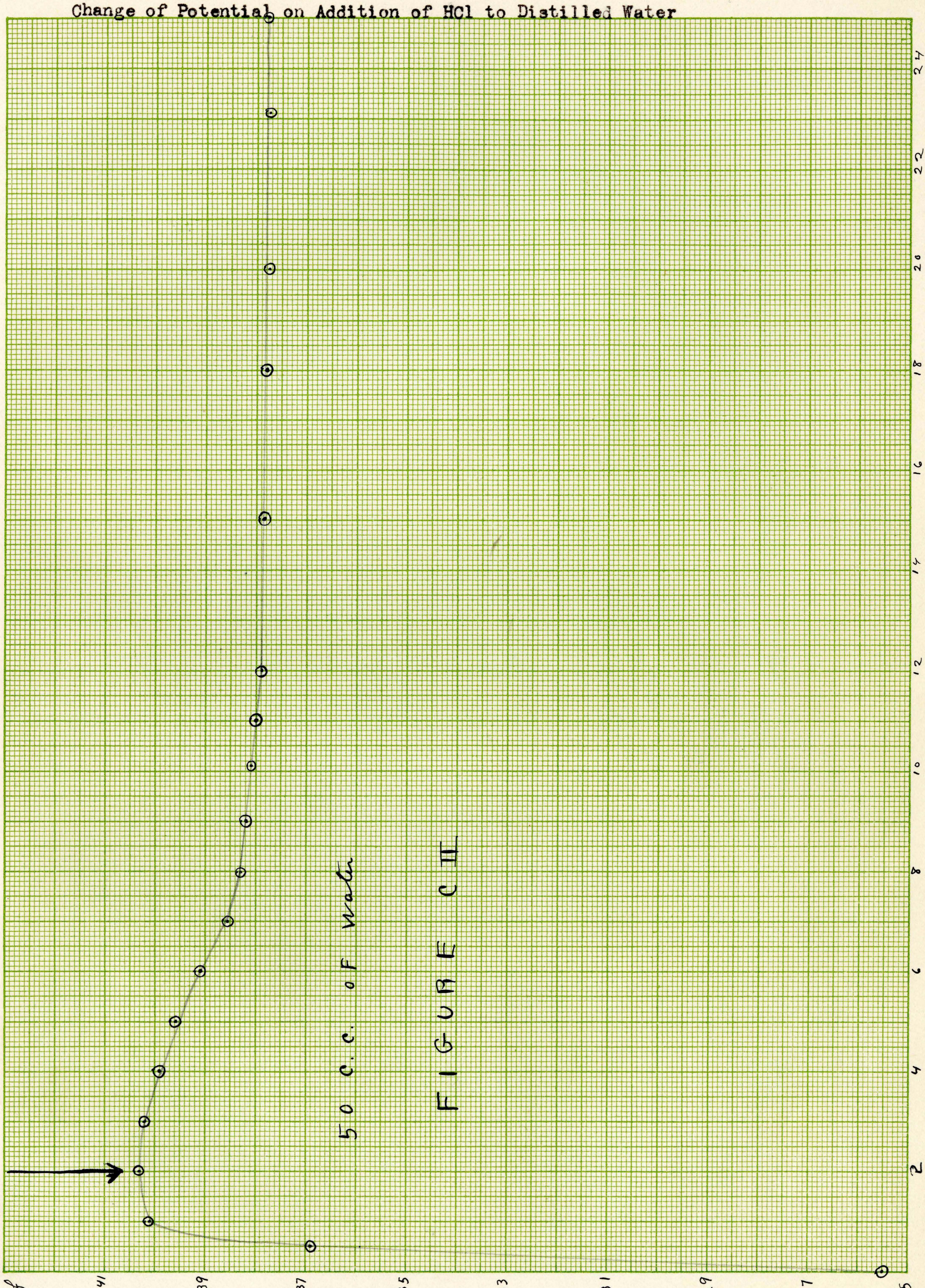
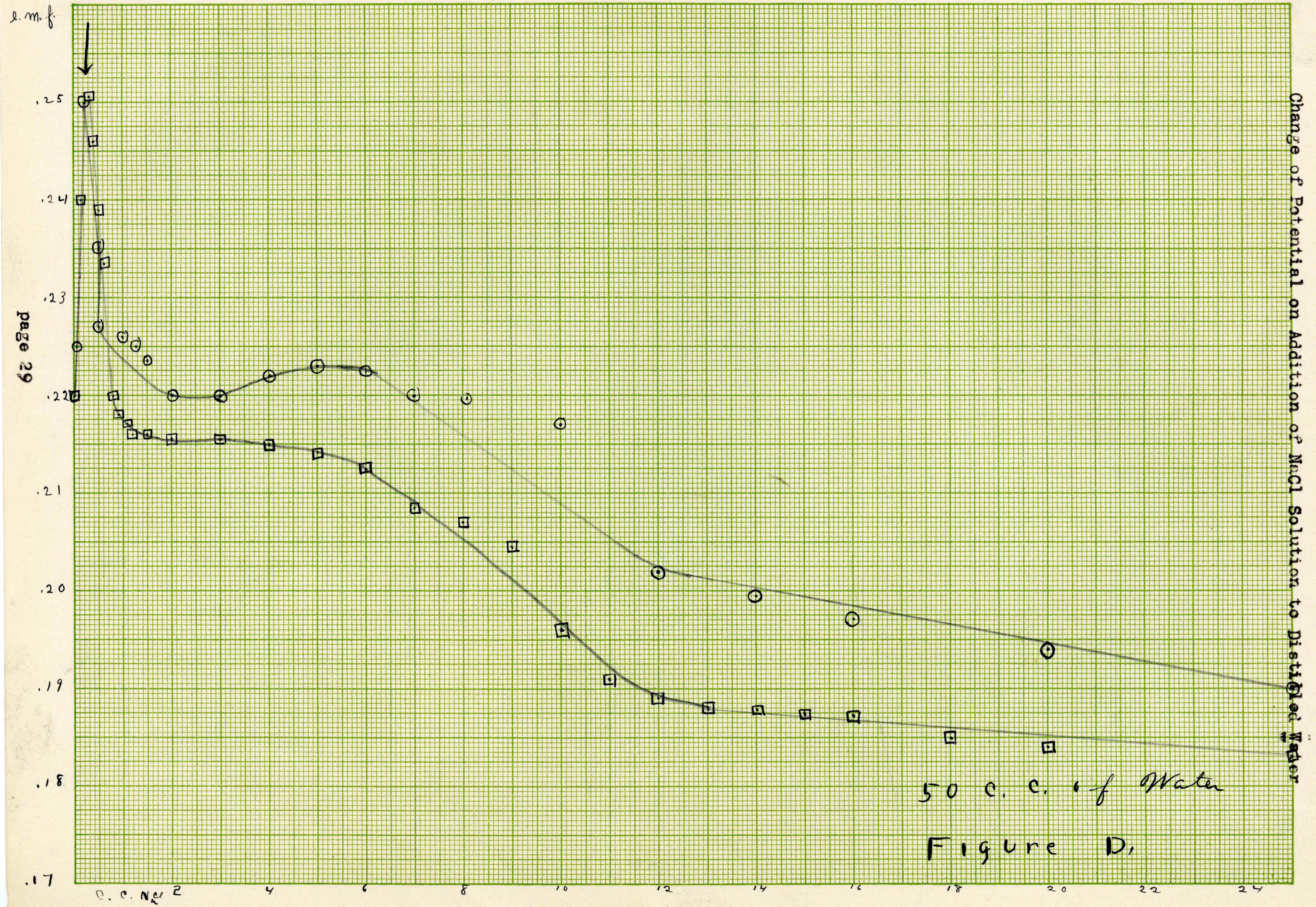


FIGURE C II

Sodium chloride added to water

Table D1

I		II	
e.m.f.	NaCl	e.m.f.	NaCl
0.240	5 drops	0.2200	1 drop
0.2504	8 "	0.2250	3 "
→ 0.2560	10 "	0.2500	7 " ←
0.2335	15 "	0.2450	10 "
0.2330	18 "	0.2350	12 "
0.2200	20 "	0.2270	15 "
0.2180	22 "	0.2260	25 "
0.2170	25 "	0.2250	30 "
0.2160	28 "	0.2200	2 c.c.
0.2160	30 "	0.2200	3 "
0.2158	2 c.c.	0.2220	4 "
0.2157	3 "	0.2230	5 "
0.2150	4 "	0.2225	6 "
0.2140	5 "	0.2200	7 "
0.2125	6 "	0.2197	8.1 c.c.
0.2085	7 "	0.2170	10 c.c.
0.2044	8 "	0.2020	12 "
0.1995	9 "	0.1993	14 "
0.1960	10 "	0.1970	16 "
0.1910	11 "	0.1942	20 "
0.1890	12 "	0.1901	25 "
0.1880	13 "		
0.1882	14 "		
0.1872	15 "		
0.1860	16 "		
0.1850	18 "		
0.1840	20 "		
0.1830	25."		



Change of Potential on Addition of NaCl Solution to Distilled Water

50 c. c. of Water

Figure D,

Table D

0.0995 N. HCl titrated into 25 ml. of 0.0989 N. NaCl and 25 ml. of distilled water.

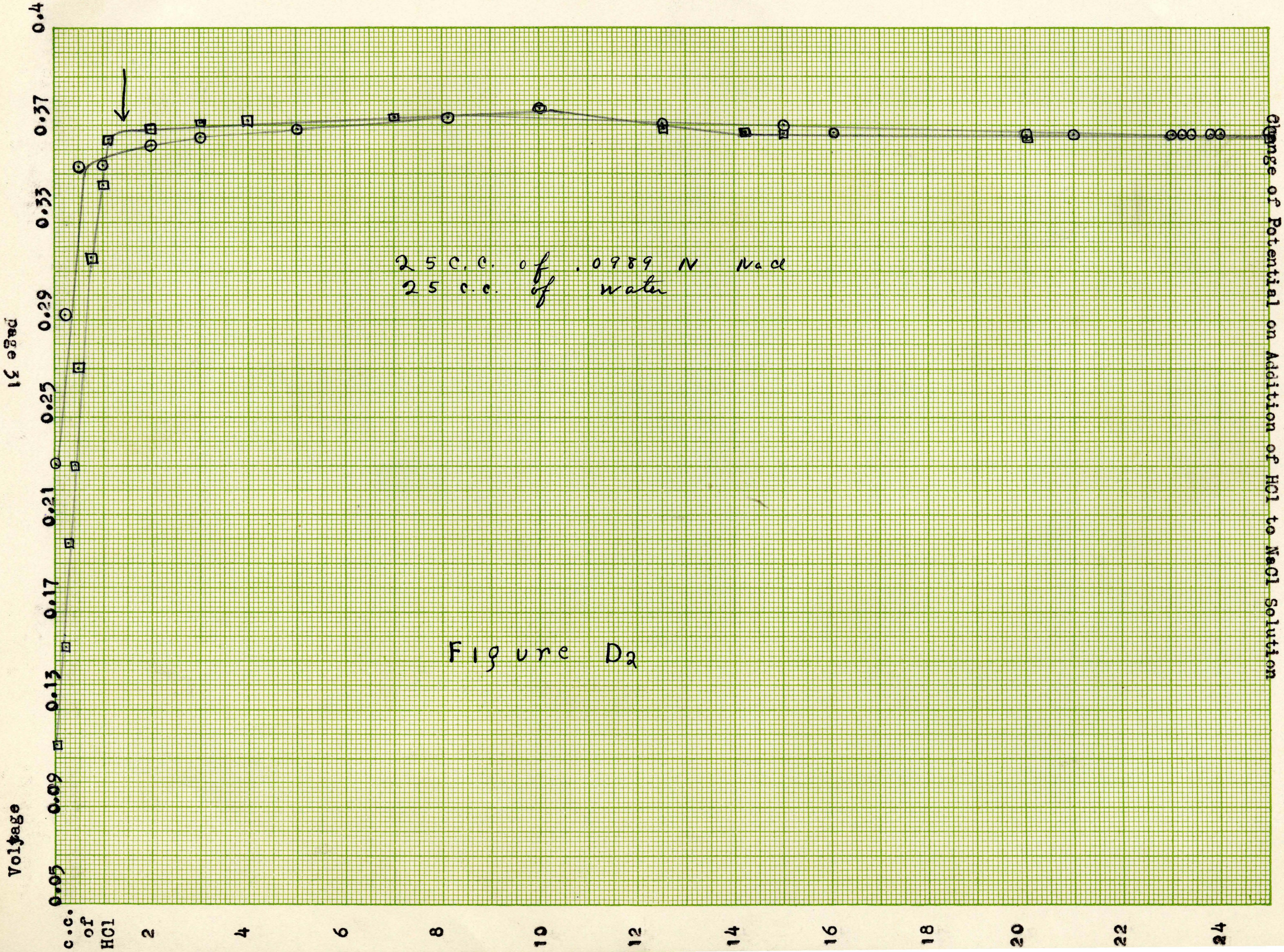
I

e.m.f.	ml. HCl
0.2308	0.0
0.2920	0.18
0.3530	10 drops
0.3535	20 "
0.3620	2.0
0.3650	3.0
0.3690	5.0
→ 0.3780	8.1
0.3775	10.0
0.3705	12.5
0.3700	15.05
0.3670	16.05
0.3660	20.0
0.3660	21.0
0.3660	23.0
0.3660	23.2
0.3660	23.4
0.3660	23.8
0.3660	24.0
0.3660	25.0

II

e.m.f.	ml. HCl
0.0600	0.0
0.1150	1 drop
0.1550	3 "
0.1980	5 "
0.2300	7 "
0.2700	10 "
0.3150	15 "
0.3450	20 "
0.3680	2.0
0.3710	3.0
0.3720	4.0
0.3730	7.0
0.3760	10.0 ←
0.3690	12.6
0.3670:	14.2
0.3660	15.0
1.3660	20.0
0.3660	25.0

Change of Potential on Addition of HCl to NaCl Solution



25 c.c. of .0989 N NaCl
25 c.c. of water

Figure D2

The following series of titrations have for their objective the reduction of ruthenium tetroxide with HCl as the reducing agent. The reduction was observed by the use of a potentiometer. The procedure followed in the five series of the titrations was to titrate 0.0995 normal HCl into a beaker containing 10 ml. of ruthenium tetroxide solution and 40 ml. of distilled water.

Summary

Series I

In this series of titrations there are no breaks in the curve because the concentration of the ruthenium tetroxide in the solution was so small that it was impossible to get accurate differences in potentials. The curves seem to have the general shape of a parabola. The potential rises with increase in the concentration of the HCl. Its rise is steepest at those points where the concentration of HCl is the lowest.

Methods of Analysis

In analyzing a solution of ruthenium tetroxide two ten ml. samples were added to two small beakers containing some concentrated HCl. The non-volatile ruthenium chloride formed were evaporated in two previously weighed silica boats. Placing the silica boats containing the solid ruthenium chloride in an electric reducing furnace a hydrogen stream reduced the ruthenium chloride to metallic ruthenium at temperatures above 300°C. The metallic ruthenium was weighed and the molarity of the solution calculated by proportion. The other solutions were analyzed by the same method with the results shown in later pages.

Table E

	I	II
Wgt. of boat	7.27613	7.16435
Wgt. of boat Ru	7.28948	7.17767
Wgt. of Ru in ten ml.	0.01335	0.01332

The mean average weight is 0.01333 grams of ruthenium in ten ml.

The molatity of the solution is 0.0130

10 c.c. of RuO^{4}_{-} solution

50 c.c. of water

Table E

I.e.m. f.	c.c. HCl	II.e.m.f.	c.c. HCl
0.7748	0.0	0.7705	0.0
0.8232	1.46	0.8138	1.0
0.8375	2.98	0.8293	2.0
0.8470	4.42	0.8370	3.0
0.8538	6.02	0.8427	4.0
0.8590	8.0	0.8480	5.0
0.8610	10.0	0.8520	6.0
0.8660	11.97	0.8547	7.0
		0.8580	7.95
		0.8582	9.0
		0.8605	10.0
		0.8632	11.0

