

1927

Reduction by hydrogen

R. B. Waite

Iowa State College

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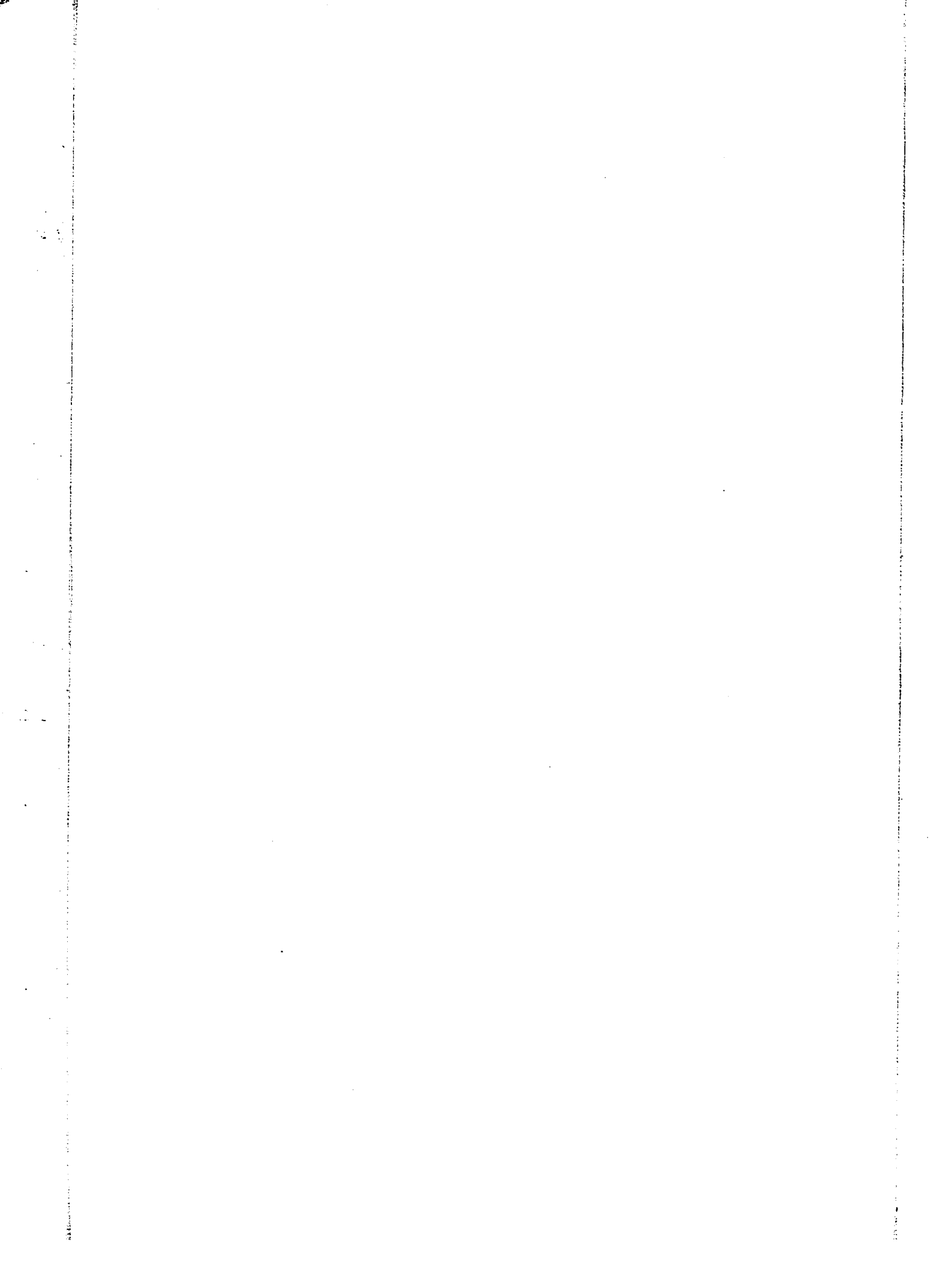