Ruthenium Tetroxide Solution Titrated with HCl

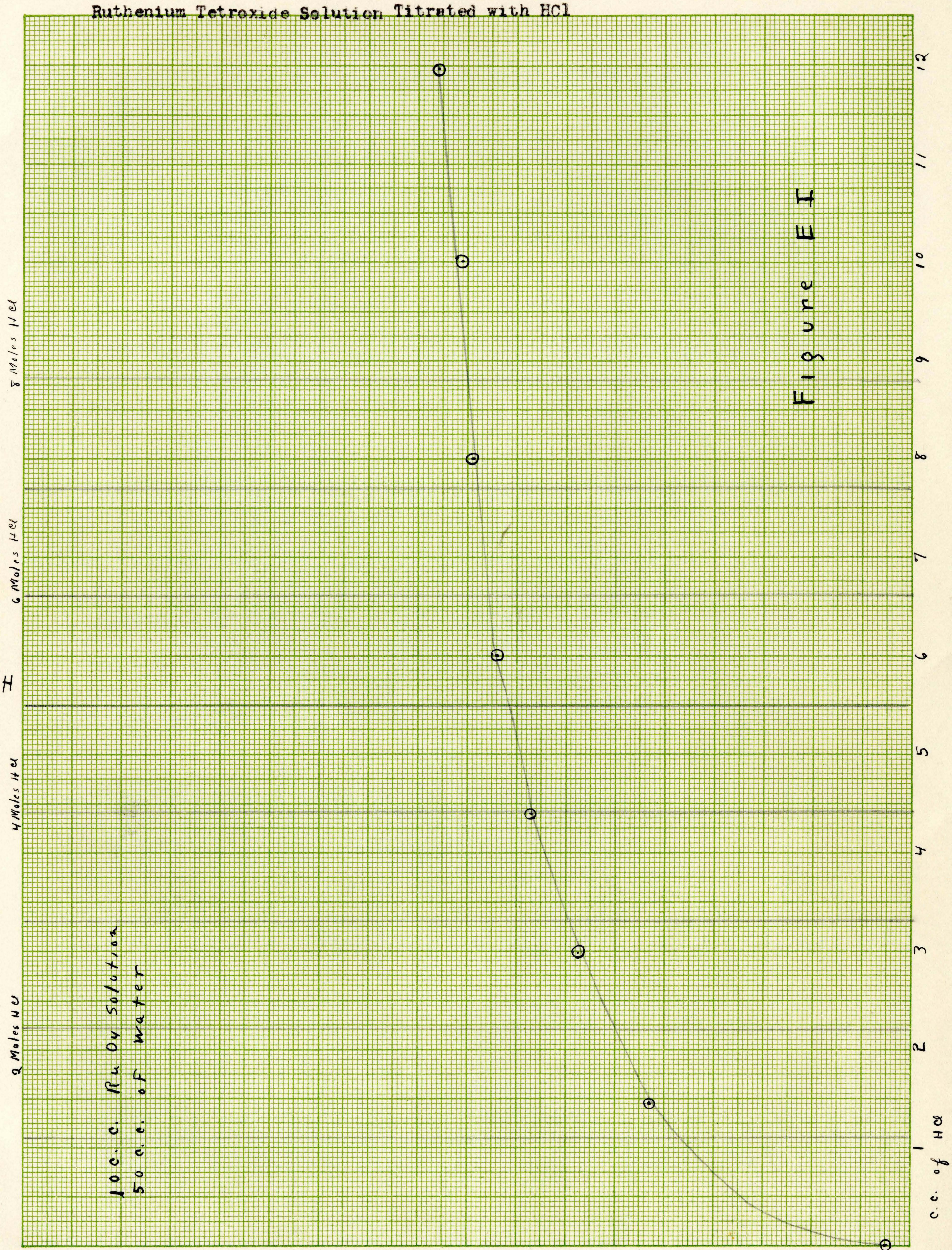


Figure EI

Ruthenium Tetroxide Solution Titrated with HCl

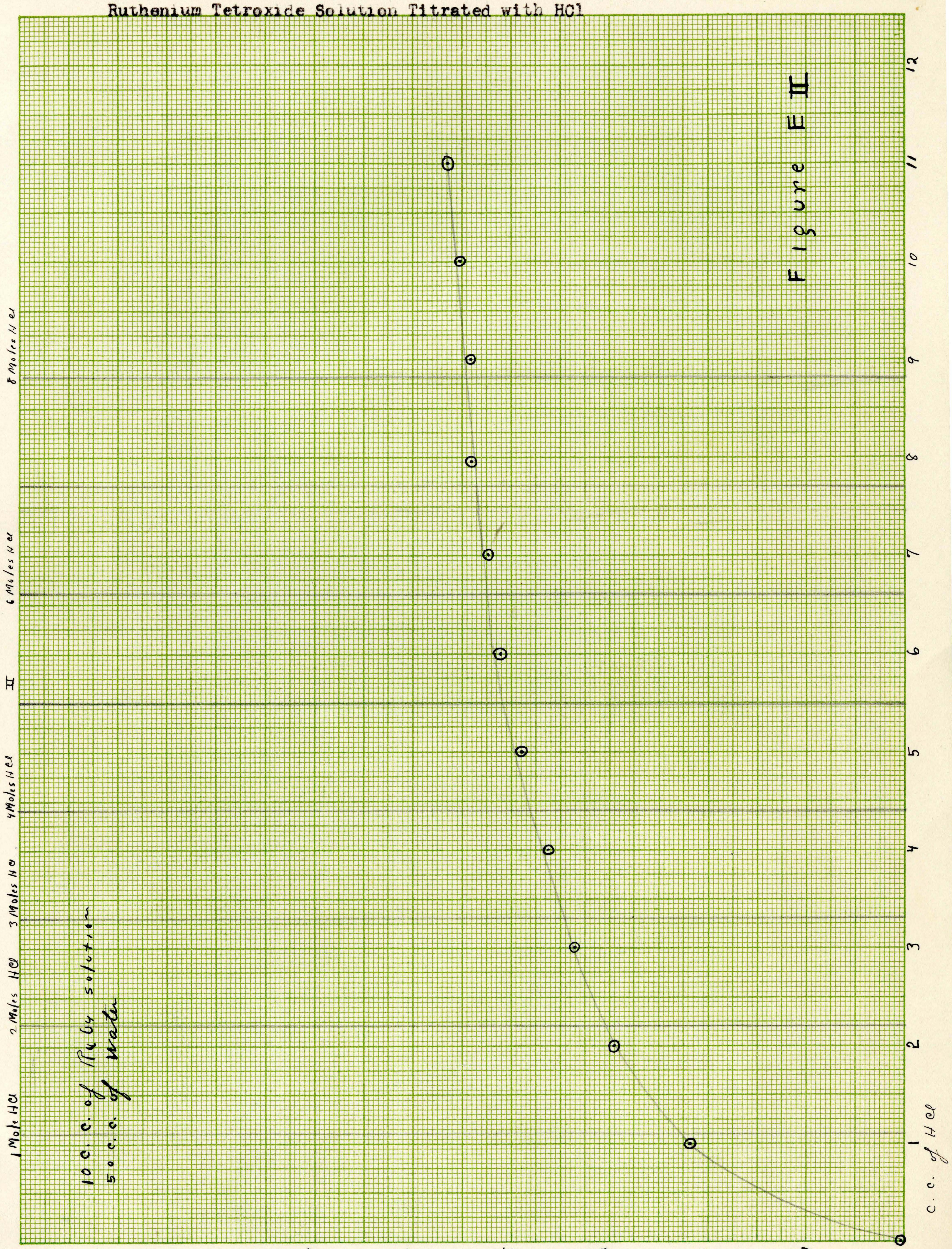


Table F

Two samples of ten c.c. of ruthenium tetroxide stock solution.

	I	II
Wgt. of boat	7.16452	7.27615
Wgt. of boat Ru.	7.19244	7.30381
Wgt. of ruthenium in ten c.c.	0.02792	0.02746

Mean average is 0.02768 grams of ruthenium in ten c.c.

Molarity of the solution is 0.0272.

Summary of the second series.

The titration of a new solution of ruthenium tetroxide with HCl gave the same type of curve as those obtained for the preceding series. There is a weak minimum in the curve at the point where there are equal number of HCl and ruthenium tetroxide molecules in the solution. It is not sharp enough for anyone to say with any degree of certainity that it is a real break. In order to find the effect of time on the potential readings, enough HCl was titrated into the solution to give about seven molecules of HCl to one of ruthenium tetroxide. The curves show that time plays an important part in the potential. Since time had to be considered the potential readings of the following experiments were recorded only after a sufficent amount of time had elapsed for the potential to reach equilibrium. When the potential was plotted as a function of time the curve seemed to be a hyperbola.

10 c.c. of RuO^4 solution

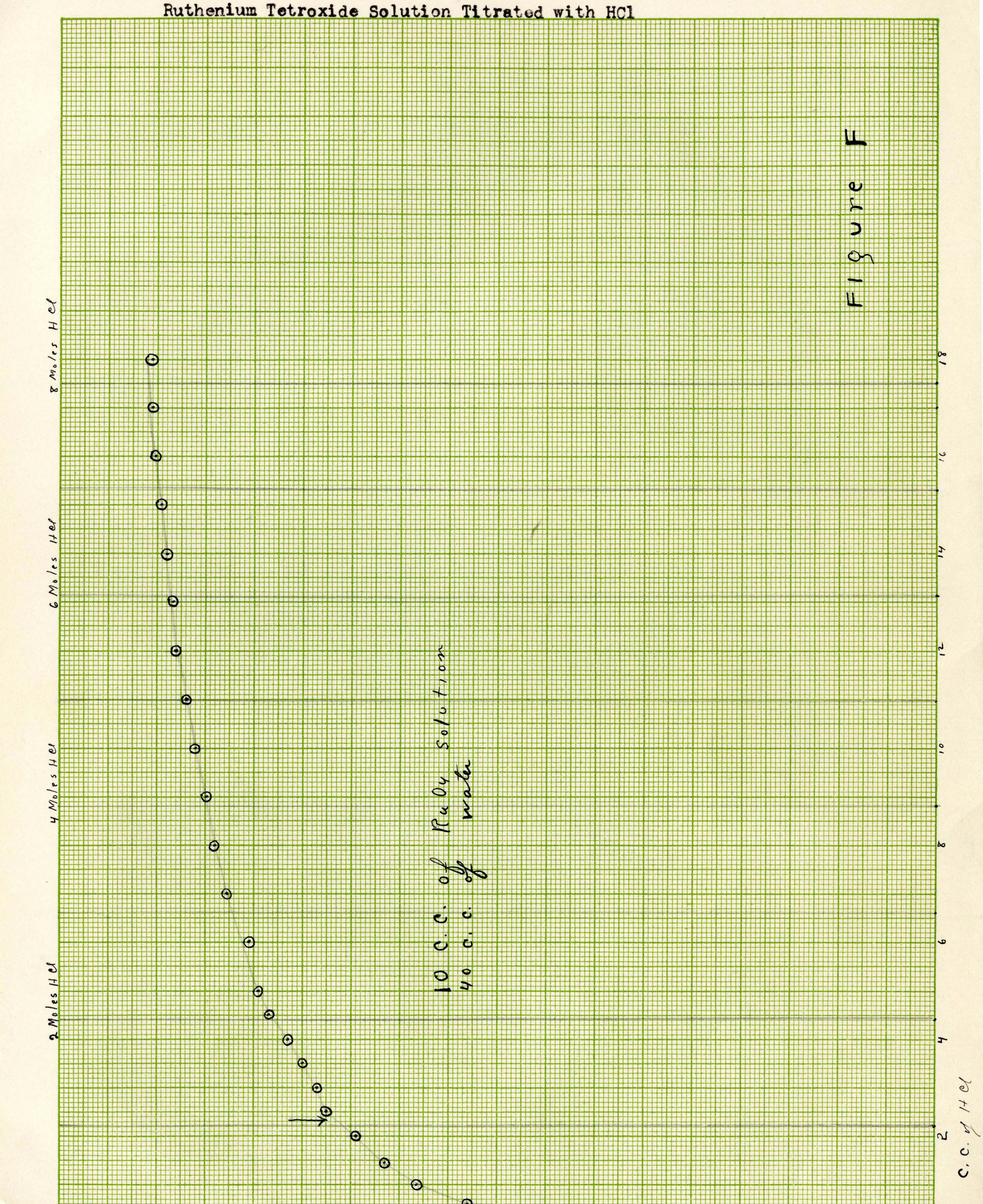
Table F

40 c.c. of water

I

e.m.f.	c.c. HCl
0.7850	0.0
0.7960	0.1
0.8040	0.3
0.8135	0.5
0.8160	0.6
0.8265	1.0
0.8330	1.46
0.8390	2.0
0.8450	2.52 ←
0.8470	3.0
0.8500	3.5
0.8532	4.0
0.8570	4.5
0.8590	5.0
0.8610	6.0
0.8655	7.02
0.8680	8.0
0.8698	9.0
0.8720	10.0
0.8740	11.03
0.8760	12.0
0.8768	13.02
0.8780	14.0
0.8792	15.0
0.8802	16.0
0.8810	17.0
0.8813	18.0

Ruthenium Tetroxide Solution Titrated with HCl



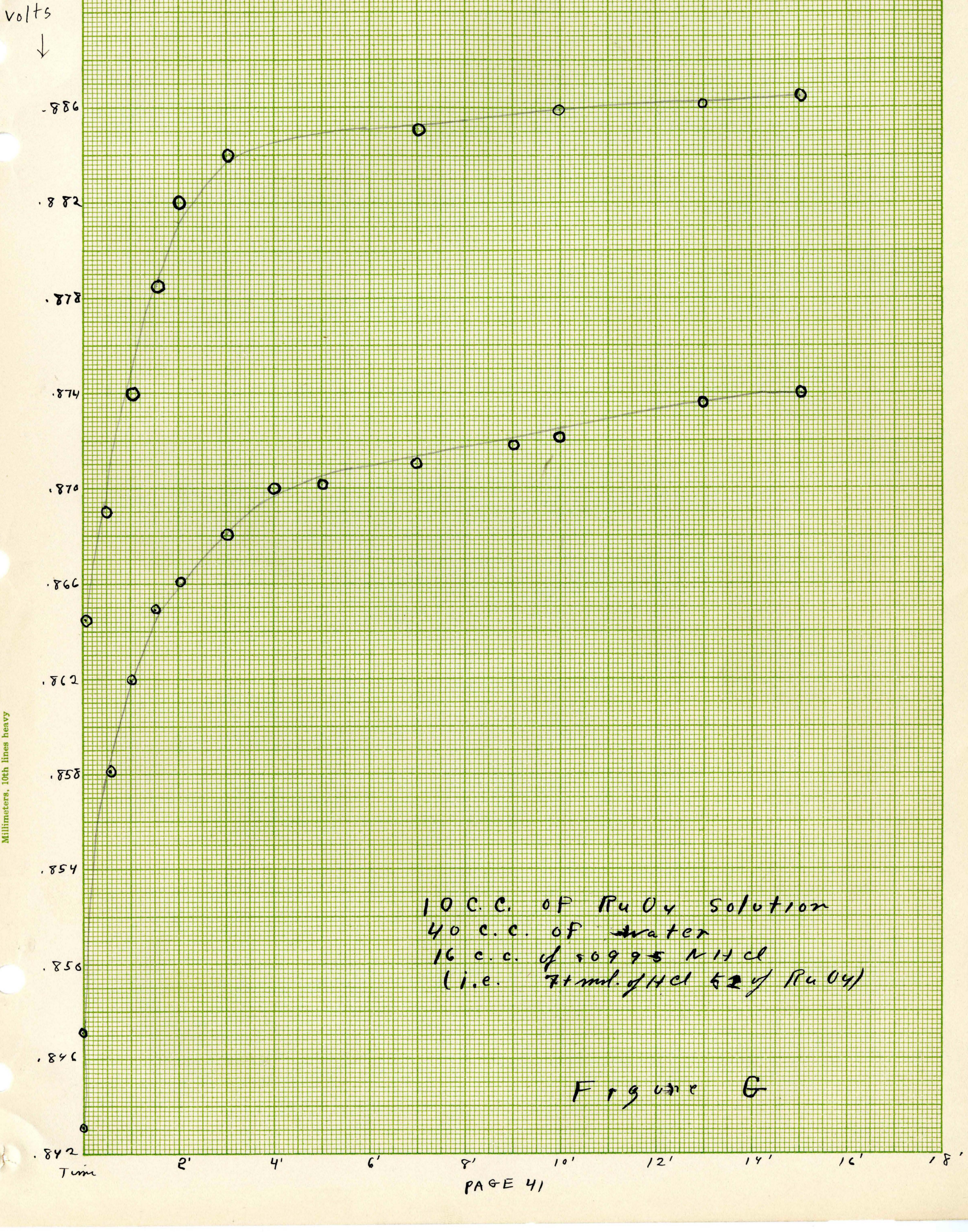
10 c.c. of RuO4 solution
40 c.c. of water

Figure F

Table - G

e.m.f.	time	e.m.f.	time
0.847	0	0.8645	0
0.858	30"	0.8690	30"
0.862	60""	0.8740	60"
0.865	90"	0.8785	90"
0.866	2'	0.8820	2'
0.868	3'	0.8840	3'
0.8693	4'	0.8850	7'
0.8700	5'	0.8860	10'
;0.8718	8'	0.8862	13'
0.8722	10'	0.8865	15'
0.8737	15'		
0.8740	15'-30"		

Change of potential of RuO_4 solution and HCl with Time.



10 C.C. of RuO_4 Solution
40 c.c. of water
16 c.c. of .0995 N HCl
(i.e. 7+ mol. of HCl 52 of RuO_4)

Figure G

Series III Analysis Table H

Two samples of ten c.c. of ruthenium tetroxide solution

	I	II
Wgt. of boat	7.16463	7.27581
Wgt. of boat + Ru.	7.19410	7.30508
Wgt. of ruthenium in ten c.c.	0.02947	0.02927

Mean average is 0.02937 grams of ruthenium in ten c.c.

Molarity of the solution is 0.02888.

Summary

In this series a weak minimum is observed when there are equal numbers of HCl and ruthenium tetroxide molecules in the solution. This indicates that a rapid change of electrons occur at this point possibly due to the formation of a halide. In the first three series of titrations the changes observed at the point when the number of HCl and ruthenium tetroxide molecules are equal are as follows:

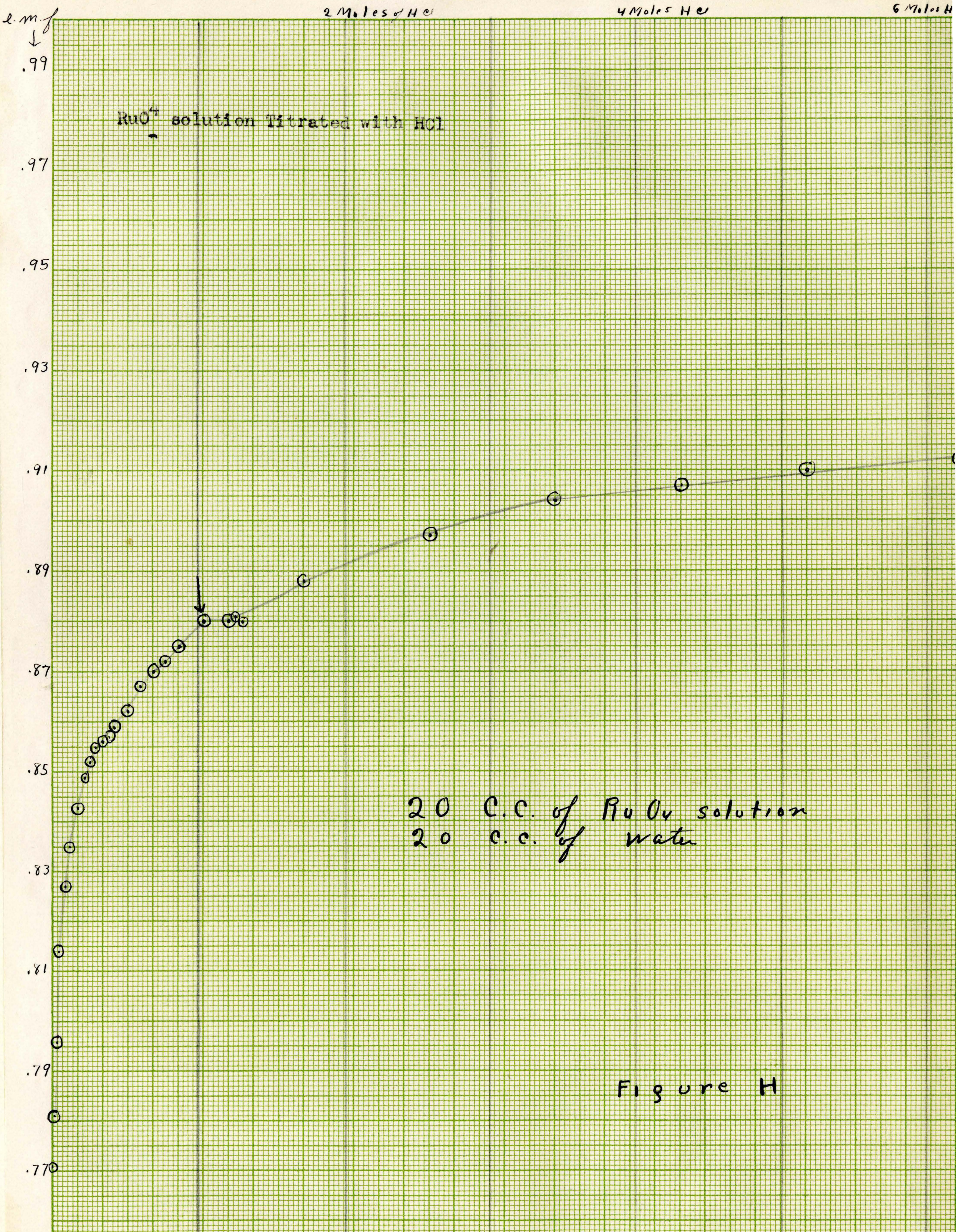
Series I	no minimum	solution 0.0130 M.
Series II	weak minimum	solution 0.0272 M.
Series III	weak minimum	solution 0.02888 M.

20 c.c. of RuO^4 solution

Table H

20 c.c. of water

e.m.f.	c.c. of HCl
0.7710	0.0
0.7810	0.05
0.7960	0.1
0.8140	0.2
0.8190	0.25
0 8270	0.5
0.8350	0.75
0.8430	1.0
0.8490	1.25
0.8520	1.5
0.8550	1.75
0.8560	2.0
0.8570	2.25
0.8590	2.5
0.8620	3.0
0.8670	3.5
0.8700	4.0
0.8720	4.5
0.8750	5.0
0.8800	6.16 ←
0.8800	7.0
0.8810	7.1
0.8800	7.5
0.8880	10.0
0.8970	15.0
0.9040	20.0
0.9070	25.0
0.9100	30.0
0.9120	36.0



RuO_4 solution Titrated with HCl

20 C.C. of RuO_4 solution
20 c.c. of water

Figure H

Series IV Table J

Two samples of ten c.c. of ruthenium tetroxide solution.

	I	II
Wgt. of boat	7.27610	7.16455
Wgt. of boat plus Ru.	7.31170	7.20035
Wgt. of ruthenium in ten c.c.	0.03560	0.03580

Mean average is 0.03570 grams of ruthenium in ten c.c.

Molarity of the solution is 0.03506

Summary

In curves I, III, IV a sharp minimum can be recognized at the point where there are equal numbers of HCl and ruthenium tetroxide molecules. Curve II shows a slight minimum. This leads to a discrepancy between this work and the previous work by McConnell(18) who found a maximum at the same point. This discrepancy seems to be caused by the fact that some free chlorine must have been present in his ruthenium tetroxide solution. In curves VI and VII where chlorinated distilled water was used instead of ordinary distilled water, a maximum was obtained at the same point. Likewise the voltage agrees with his recorded potentials and the curves obtained are similiar to his.

10 c.c. of RuO^4 solution

40 c.c. of water

Table - J-I and J-II

I

e.m.f.	c.c. HCl
0.6850	0.0
0.7020	1 drop
0.7450	3 "
0.7650	5 "
0.7800	0.5
0.7910	0.7
0.7995	1.0
0.8030	1.38
0.8190	2.05
0.7995	2.5
0.7900	2.6 ←
0.7970	2.7
0.7995	2.8
0.7980	3.0
0.7980	3.1
0.8030	3.5
0.8070	4.0
0.8090	4.5
0.8140	5.0
0.8220	6.0
0.8250	7.0
0.8290	8.0
0.8320	9.0
0.8350	10.0
0.8375	11.0
0.8410	12.0
0.8480	15.0
0.8510	17.0
0.8540	20.0
0.8570	23.0

II

e.m.f.	c.c. HCl
0.7995	0.0
0.8120	0.1
0.8220	0.24
0.8380	0.4
0.8430	0.6
0.8450	0.8
0.8450	1.0
0.8469	1.3
0.8460	1.5
0.8490	1.8
0.8470	2.0
0.8470	2.1
0.8510	2.5 ←
0.8520	3.0
0.8540	3.5
0.8540	4.0
0.8560	4.5
0.8590	5.0
0.8625	6.0
0.8640	7.0
0.8660	8.0
0.8670	9.0
0.8700	11.0
0.8730	13.0
0.8740	15.0
0.8760	17.0
0.8770	19.0
0.8775	21.0
0.8780	23.0

Ru O^4 Solution Titrated with HCl

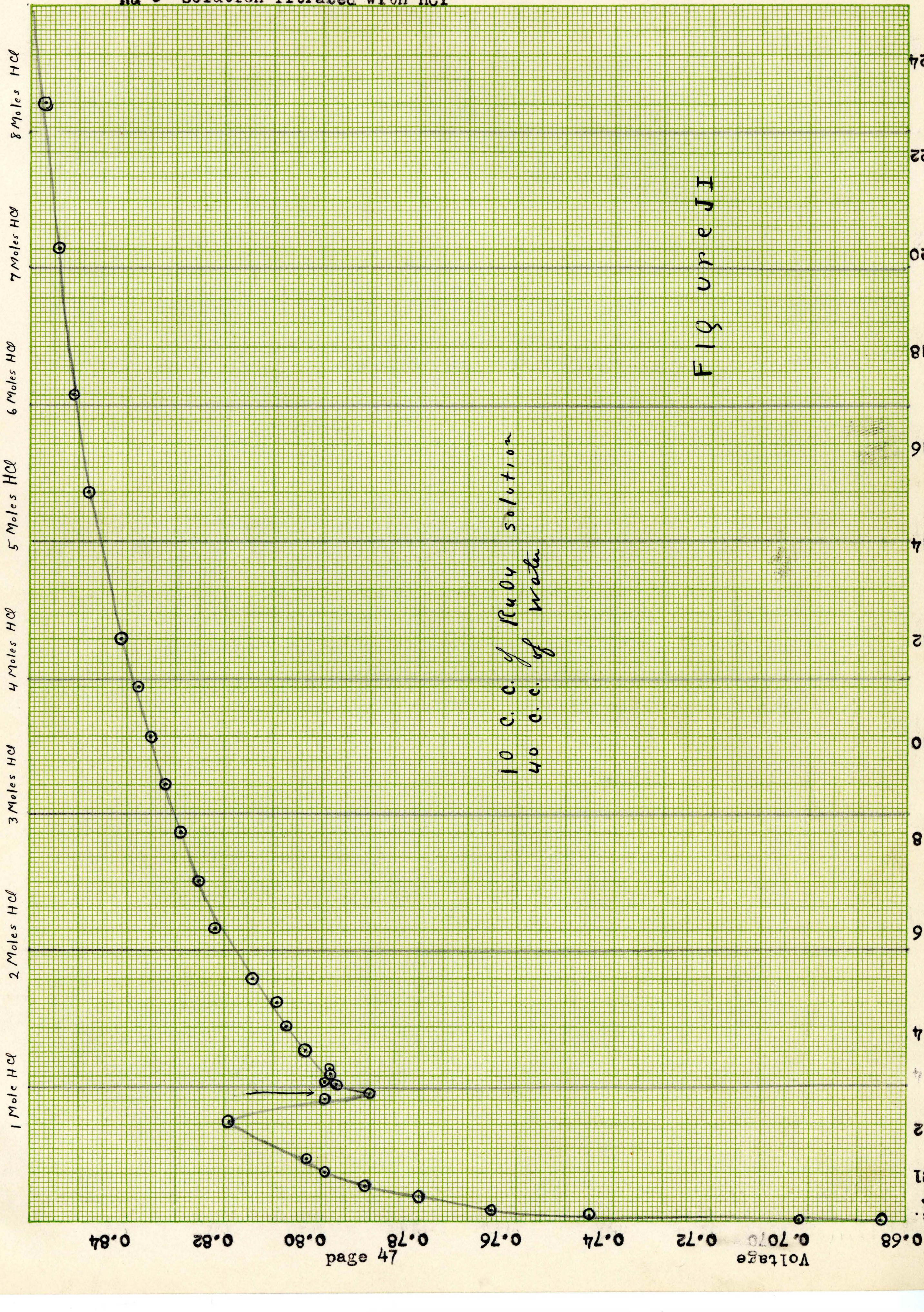


Figure II

RuO$_4$ Solution Titrated with HCl

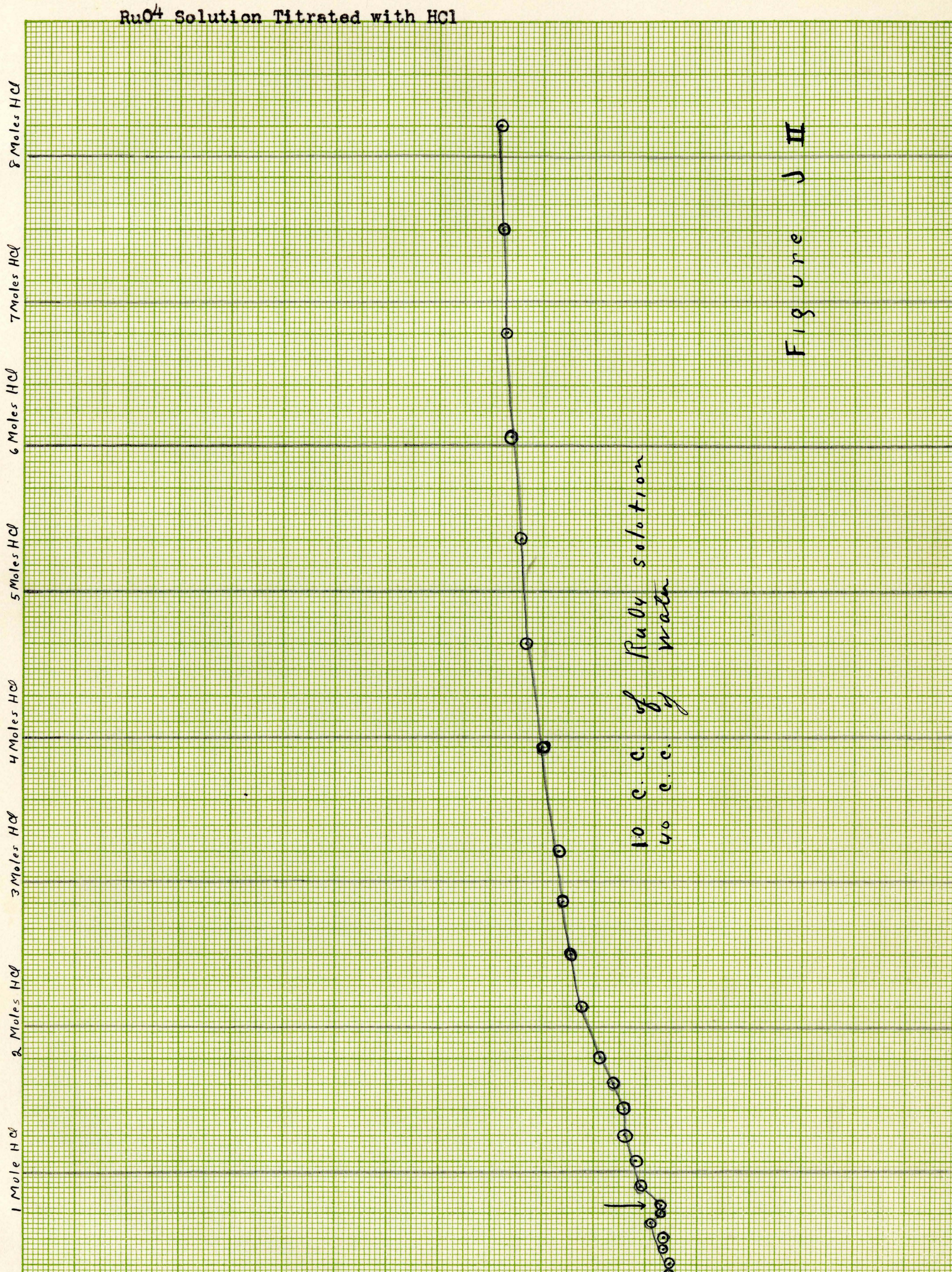


Figure J II

page 48

10 c.c. of RuO^4 solution

40 c.c. of water

Table - J-III - J-IV

III

e.m.f.	c.c. HCl
0.8300	0.0
0.8490	0.15
0.8620	0.40
0.8680	0.6
0.8440	0.8
0.8430	1.0
0.8450	1.4
0.8470	1.7
0.8470	1.9
0.8450	2.0
0.8460	2.1 ←
0.8460	2.2
0.8450	2.3
0.8470	2.5
0.8480	2.7
0.8485	2.9
0.8530	4.0
0.8570	5.0
0.8605	6.0
0.8660	8.0
0.8690	10.0
0.8720	12.0
0.8740	14.0
0.8760	16.0
0.8790	20.0
0.8805	24.0

IV

emf	c.c. HCl
0.8745	0.0
0.8850	0.1
0.9000	0.5
0.9080	0.9
0.9050	1.2
0.9000	1.5
0.8970	1.8
0.8920	2.0
0.8880	2.1
0.8830	2.2
0.8790	2.3
0.8760	2.4
0.8740	2.6 ←
0.8740	3.1
0.8740	3.5
0.8740	4.0
0.8745	5.0
0.8780	6.0
0.8860	10.0
0.8930	15.0
0.8980	20.0
0.9050	25.0