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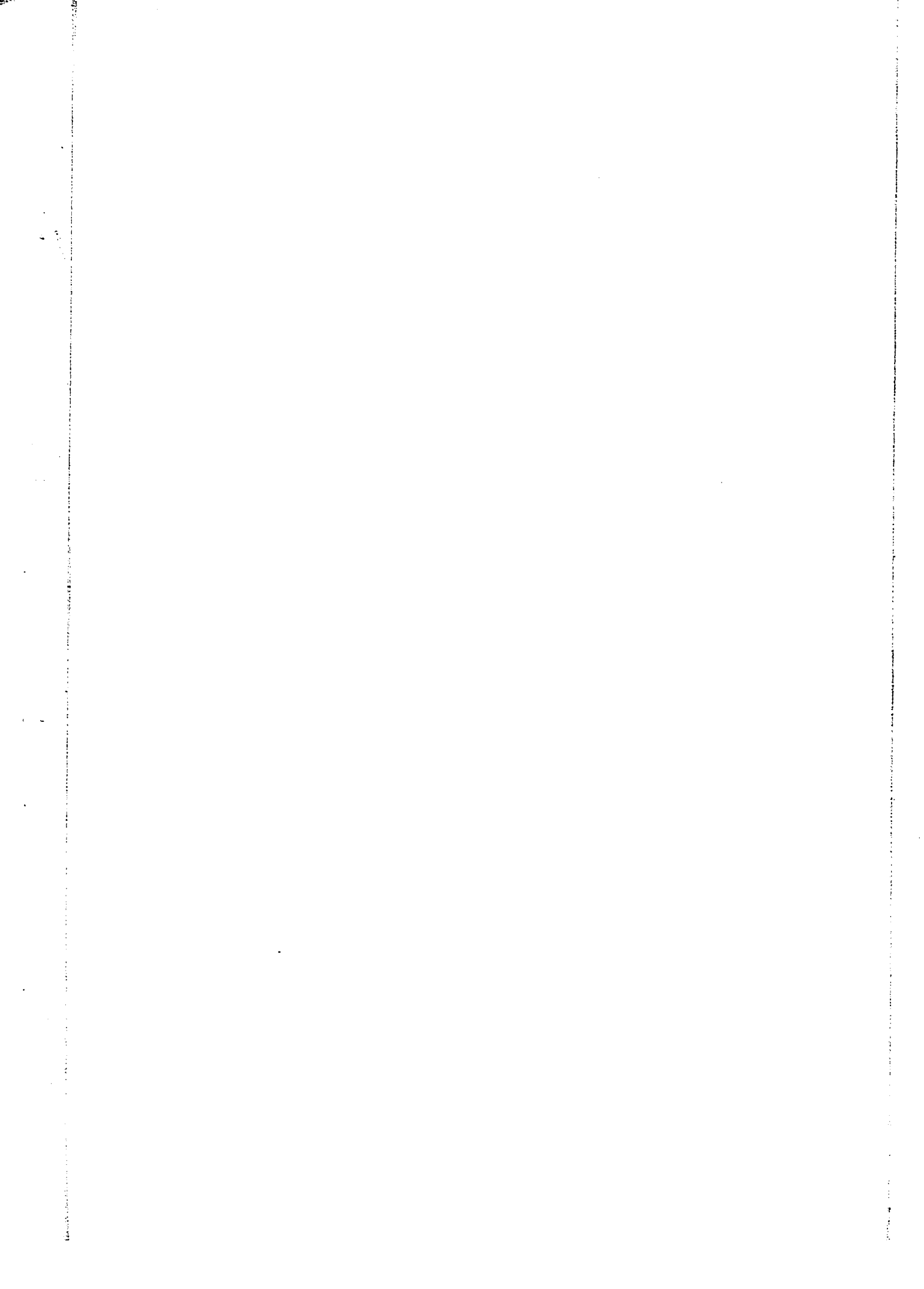
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REDUCTION BY HYDROGEN