RuO$^{4}_{-}$ Solution Titrated with HCl

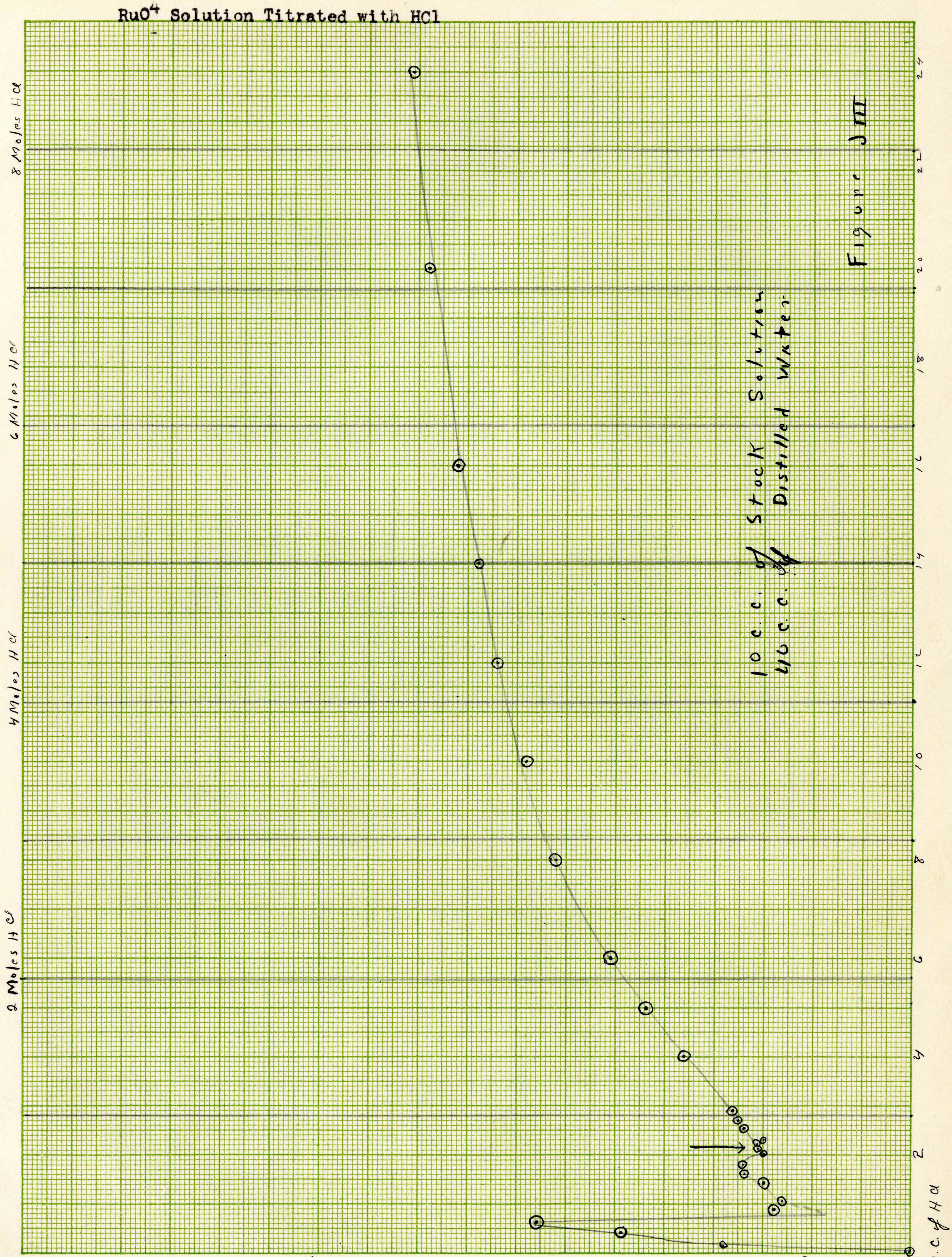


Figure III

RuO_4 Solution Titrated with HCl

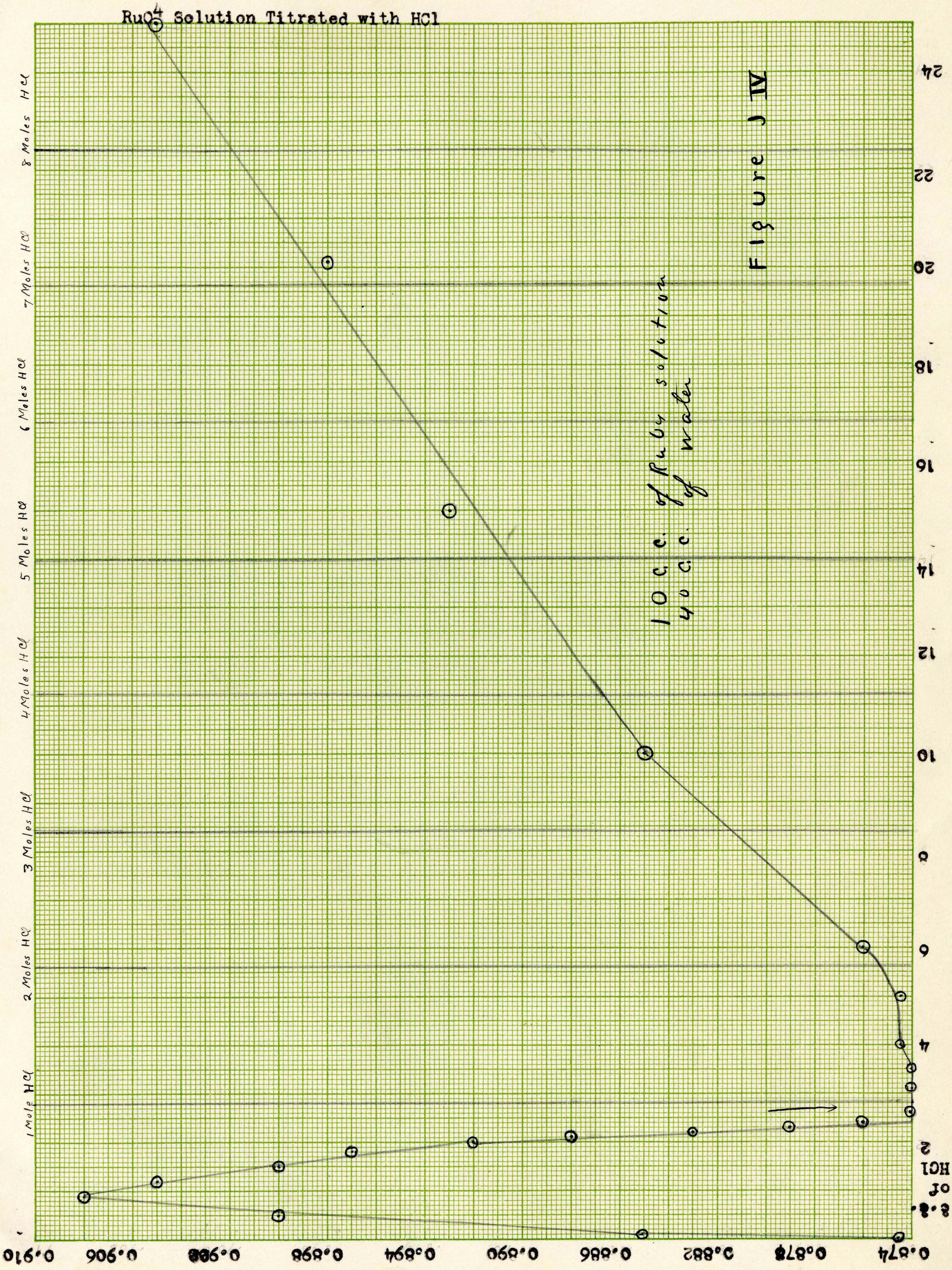


Figure J IV

IV

Table J-VI. J-VII

Table - - VI

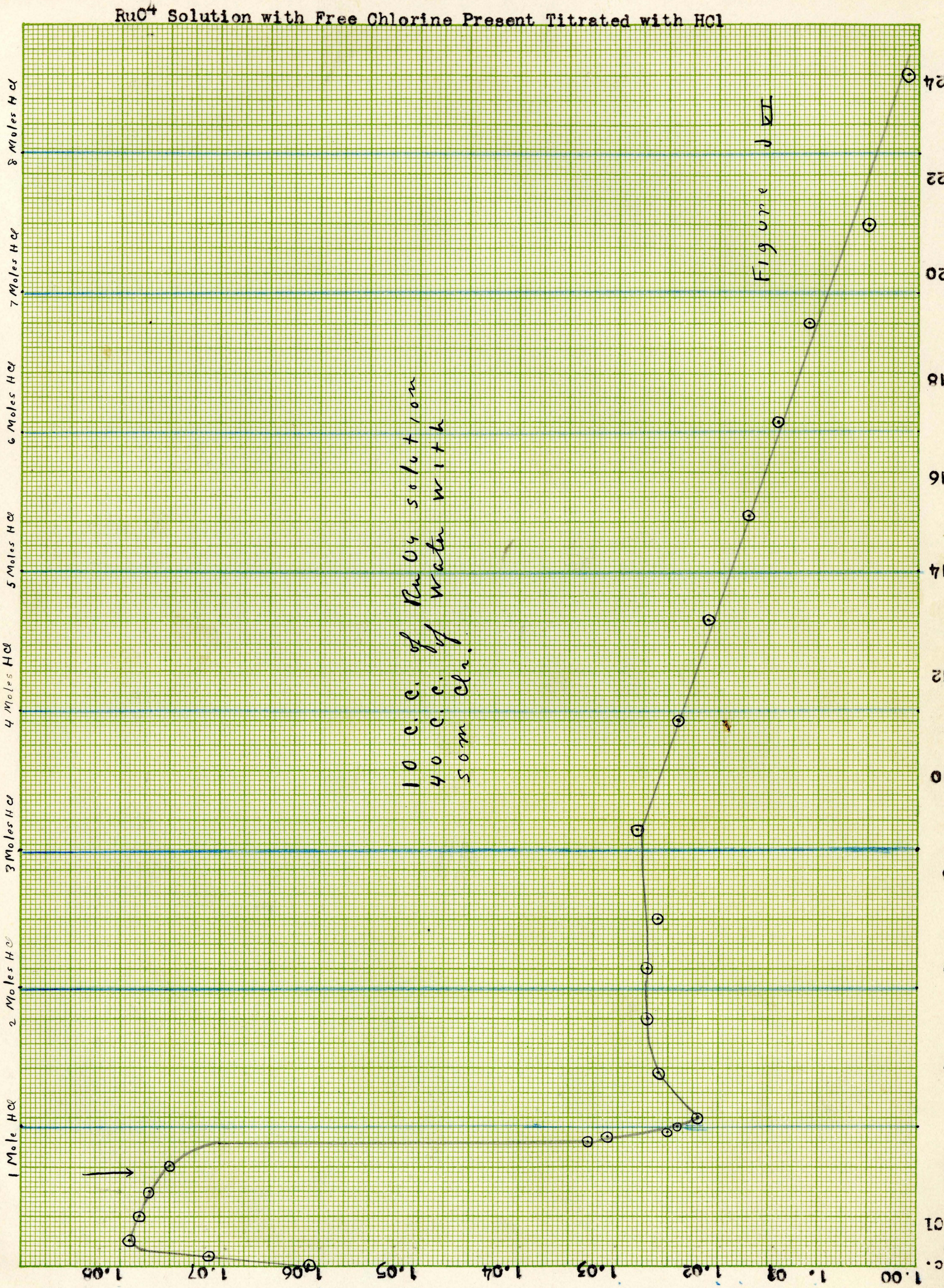
e.m.f.	c.c. of HCl
1.061	0.00
1.071	0.20
1.079	0.50
1.078	1.00
1.077	1.50
1.075	2.00 ←
1.033	2.50
1.031	2.60
1.025	2.70
1.024	2.80
1.022	3.00
1.026	3.91
1.027	5.00
1.027	6.01
1.026	7.00
1.028	8.81
1.024	11.00
1.021	13.00
1.017	15.12
1.014	17.05
1.011	19.00
1.005	21.00
1.001	23.02

Table - - VII

e.m.f.	c.c. of HCl
1.045	0.00
1.050	0.20
1.053	0.50 ←
1.045	1.00
1.035	1.50
1.040	2.00
1.043	2.50
1.039	2.70
1.039	2.80
1.037	2.90
1.035	3.10
1.035	4.01
1.036	5.02
1.036	6.00
1.032	7.00
1.031	8.00
1.030	9.01
1.027	10.00
1.024	11.01
1.022	12.00
1.020	13.00
1.018	14.00
1.016	16.00
1.013	18.02
1.008	20.11
1.004	22.00
1.001	24.02

This was carried out by using 40 c.c. of chlorinated water, 10 c.c. of the stock solution, which was partially decomposed.

RuC^4 Solution with Free Chlorine Present Titrated with HCl



RuO^4 Solution with Free Chlorine Present Titrated with HCl

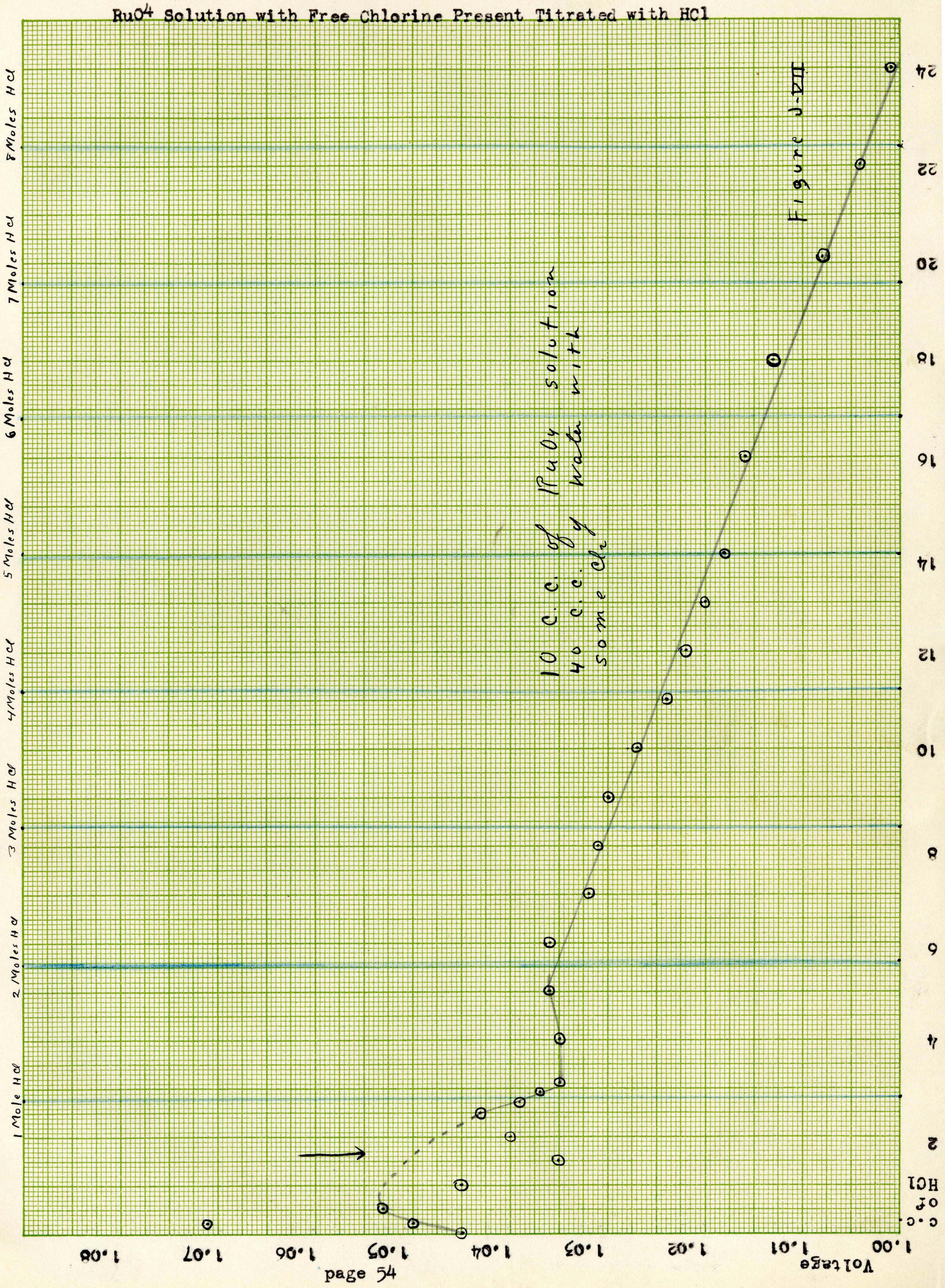


Table K

Fifth series

Two samples of ten c.c. of ruthenium tetroxide solution.

Wgt. of boat	7.16441	7.27601
Wgt. of boat plus Ru.	7.22024	7.33166
Wgt. of Ru. in ten c.c.	0.05583	0.05565

Mean average is 0.05579 grams of ruthenium in ten c.c.

Molarity of the solution is 0.0548.

Summary

The curves I, II, IV show a minimum at the point where there are equal numbers of HCl and ruthenium tetroxide molecules in solution. The third titration, III, which was carried out using chlorinated water instead of distilled water shows a maximum at the same point. This seems to confirm the suspicion that McConnell(18) had some free chlorine present in his ruthenium tetroxide solution. The puzzling fact is that there are no compound of ruthenium known in which it has a valence of VII and one chlorine atom attached to it. At the point where ruthenium has a valence of IV there is no break in the curve. Although RuO^2 and $RuCl^4$ have been isolated, yet at the point where this should be present in the solution there is no sharp change of potential.

10 c.c. of RuO^4 solution
40 c.c. of water

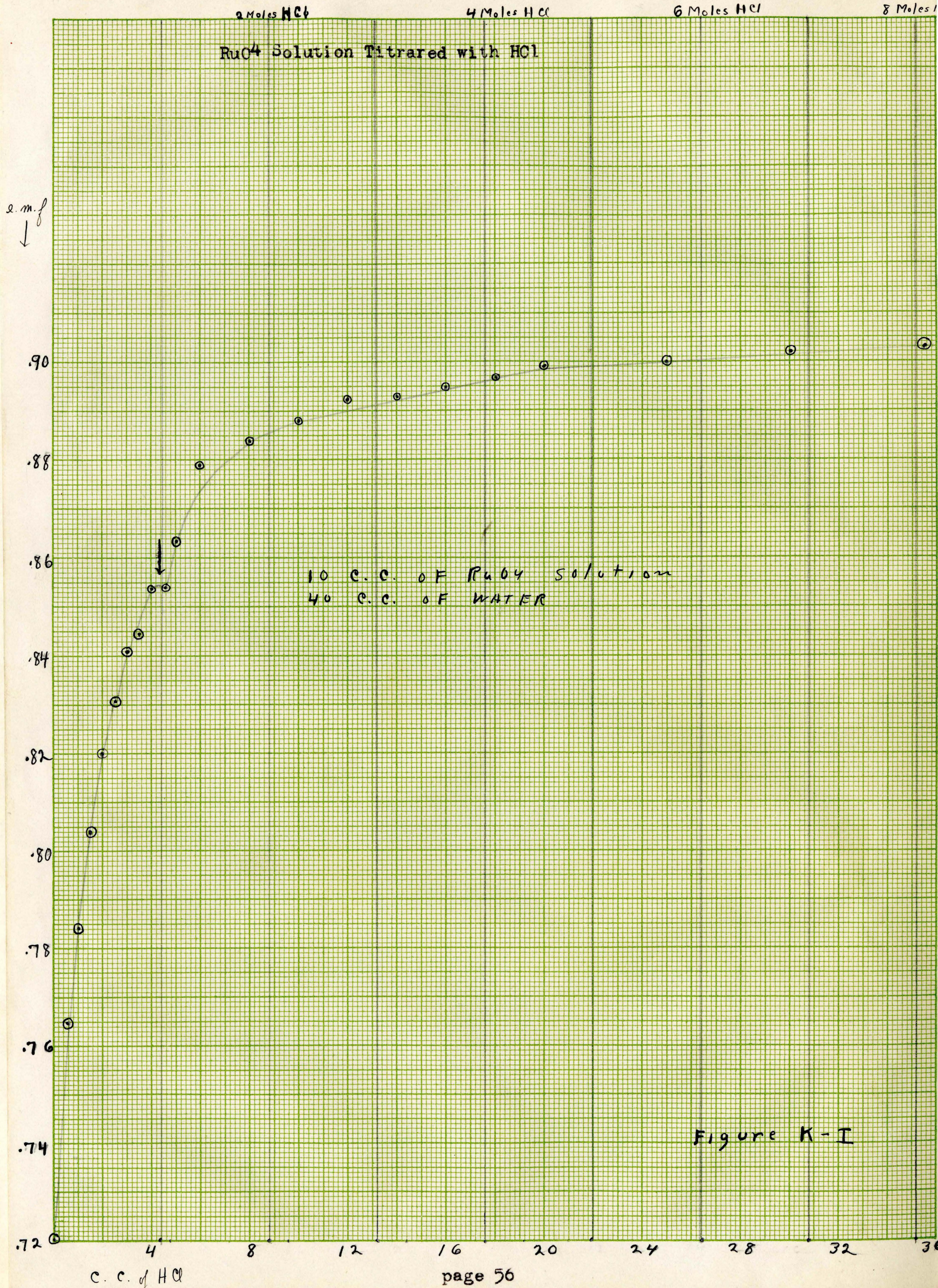
Table K-I - K-II

I

e.m.f.	c.c. HCl
0.7200	0.0
0.7650	0.5
0.7890	1.0
0.8080	1.5
0.8200	2.0
0.8320	2.5
0.8420..	3.0
0.8490	3.5
0.8580	4.0 ←
0.8590	4.5
0.8670	5.0
0.8690	5.5
0.8730	6.0
0.8750	6.5
0.8770	7.0
0.8790	8.0
0.8840	10.0
0.8880	12.0
0.8920	14.0
0.8950	16.0
0.8970	18.0
0.8990	20.0
0.9002	25.0
0.9020	30.0
0.9035	35.0

II

e.m.f.	c.c. HCl
0.7490	0.0
0.8550	1.1
0.8660	2.0
0.8660	2.5
0.8700	3.0
0.8710	3.4
0.8720	3.6
0.8740	3.8
0.8750	4.0
0. 8740	4.1
0.8730	4.2 ←
0.8730	4.3
0.8745	4.45
0.8745	4.65
0.8770	6.0
0.8870	9.0
0.8920	12.0
0.8940	15.0
0.8960	18.1
0.8970	21.0
0.8990	24.0
0.9110	30.0
0.9130	35.0



RuO4 Solution Titrared with HCl

Figure K-I

RuO^4 Solution Titrated with HCl

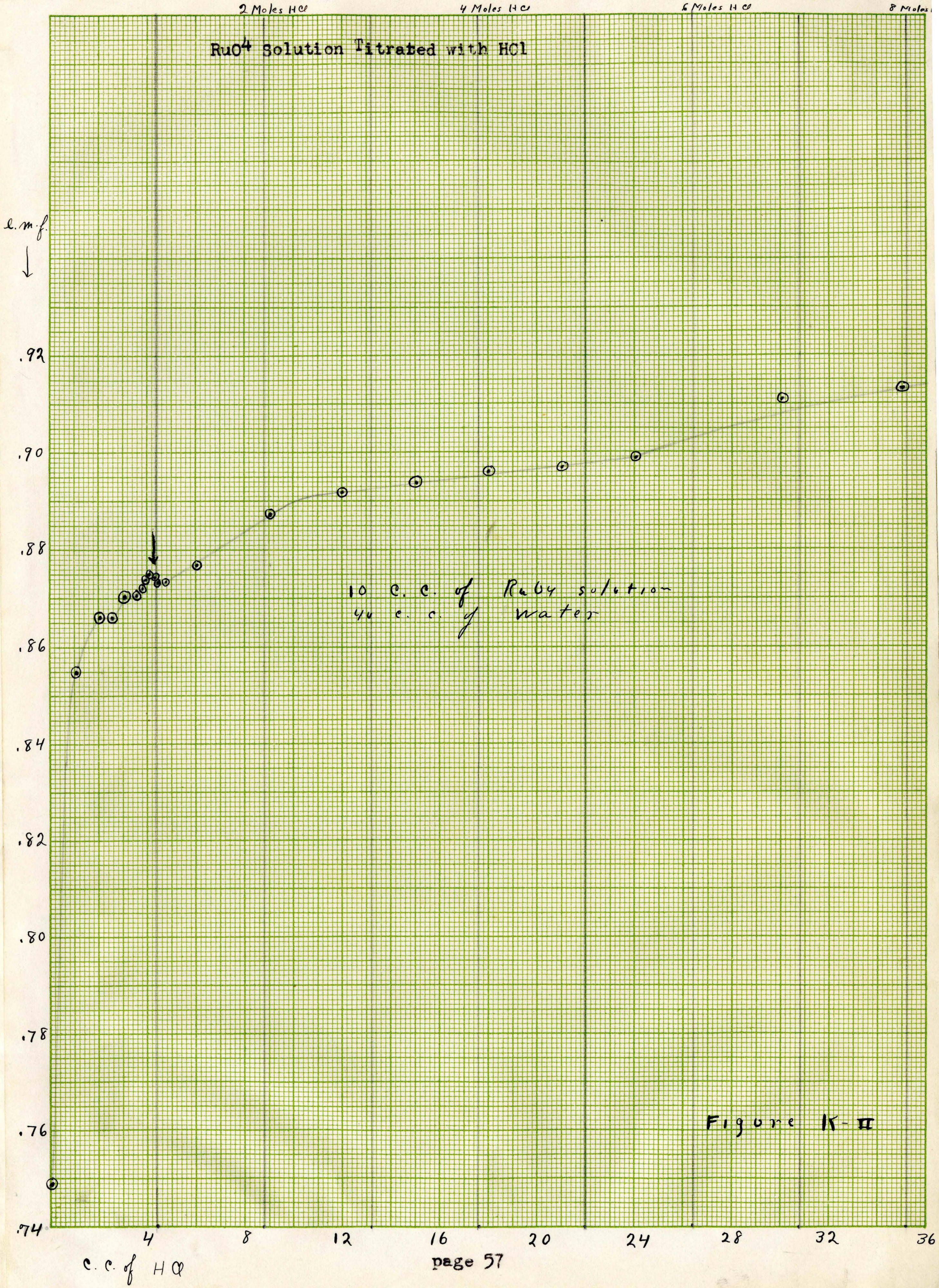


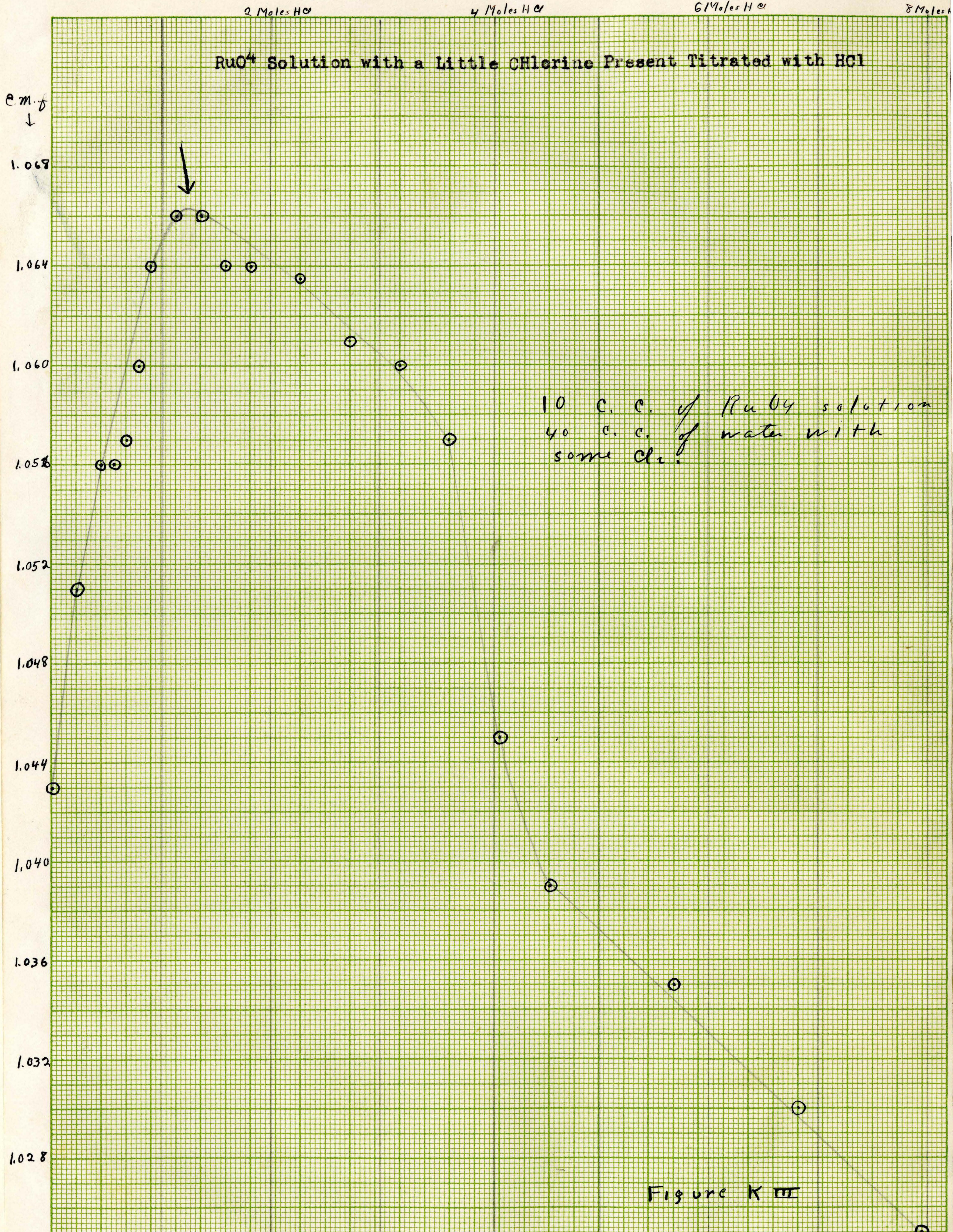
Figure K-II

Table K-III-K-IV

III		IV	
e.m.f.	c.c. HCl	e.m.f.	c.c. HCl
1.0430	9.9	0.7950	0.0
1.0510	1.0	0.8550	1.0
1.0560	2.0	0.8700	2.0
1.0560	2.5	0.8780	3.0
1.0570	3.0	0.8810	3.4
1.0600	3.5	0.8820	3.8
1.0640	4.0	0.8840	4.0
1.0660	5.0 ←	0.8850	4.3 ←
1.0660	6.0	0.8870	5.0
1.0640	7.0	0.8900	6.0
1.0640	8.0	0.8935	8.0
1.0635	10.0	0.8990	10.0
1.0610	12.0	0.9040	12.0
1.0600	14.0	0.9070	14.0
1.0570	16.0	0.9090	16.0
1.0450	18.0	0.9110	18.0
1.0390	20.0	0.9130	20.0
1.0350	25.0	0.9150	22.0
1.0300	30.0	0.9180	25.0
1.0250	35.0	0.9200	30.0
		0.9222	35.0

III- 10 c.c. of RuO^4 solution, 40 c.c. of water, and the waterhad some free clorine present

IV- 10 c.c. of RuO^4 solution, 40 c.c. of water.



RuO^4 Solution with a Little CHlorine Present Titrated with HCl

10 c.c. of RuO4 solution
40 c.c. of water with
some Cl_2.

Figure K III

RuC^4 Solution Titrated with HCl

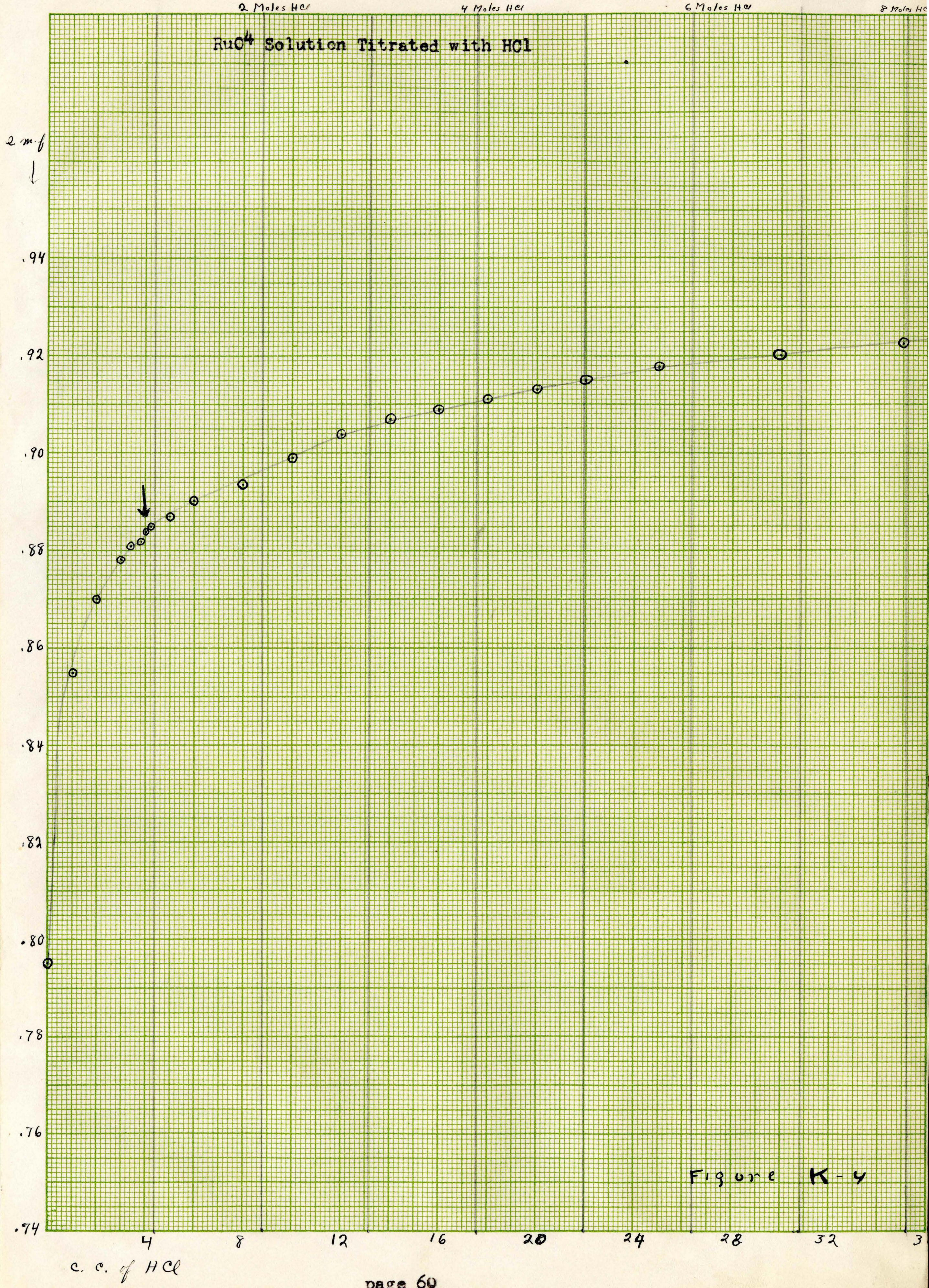


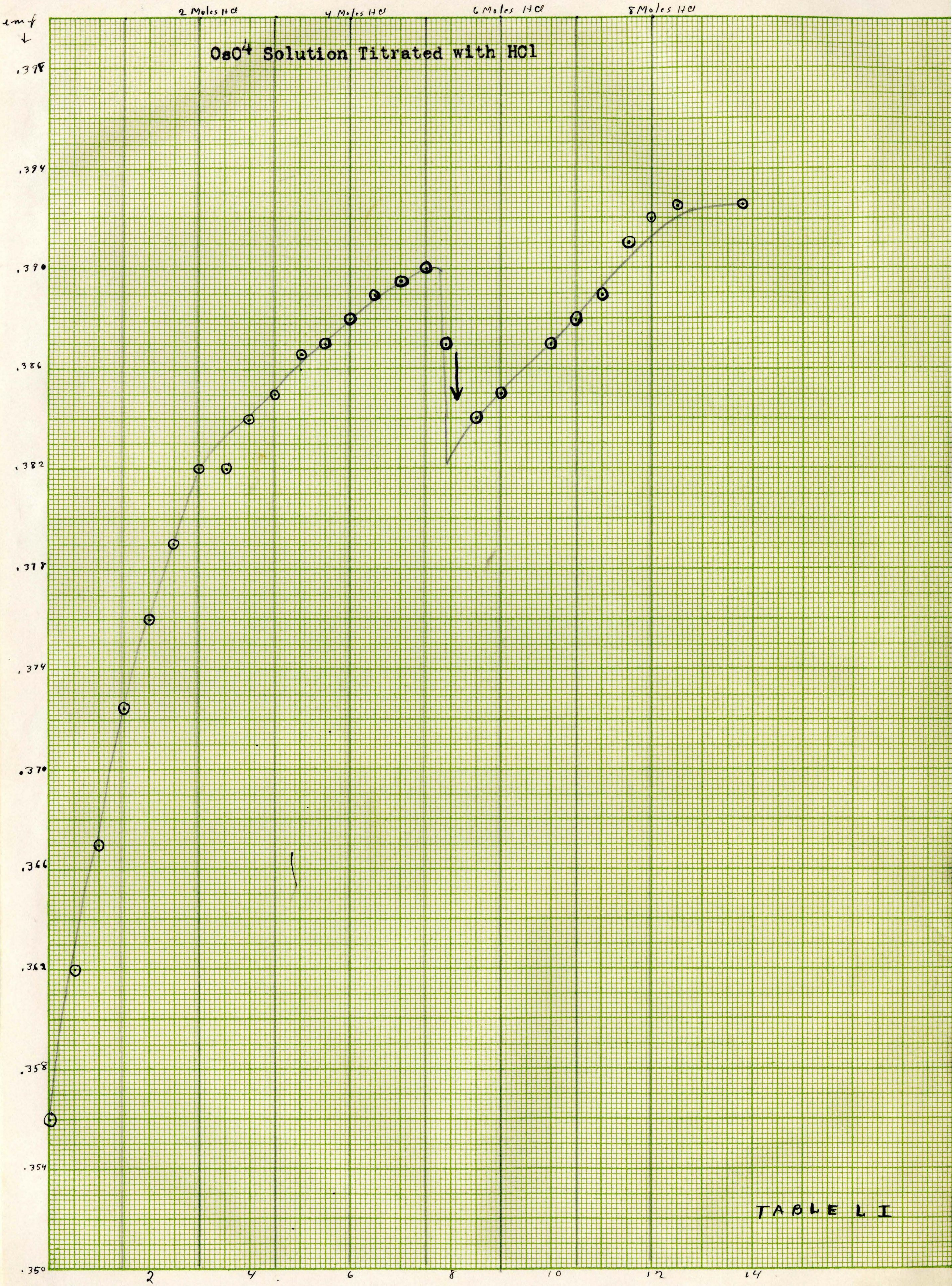
Figure K-4

10c.c. of OsO^4 solution

40c.c. of water

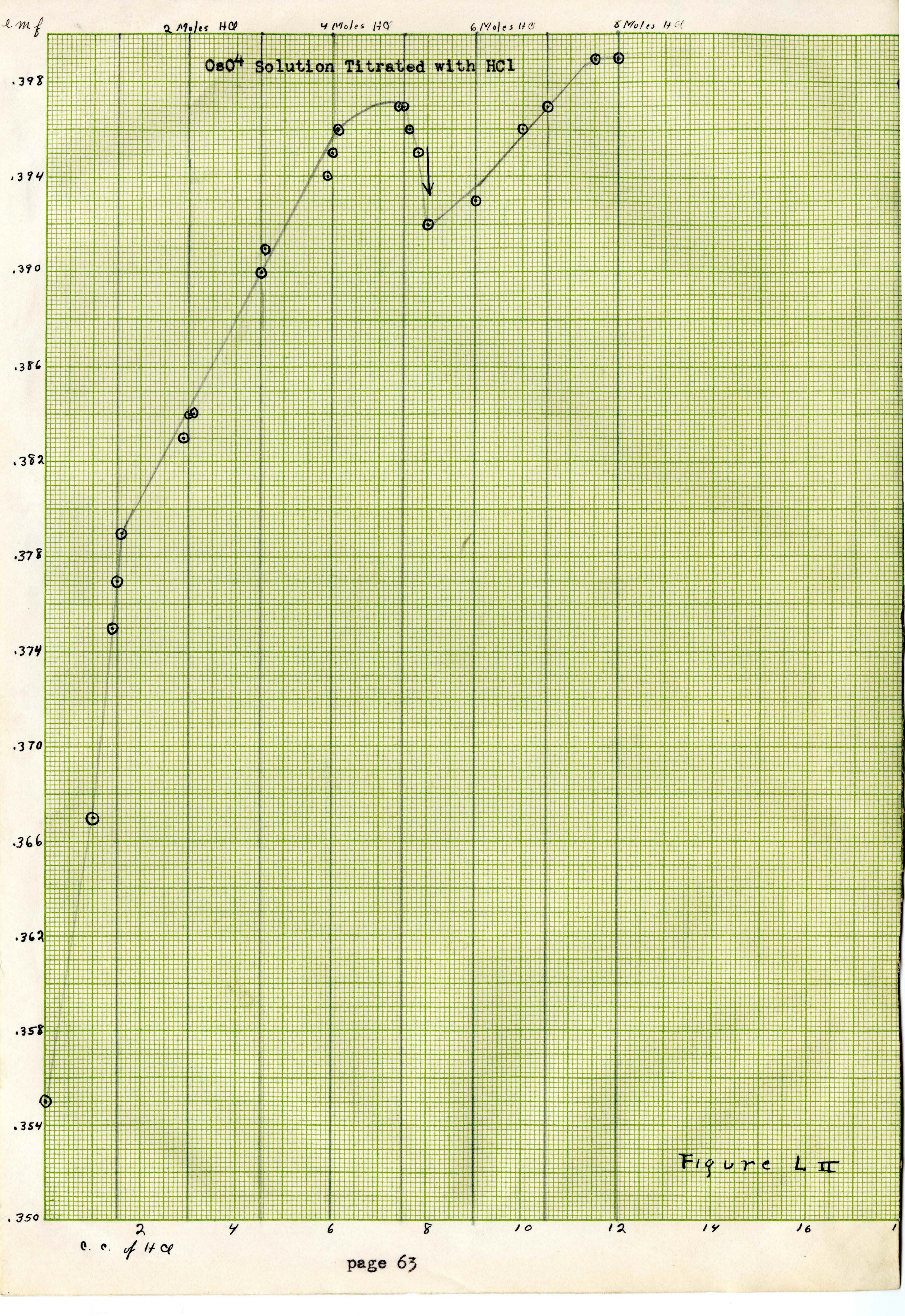
Table L

I		II		III	
e.m.f.	c.c. HCl	e.m.f.	c.c. HCl	e.m.f.	c.c. HCl
0.3560	0.0	0.3550	0.0	0.3530	0.0
0.3620	0.5	0.3670	1.0	0.3670	1.0
0.3670	1.0	0.3750	1.4	0.3725	1.5
0.3725	1.5	0.3770	1.5	0.3800	2.5
0.3760	2.0	0.3790	1.6	0.3830	3.0
0.3790	2.5	0.3830	2.9	0.3840	3.1
0.3820	3.0	0.3840	3.0	0.3860	4.0
0.3820	3.5	0.3840	3.1	0.3870	4.5
0.3840	4.0	0.3890	4.5	0.3880	4.6
0.3850	4.5	0.3910	4.6	0.3895	5.5
0.3865	5.05	0.3940	5.9	0.3910	6.0
0.3870	5.5	0.3950	6.0	0.3915	6.1
0.3880	6.0	0.3960	6.1	0.3930	7.0
0.3890	6.5	0.3970	7.4	0.3945	7.5 ←
0.3895	7.0	0.3970	7.5 ←	0.3930	7.6
0.3900	7.5 ←	0.3960	7.6	0.3940	7.95
0.3870	7.9	0.3950	7.8	0.3940	8.0
0.3840	8.5	0.3920	8.0	0.3960	9.0
0.3850	9.0	0.3930	9.0	0.3975	10.0
0.3860	9.5	0.3960	10.0	0.3980	10.5
0.3870	10.0	0.3970	10.5	0.3990	11.5
0.3880	10.5	0.3990	11.5	0.3995	12.0
0.3900	11.0	0.3990	12.0	0.3995	16.0
0.3910	11.5	0.3970	18.0		
0.3920	12.0				
0.3925	12.5				
0.3930	13.8				