BY

R. B. WAITE

A Thesis Submitted To The Graduate Faculty
For The Degree Of

DOCTOR OF PHILOSOPHY

Major Subject Inorganic Chemistry

Approved

Signature was redacted for privacy.

In charge of Major work.

Signature was redacted for privacy.

Head of Major Department.

Signature was redacted for privacy.

Dean of Graduate College.

Iowa State College

1927

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INTRODUCTION

It is apparent that the subject covered by the title of this thesis is extremely general, covering as it does all reactions in which hydrogen is involved. Many of these have already been investigated and some of them have become of great commercial importance. Among the latter might be mentioned the preparation of ammonia in which nitrogen, derived from the air by liquifaction and hydrogen, obtained usually by electrolysis, are made to combine directly by the Haber process; the hydrogenation of oils, in which liquid unsaturated animal and vegetable oils are treated with hydrogen to convert them into saturated compounds which have higher melting points and are therefore more desirable for household and commercial purposes; the formation of catalysts by the reduction of metal oxides by hydrogen; the recent synthetic preparation of methanol by the direct reaction of hydrogen and carbon monoxide; the manufacture of synthetic organic compounds; and many other things.

Since, as indicated, the field is so broad this work cannot, of course, be comprehensive and must select some particular phase for a special study. The phase that we are interested in and the one whose consideration led to the beginning of this work is the effect which variations of pressure have upon some of the reactions of hydrogen.

It has long been known that in many cases the results

obtained in chemical reactions are greatly affected by the pressure at which the reactions take place, but the field has not been explored as thoroughly as its importance would seem to justify.

The work done shows that some reactions that were previously considered impossible will take place under the influence of pressure and that others, which at atmospheric pressure go too slow to ever be of any use, can be speeded up by the use of pressure to where they become important both scientifically and industrially.

Of the latter there are a number which are well known. Among these are the manufacture of ammonia mentioned above; the cracking of petroleum oils; the contact process for making sulphuric acid and many others. The pressure effect in each of these industries has been worked out as an individual problem and more or less empirically in most cases. The effect of pressure on chemical reactions as a field for systematic scientific research is just beginning to be appreciated.

In view of these facts the work which is to be described here was taken up in the hope that something could be added to the present knowledge of the effect of pressure upon the reducing action of hydrogen.

REVIEW AND DISCUSSION OF THE LITERATURE

EARLY WORK:- The first known attempt to study the

effect of pressure on a chemical reaction was made by C. Babbage in 1813 (15). He drilled a hole thirty inches deep and six inches wide in limestone, put in an acid and plugged up the hole. No conclusions were drawn. In 1859 M. N. BeMetoff (2) reports that Babinet (no reference) had already proven that the liberation of hydrogen by metals could be stopped by pressure. He himself finds that hydrogen under pressure will precipitate silver from silver nitrate but not from silver sulphate, but says that Ozann (no reference) reports that hydrogen from an electrical cell will separate silver from silver sulphate. His method was to use a bent glass tube with the salt solution in one arm and zinc and hydrochloric acid in the other. Mellor (15) quotes him as saying in 1864 (no reference) that, if salts like zinc sulphate, copper sulphate and silver sulphate be exposed to hydrogen under great pressure--up to 7100 atmospheres--the metal is precipitated.

Cailletet (3) says that the reaction of sodium amalgam on water in a closed glass tube with manometer slows up and finally stops. Also that pressure causes the action between hydrochloric acid and zinc to cease. Ipatiev (12) reports to have precipitated nickel, cobalt, lead etc., from solutions of their salts in this manner.

Nernst and Tammen (17) tested the effect of pressure on the action of acids on a large number of metals by sealing them

up in glass tubes with a manometer and found that in most cases the reaction slowed up and seemed to stop after a time.

LATER WORK:- The most of the later work on pressure can be divided into five classes as follows:

1. Research upon the effect of pressure on the reactions of a single industry as those on the preparation of ammonia already mentioned.

11. Investigations of the effect of pressure upon physical phenomena such as melting point, solubility, transition points, conductivity etc. In this field there has been a great deal of very careful and systematic work done. Among the leaders should be mentioned Bridgeman, McKey, Cohen and MacInnis and their collaborators.

111. Determination of the effect of pressure on the E. M. F. of galvanic cells.

Lewis and Randal (13), Loomis and Acree (14) and Elles (9) have all studied the effect of pressure on the change of the potential of the hydrogen electrode and all have found it to agree with the equation

$$E = \frac{RT}{2F} \ln \frac{P_2}{P_1}$$

where E is the change in E. M. F. of the cell pro-

duced by changing the pressure from one atmosphere to p atmospheres.

Tammen and Dickman (20) measured changes of potential of 0.1 N hydrogen electrode for pressures up to 3000 Kg. per sq. Cm. The potentials nearly coincided with those calculated on the assumption that hydrogen is a perfect gas. If corrections for the deviation are made the values calculated are too high.

Ernst Cohen and L. R. Sinnige (7) have investigated the effect of pressure on the cell cadmium/cadmium sulphate/12.5% cadmium amalgam up to 1000 atmospheres. They found that the change of E. M. F. per atmosphere of pressure change was 0.0000196 V (one place gives 0.0000196); that the volume change in passing 1 F through this cell is -1.656 C. C.; and that the change of E. M. F. with pressure agrees with the equation

$$E_{\pi} - E_0 = \pi(V_1 - V_2)$$

for this and also for the Clark cells.