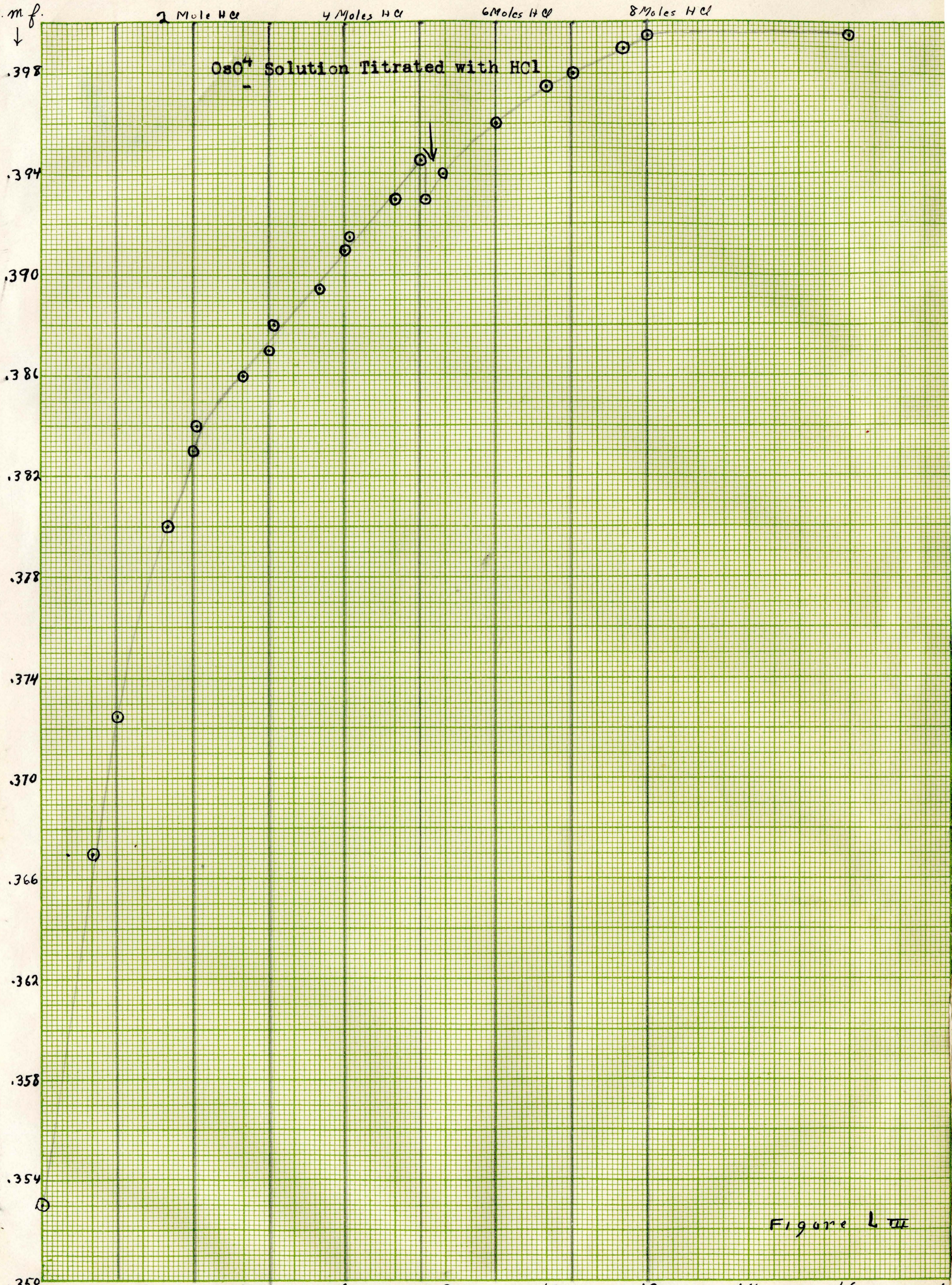
OsO⁴ Solution Titrated with HCl

TABLE L I



OsO^4 Solution Titrated with HCl

Figure L II



OsO$_4^-$ Solution Titrated with HCl

Figure LIII

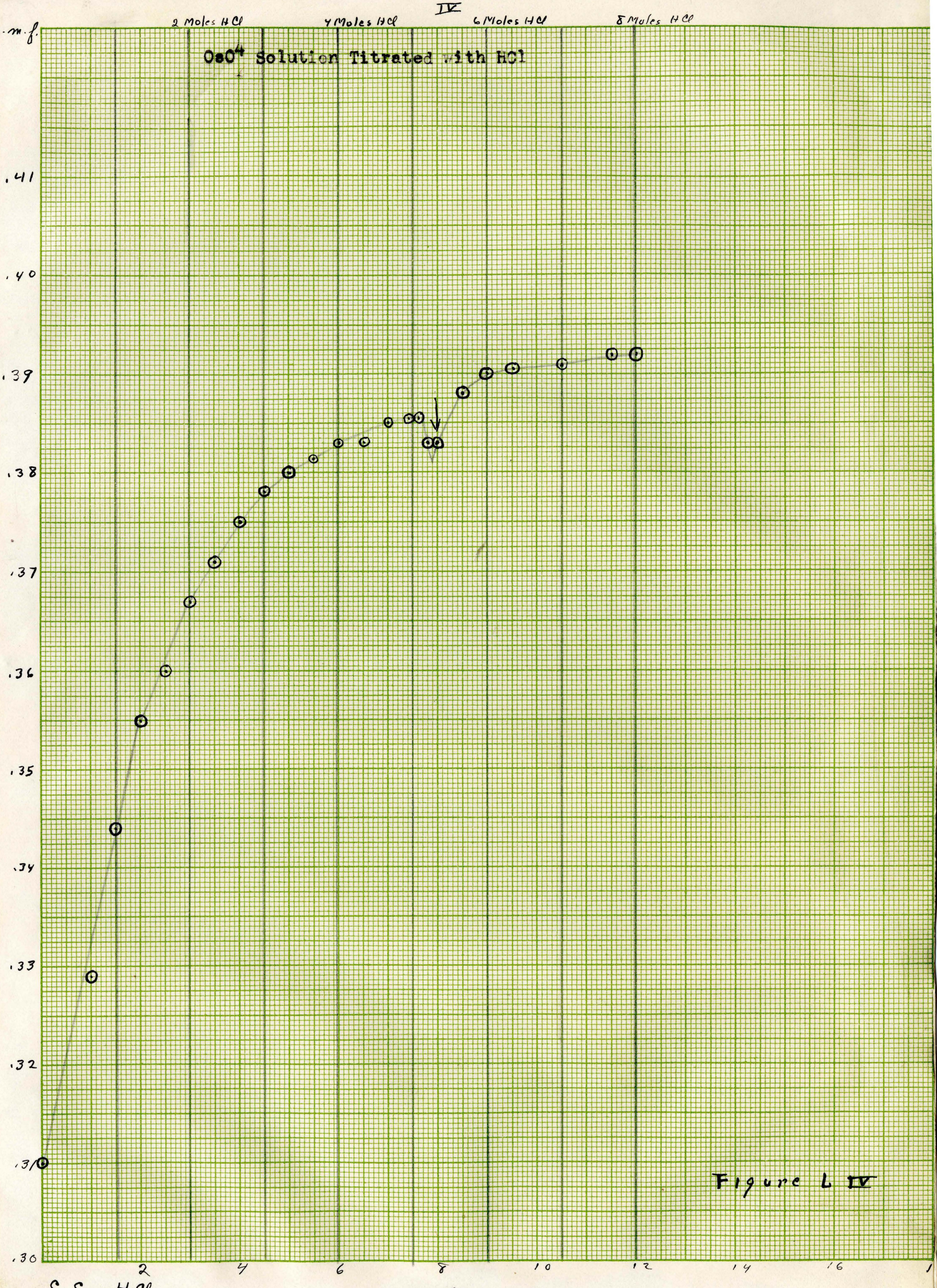
10 c.c. of OsO^4 solution

40 c.c. of water

Table 4

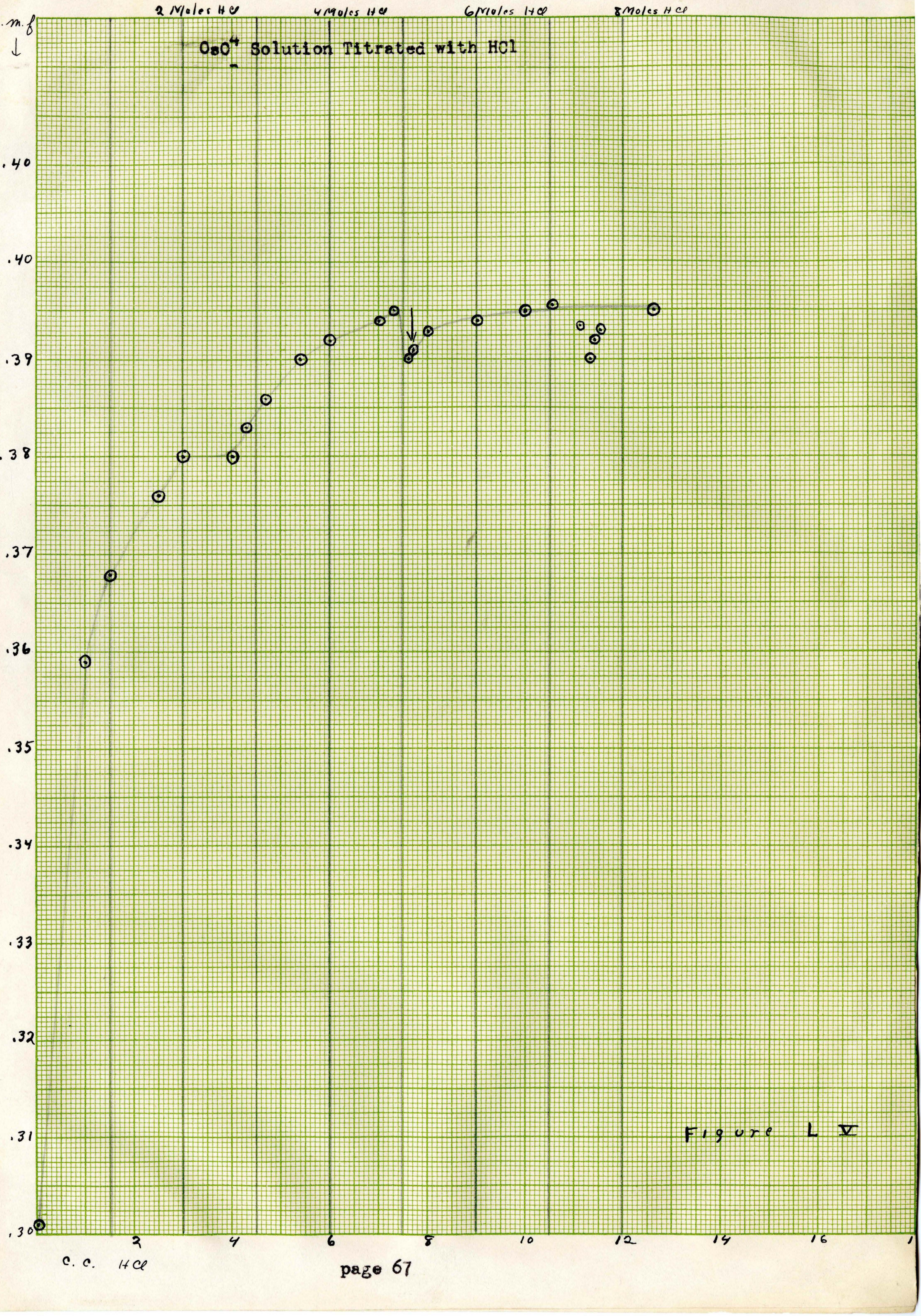
IV		V		VI	
e.m.f.	c.c. HCl	e.m.f.	c.c. HCl	e.m.f.	c.c. HCl
0.3100	0.0	0.3010	0.0	0.2700	0.0
0.3290	1.0	0.3590	1.0	0.3450	1.0
0.3440	1.5	0.3680	1.5	0.3590	1.4
0.3550	2.0	0.3760	2.5	0.3670	1.6
0.3600	2.5	0.3800	3.0	0.3710	2.2
0.3670	3.0	0.3800	4.0	0.3760	2.7
0.3710	3.5	0.3830	4.3	0.3820	3.0
0.3750	4.0	0.3860	4.7	0.3840	3.3
0.3780	4.5	0.3900	5.4	0.3870	3.9
0.3800	5.00	0.3920	6.0	0.3890	4.5
0.3815	5.5	0.3940	7.0	0.3910	4.9
0.3830	6.0	0.3950	7.3	0.3930	5.5
0.3830	6.5	0.3900	7.6 ←	0.3950	5.9
0.3850	7.0	0.3910	7.7	0.3960	6.4
0.3855	7.4	0.3930	8.0	0.3980	7.0
0.3855	7.55 ←	0.3940	9.0	0.3990	7.4
0.3860	7.6	0.3950	10.0	0.3970	7.7 ←
0.3830	7.8	0.3955	10.55	0.3970	7.8
0.3830	8.0	0.3935	11.1	0.3860	8.0
0.3880	8.5	0.3900	11.3	0.3990	8.2
0.3900	9.0	0.3920	11.4	0.4000	8.7
0.3905	9.5	0.3930	11.5	0.3985	9.0
0.3910	10.5	0.3950	12.6	0.3980	9.5
0.3920	11.5			0.3965	10.0
0.3920	12.0			0.3990	10.5
				0.4015	11.0
				0.4010	11.2
				0.4020	11.7
				0.4025	12.0
				0.4040	14.8

IV



OsO^4 Solution Titrated with HCl

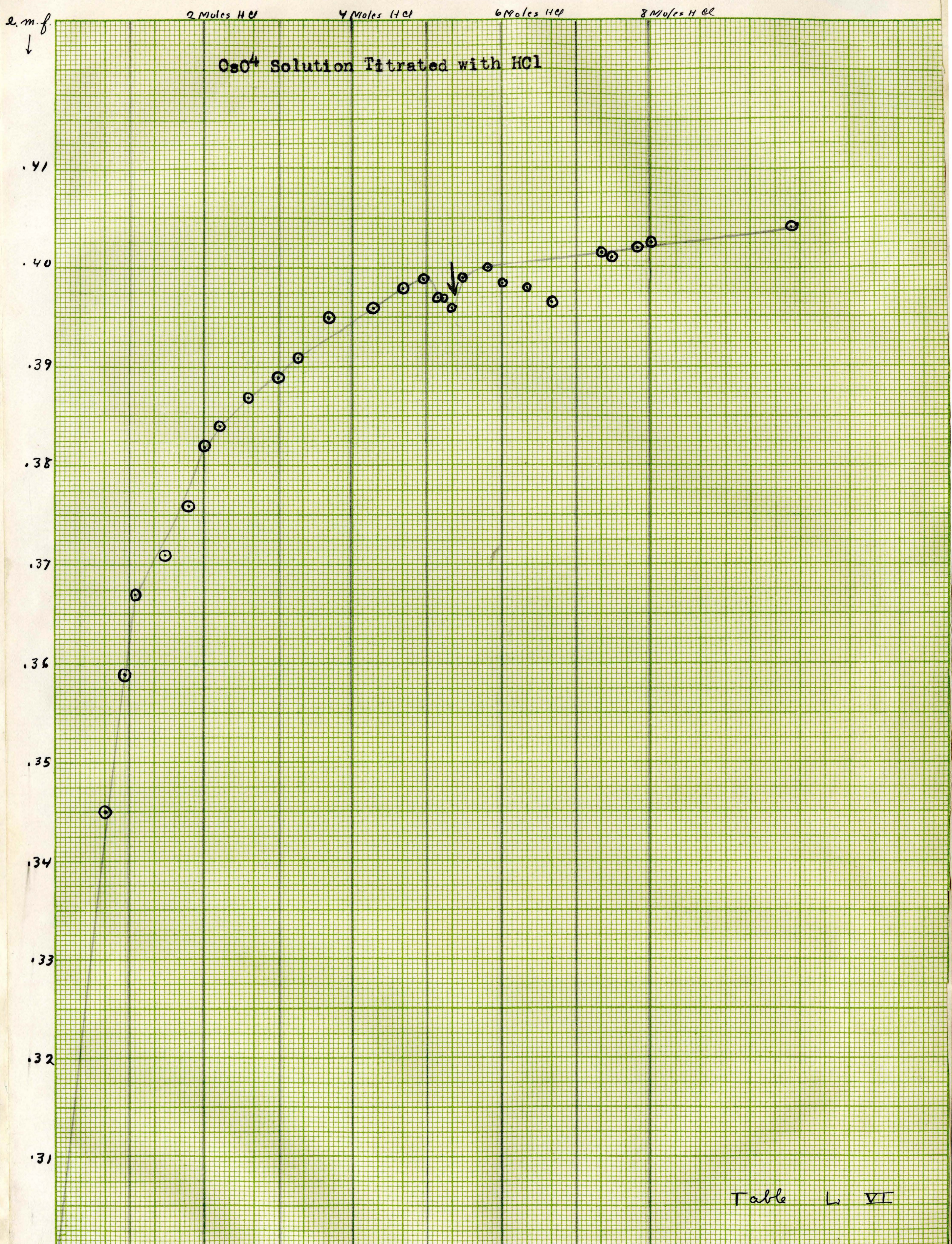
Figure L IV



OsO^4_- Solution Titrated with HCl

Figure L V

VI



OsO^4 Solution Titrated with HCl

2.7 ⊙

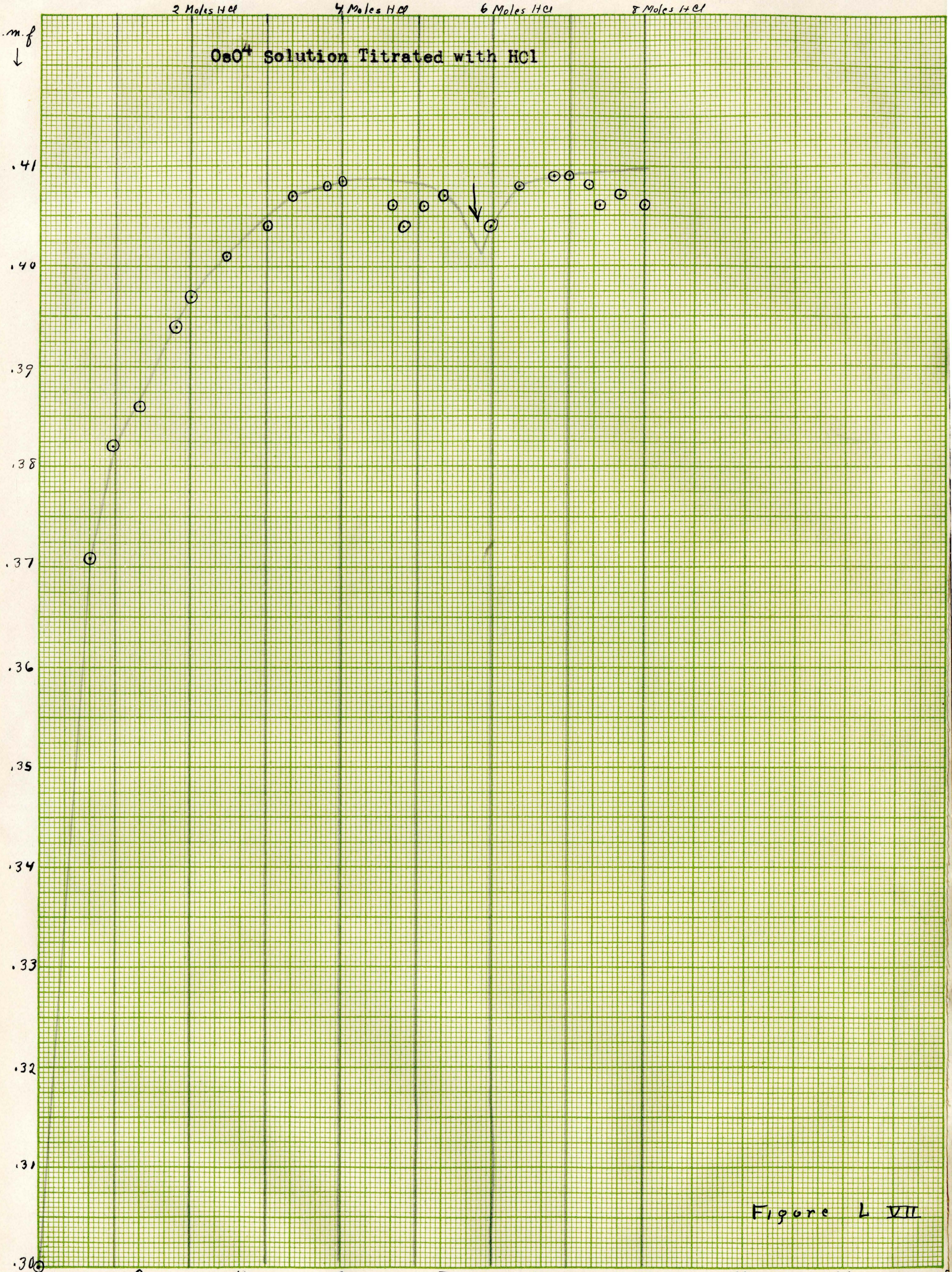
10 c.c. of OsO^4 solution

40 c.c. of water

Table 1

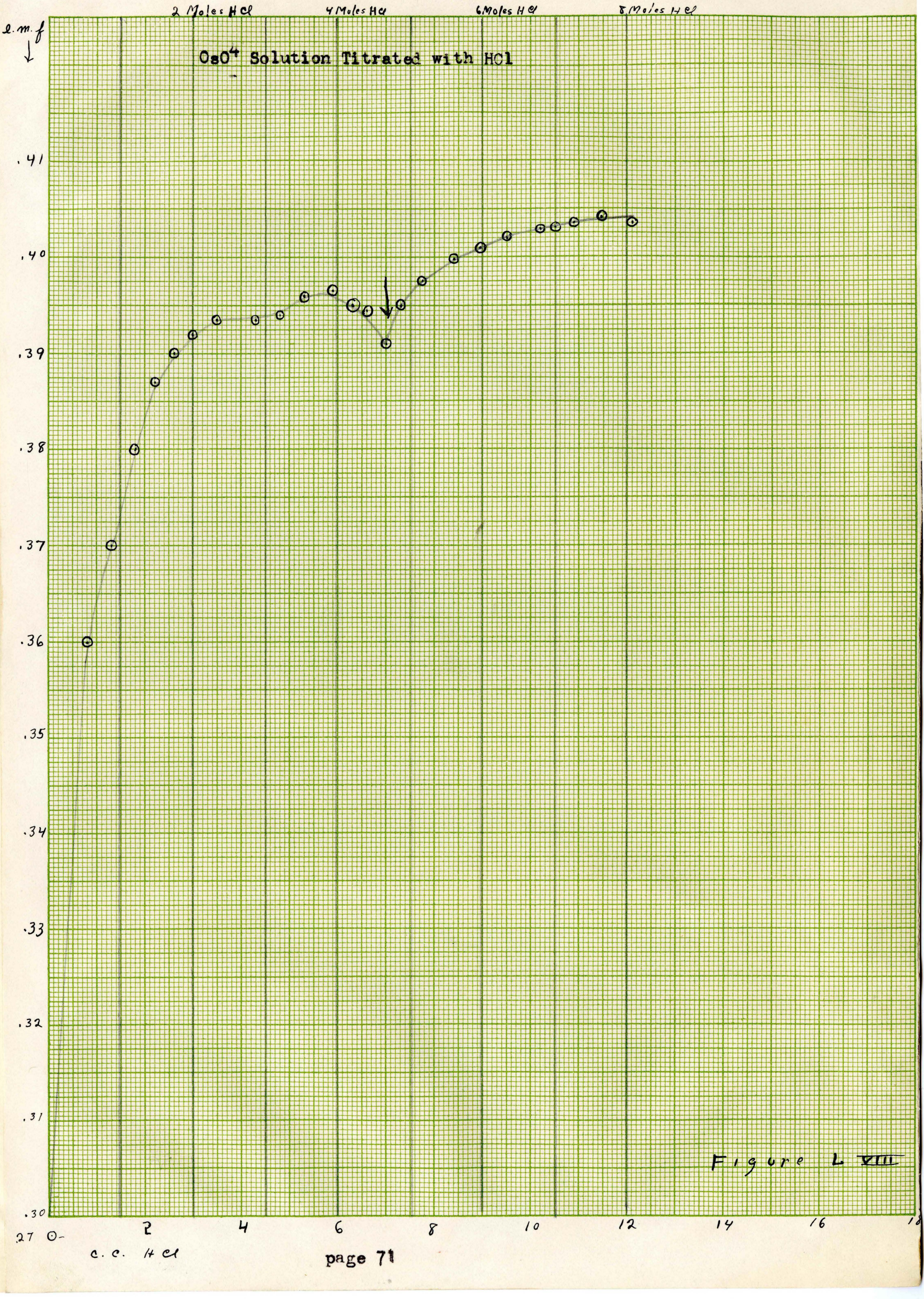
VII		VIII		VIIII	
e.m.f.	c.c. HCl	e.m.f.	c.c. HCl	e.m.f.	c.c.HCl
0.3000	0.0	0.2700	0.0	0.2400	0.0
0.3710	1.0	0.3600	0.8	0.3680	0.9
0.3820	1.45	0.3700	1.3	0.3790	1.3
0.3860	2.0	0.3800	1.8	0.3860	1.7
0.3940	2.7	0.3870	2.2	0.3920	2.4
0.3970	3.0	0.3900	2.6	0.3940	3.0
0.4010	3.7	0.3920	3.0	0.3980	3.8
0.4040	4.5	0.3935	3.5	0.3980	4.4
0.4070	5.0	0.3935	4.3	0.3965	4.8
0.4080	5.7	0.3940	4.8	0.3970	5.4
0.4085	6.0	0.3960	5.3	0.3970	6.1
0.4060	7.0	0.3965	5.9	0.3940	6.8
0.4040	7.2 ←	0.3950	6.3	0.3920	7.2 ←
0.4060	7.6	0.3945	6.6 ←	0.3940	7.4
0.4070	8.0	0.3910	7.0 ✓	0.3950	7.8
0.4040	8.95	0.3950	7.3	0.3965	8.4
0.4080	9.5	0.3980	7.75	0.3965	9.0
0.4090	10.2	0.3998	8.4	0.3975	10.0
0.4090	10.5	0.4010	8.95	0.3980	10.5
0.4080	10.9	0.4020	9.5	0.3995	11.0
0.4060	11.1	0.4030	10.2	0.4000	11.5
0.4070	11.5	0.4032	10.5	0.3995	12.05
0.4060	12.0	0.4035	10.9		
		0.4040	11.47		
		0.4035	12.1		

VII



OsO^4 Solution Titrated with HCl

Figure L VII



OsO^4 Solution Titrated with HCl

Figure L VIII

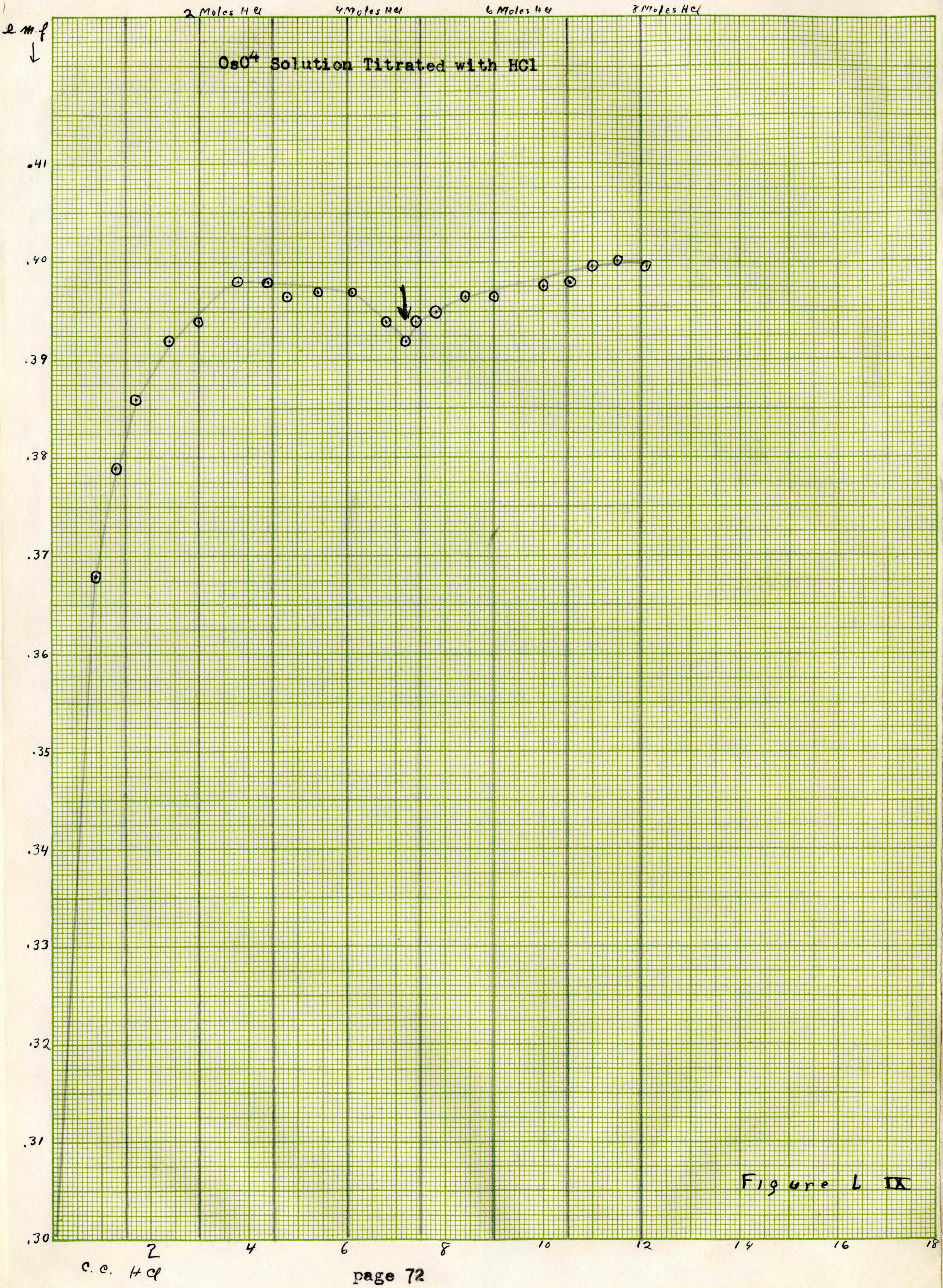

OsO^4 Solution Titrated with HCl
e.m.f
2 Moles HCl
4 Moles HCl
6 Moles HCl
8 Moles HCl
.41
.40
.39
.38
.37
.36
.35
.34
.33
.32
.31
.30
2
4
6
8
10
12
14
16
18
c.c. HCl

Figure L IX

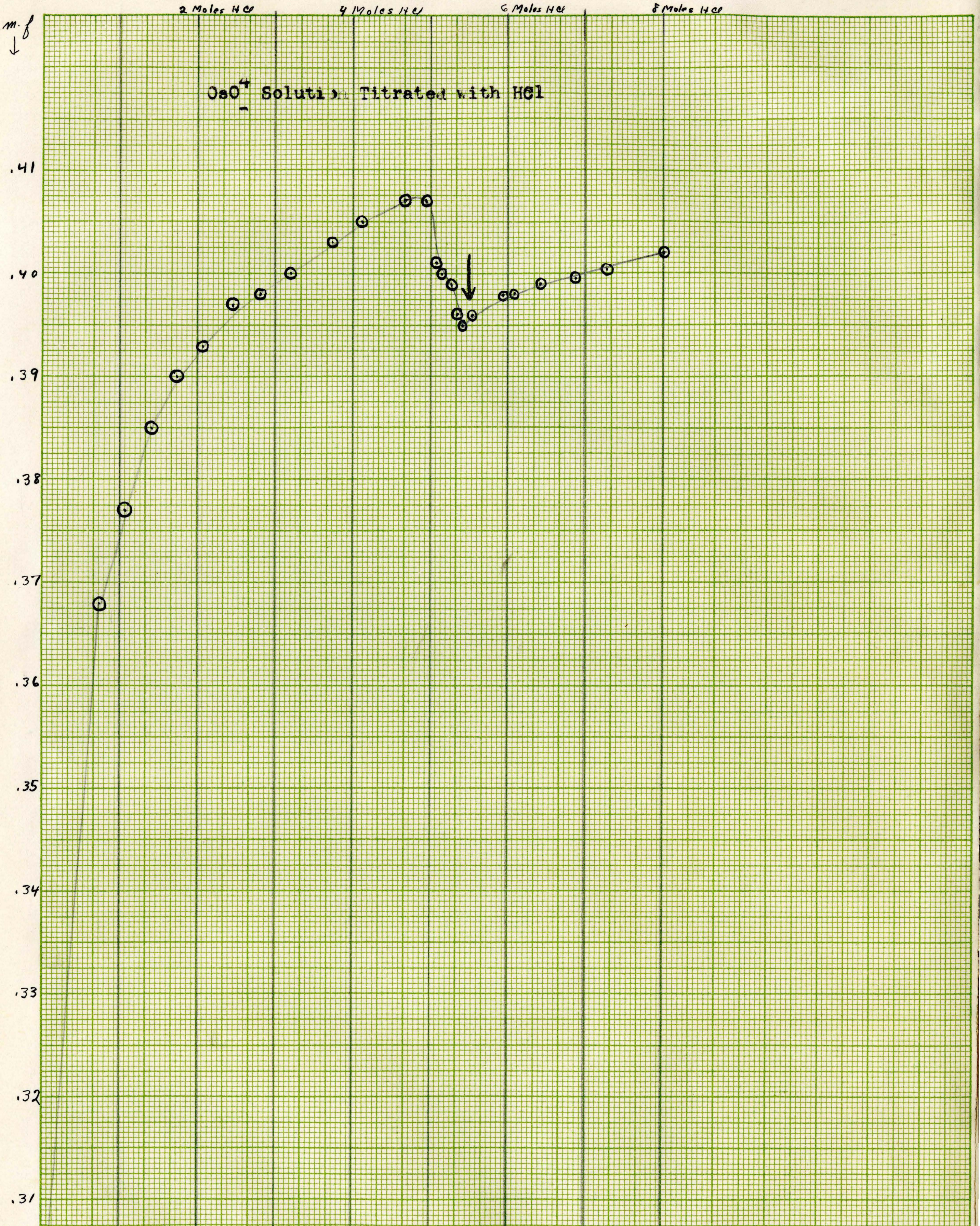
10 c.c. of OsO^4 solution

Table L

40 c.c. of water

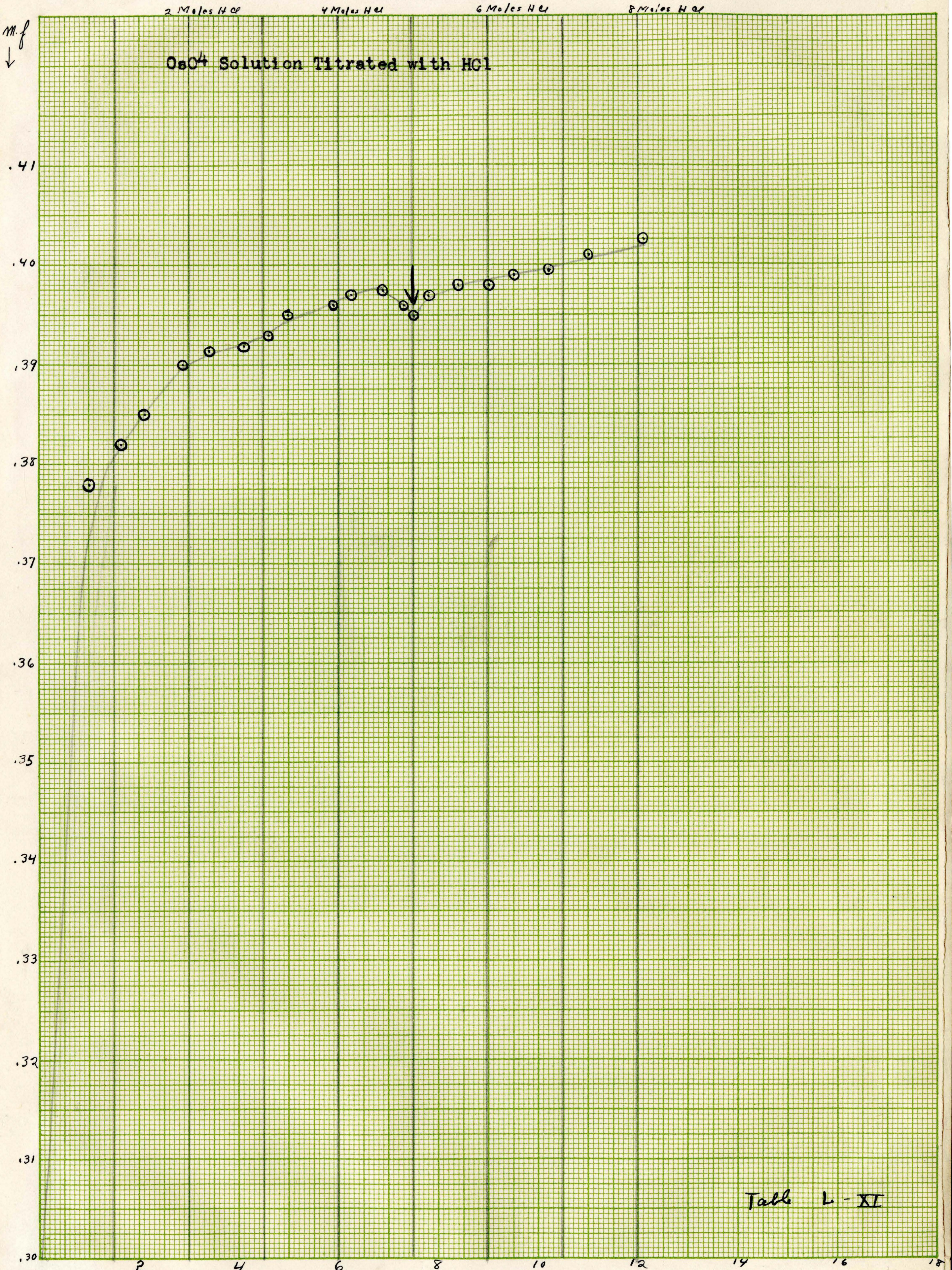
X		XI		XII	
e.m.f.	c.c. HCl	e.m.f.	c.c. HCl	e.m.f.	c.c. HCl
0.2 - 0.6	0.0	0.2050	0.0	0.3000	0.0
0.3780	1.0	0.3680	1.1	0.3605	1.0
0.3820	1.65	0.3770	1.6	0.3770	2.1
0.3850	2.1	0.3850	2.1	0.3820	2.6
0.3900	2.9	0.3900	2.6	0.3870	3.1
0.3915	3.4	0.3930	3.1	0.3900	4.0
0.3920	4.1	0.3970	3.7	0.3915	4.5
0.3930	4.6	0.3980	4.2	0.3920	5.5
0.3950	5 0	0.4000	4.8	0.3940	6.0
0.3960	5.9	0.4030	5.6	0.3960	7.2
0.3970	6.25	0.4050	6.2	0.3960	7.4
0.3975	6.9	0.4060	7.0	0.3970	7.5 ←
0.3960	7.3 ←	0.4070	7.4	0.3910	7.7
0.3950	7.5	0.4010	7.6 ←	0.3910	7.9
0.3970	7.7	0.4000	7.7	0.3960	8.6
0.3980	8.4	0.3990	7.9	0.3980	9.3
0.3980	9.0	0.3960	8.0	0.3990	10.2
0.3990	9.55	0.3950	8.1	0.4015	11.3
0.3995	10.2	0.3970	8.3	0.4030	12.0
0.4010	11.0	0.3980	8.9		
0.4025	12.1	0.3980	9.1		
		0.3990	9.6		
		0.3995	10.3		
		0.4005	10.9		
		0.4020	12.0		

IV

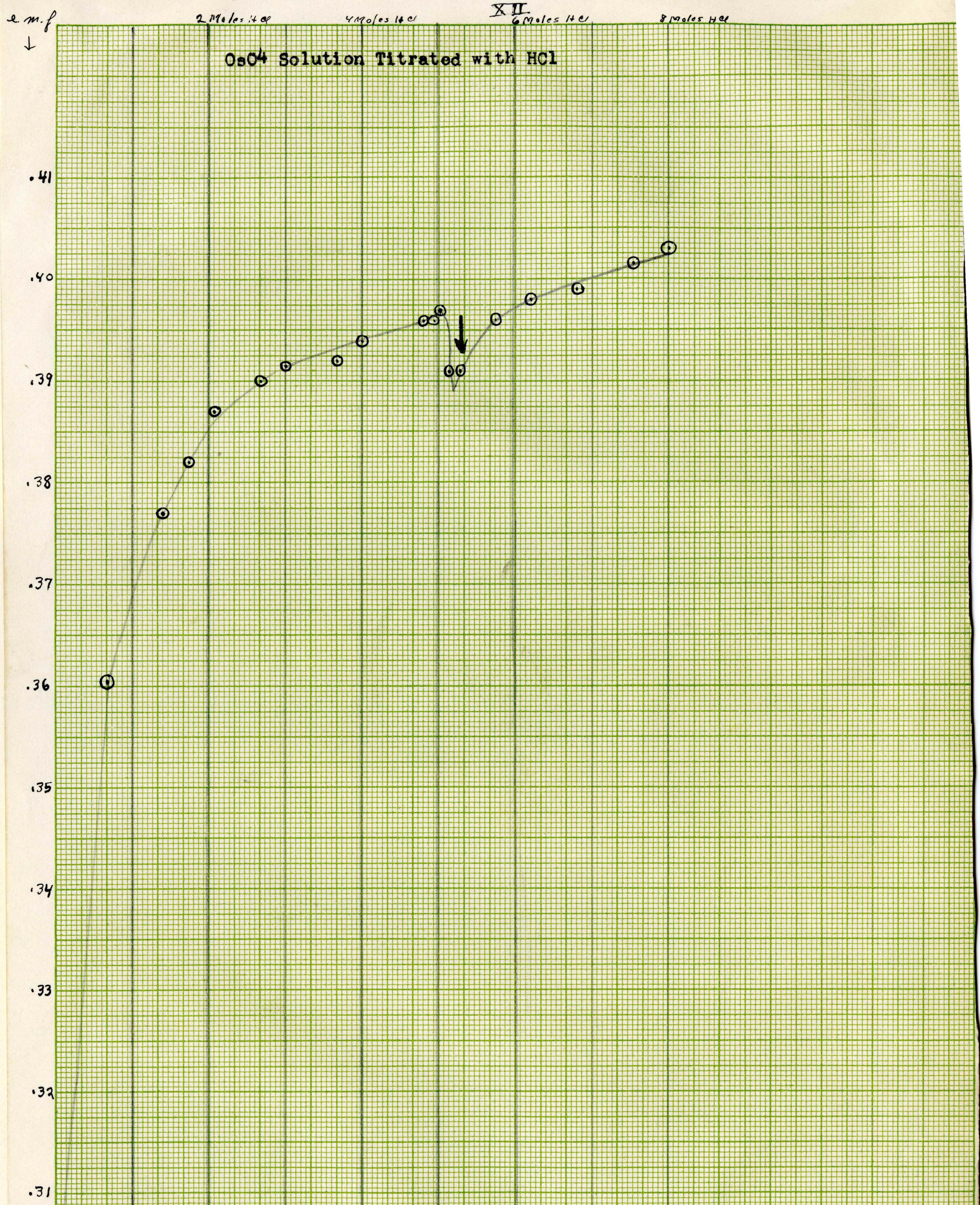


OsO^{4}_{-} Solution Titrated with HCl

XI



OsO^4 Solution Titrated with HCl



OsO^4 Solution Titrated with HCl

Because osmium tetroxide resembles ruthenium tetroxide, it was thought that it would give a curve similiar to the one obtained for the latter. The osmium tetroxide, which was obtained from J. T. Baker Co., came in a glass capsule. After scratching it with a file it was weighed. Breaking the capsule in two the contents were emptied into 250 ml. of water. In order to know the amount of osmium tetroxide in the solution the empty capsule was weighed again. The difference in the two weights gave the amount added to the water.

Wgt. of capsule with osmium tetroxide	6.15955
Wgt. of capsule	5.23003
Wgt. of the osmium tetroxide	0.92592

The molarity of the solution is 0.0146

Summary

The initial voltages when no HCl was present in the solution varied as the following table will show.

Experiment	Voltage at which galvanometer is not deflected
I	0.3560
II	0.3550
III	0.3530
IV	0.3100
V	0.3010
VI	0.2700
VII	0.3000
VIII	0.2700
IX	0.2400
X	0.2 - 0.6
XI	0.2050
XII	0.3000

The point at which the minimum occurred is when the solution contains five molecules of HCl to one of osmium tetroxide. The potential is almost constant at this place. The drop in potential averages about 0.004 volts. The tables as follows will explain this:

Experiment	Voltage of the minimum	Change of potential
I	0.3840	0.0060
II	0.3950	0.0010
III	0.3930	0.0015
IV	0.3830	0.0025
V	0.3900	0.0050
VI	0.3960	0.0030
VII	0.4040	0.0045
VIII	0.3910	0.0035
IX	0.3920	0.0050
X	0.3950	0.0025
XI	0.3950	0.0060
XII	0.3910	0.0050
Average	0.3985	0.0035

As soon as HCl is added the voltage becomes constant.

Conclusions

When ruthenium tetroxide is titrated with HCl a minimum occurs at the point where equal number of HCl and ruthenium tetroxide molecules are present in the solution. The average drop in potential at this point is 0.006 volts. In two cases it was as much as 0.03 volts. The minimum does not always occur at the same potential but between the range of 0.7900- 0.8740 volts. The average potential at which the minimum occurred was 0.845 volts.

It seems the drop of potential depends on the concentration of the ruthenium tetroxide solution. The following table will show it:

Series	The point where there are equal number of HCl and RuO^4 mol.	Molarity of the RuO^4 solution.
I	no minimum	0.0130
II	weak minimum	0.0270
III	weak minimum	0.02888
IV	sharp minimum	0.03506
V	sharp minimum	0.05565

Time plays an important part in the potential. For a period of 15 minutes the average rise in potential for one minute was 0.002 volts. The increase in potential during the first minute was 0.015 volts.

If chlorine is present in the solution, a maximum is obtained at the same point where a minimum occurs. The voltage at which this maximum occurs is almost constant. The voltage in three determinations and with two different solutions were as follows:

Voltage at which the maximum occurred.	Molarity of the solution.
1.078	0.03506
1.053	0.03506
1.066	0.05565

McConnell's conclusion (18), that a break in the potential occurred at the point where equal HCl and ruthenium tetroxide molecules are present in the solution. is confirmed but it is not a maximum unless chlorine is present. If no chlorine is present, it is a minimum.

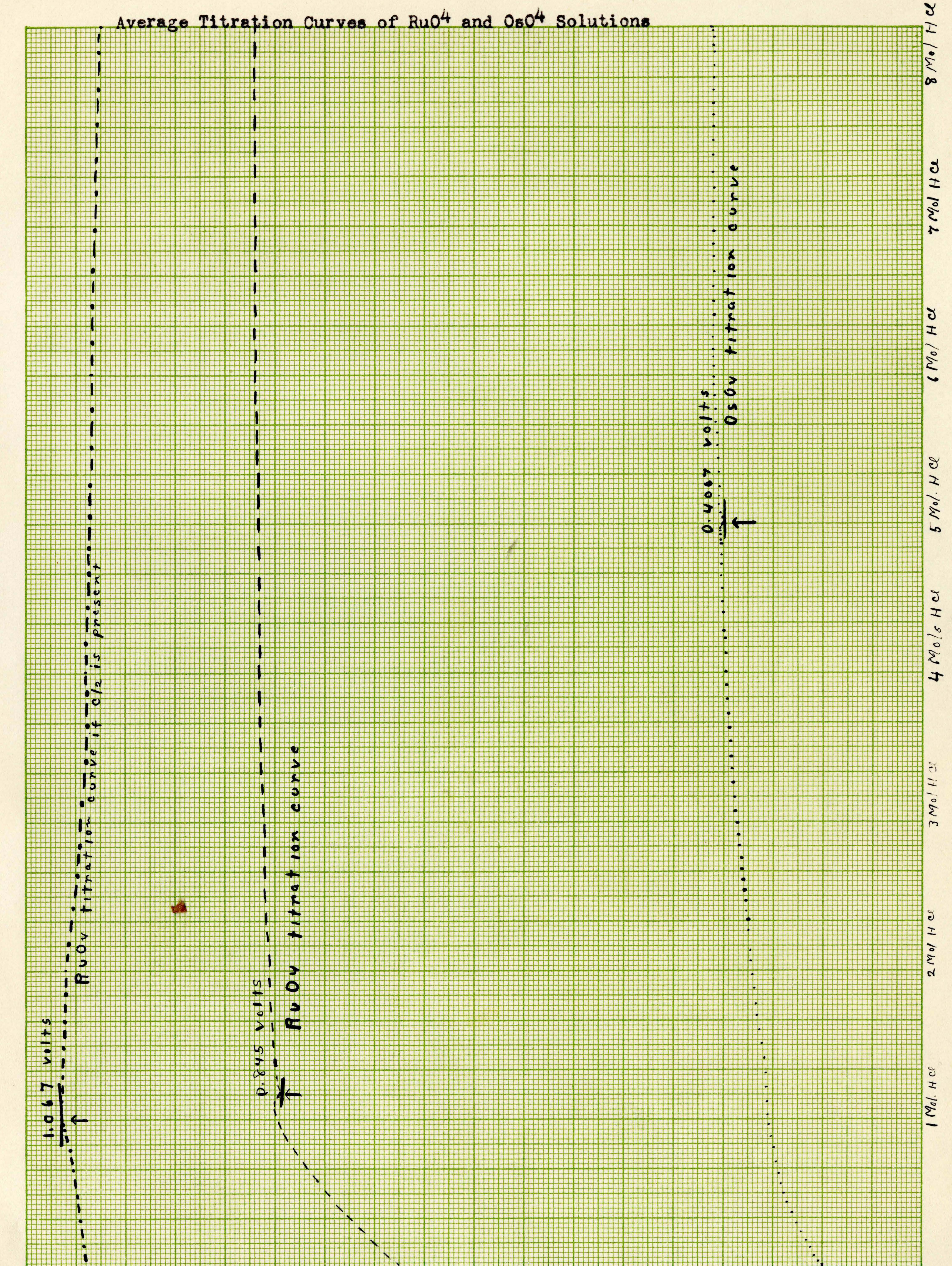
Conclusions

The titration curve for osmium tetroxide is similiar to the one obtained for ruthenium tetroxide because there is a minimum on each curve and the potential increases with each addition of HCl. The differences between the two curves are as follows:

Curve	Point where minimum is observed	Decrease in potential (average)	Average voltage of the minimum
Ruthenium tetroxide	1 HCl to 1 RuO^4	0.006	0.8450
Osmium tetroxide	5 HCl to 1 OsO^4	0.004	0.3985

Another point of interest is the fact that the voltage of the osmium tetroxide solution varied between rather large limits. This may be due to the oxidizing action of osmium tetroxide on the faint traces of impurties present in the water. It seems that if chemically pure water was used there ought to be no voltage detected. In each curve, no matter what the initial voltage was, for any definite amount of HCl added to the solution the potential was almost the same. The following graph will clearly point out the similiarities and differences. Each curve represents an average curve.

Average Titration Curves of RuO^4 and OsO^4 Solutions



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Prof. James Lewis Howe
Washington & Lee University
Lexington, Virginia

Dear Dr. Howe:

I had hoped to have an opportunity to write a letter to you at an earlier date to thank you for the reprints of Rinne's work and to say that I was returning Brady's thesis.

I am enclosing a short note which Prof. Young has written concerning his opinion on my work, which I asked him to examine. It seems quite probable that Brady is right in assuming that the maxima are due to the presence of free clorin with the ruthenium tetroxide as I do not recall making any attempt to remove the clorin from the distillate. It appears somewhat questionable from Brady's curves whether they are strictly reproducible.

Hope that I shall have the pleasure of seeing both you and Mrs, Howe in Chicago this summer.

Sincerely yours,

Duncan McConnell

Duncan McConnell

5213 Kenwood Avenue
Chicago, Illinois
24 May 1934.

July 11, 1933

Mr. Duncan McConnell,
5213 Kenwood Ave.,
Chicago, Ill.

Dear Mr. McConnell;

I am sorry I kept your thesis so long. I ~~was~~ was away during the spring quarter. I have been expecting you to drop in but perhaps you have done so and found me away.

Your report indicates an elaborate study and considerable work; seemingly a very creditable thesis. I have not, however, found anything which seems to be a contribution to the literature of the subject. At present, Potential-titration curves tell us very little when they exhibit maxima. It now seems that they never will, for if our present ideas are even approximately correct, such curves are not strictly reproducible.

If you wish to talk with me again, please do not hesitate to do so.

Sincerely,

T. F. Young.

Assoc. Prof. Chem.
Univ. Chicago.