G. Timofiev (21) made the same measurement for several cells and found that the change, which was never more than three milli volts, agreed with the

same equation.

Hainsworth and MacInnis (10) measured the effect of pressure on the E. M. F. of the hydrogen calomel cell up to 400 atmospheres and found the change to agree with the Nernst equation

$$E = \frac{RT}{2F} \ln p$$

where E is the change in E. M. F. of the cell produced by changing pressure from 1 to p atmospheres and also with the equation of Keyes'

$$p = \frac{RT}{V-\delta} - \frac{A}{(V-1)^2}$$

in which $\delta = Be^{-a/V}$ and a, B, A and l are characteristic constants. For hydrogen when V = cc/g, a = 2.898; B = 9.619, A = 3.91×10^4 , l = 1.18 and R = 40.72 except that above 100 atmospheres there was a slight deviation thought to be due to the solubility of hydrogen.

Hainsworth, Rowley and MacInnis (11) carried the above work to 1000 atmospheres. At the higher pressures the deviation was found to be much greater than previously noted; most of this deviation was attributed

to the deviation of hydrogen from the perfect gas laws and the rest to the effect of the solubility of hydrogen on the activity of the hydrogen ion.

IV. Determination of equilibrium constants and reaction velocities.

Several studies have been made of the effect of pressure upon equilibrium constants and reaction velocities.

Cohen and de Boer (5) have studied the effect of pressure on the speed of inversion of cane sugar by hydrochloric acid from 1 to 1500 atmospheres. The speed of the reaction was reduced 8% by 500 atmospheres, 19% by 1000 atmospheres and 26% by 1500 atmospheres. At constant acid concentration and constant sugar concentration the pressure influence may be expressed by

$$\frac{d \ln k}{d p} = \text{Constant}$$

or by the linear equation

$$K_p = a + bp$$

($a = 234$, $b = -0.0486$) with equal accuracy.

Cohen and Kaiser (6) studied the effect of pressure on the esterification velocity of 0.01 N ethyl acetate by 0.01 N sodium hydroxide at 2.40° between 1 and 1500 atmospheres. They found that the influence of pressure on the velocity of the reaction could be as well described by the linear equation given above as by the van't Hoff equation

$$\frac{d. l. k.}{dp} = \text{Constant}$$

in which K is the reaction velocity, a is the percent increase in concentration due to compressibility, p is the pressure, l is the reciprocal of the measured resistance of a 0.01 N sodium hydroxide, or sodium acetate solution.

Cohen and Valetton (8) extended the above work of Cohen and de Boer using acetic acid as a catalyst. The results show that the velocity coefficients increase with pressure but that the rate is much smaller above 1000 atmospheres. When corrections are made for compressibility it is found that velocity is independent of pressure above 1000 atmospheres.

Cohen (4) in his George Fisher Baker Non-Resident Lectureship in Chemistry at Cornell University,

discussed the above experiments. He concludes that pressure has a great influence in reaction velocities; that this effect may be positive or negative and that it is linear. He makes no use of any of the above equations.

Armstrong and Hildetch (1) found that the rate of hydrogenation of certain organic compounds in the presence of 0.1% nickel is proportional to the hydrogen pressure. This is said to indicate the reaction with molecular hydrogen and not atomic hydrogen as in this case the rate should vary as the square root of the concentration of hydrogen. For other substances the rate is less than proportional to the hydrogen concentration, indicating a reaction with the catalyst.

Williams (22) checks the equation of Plank for the variation of the equilibrium constant of a reaction with pressure

$$\frac{\partial \log K}{\partial P} = \frac{V_1 - V_2}{RT}$$

where K is calculated for concentrations which are mol fractions of the total number of molecules present including the solvent.

Rice (19) obtained a similar expression but K referred to the volume, (reported by Williams (22)).

Moesveld (16) studied the effect of pressure on the reactions, $5\text{HBr} + \text{HBrO}_3 = 3\text{Br}_2 + 3\text{H}_2\text{O}$ and the saponification of the ethyl ester of methylcinnamic acid. His conclusions were similar to those of Cohen.

Parravano and Malquori (18) studied the equilibrium conditions for the reduction of halides by hydrogen. They concluded that the reactions are reversible and come to a characteristic state of equilibrium at any temperature and pressure. The equilibrium condition is expressed by

$$\frac{\log Q}{RT} + \log p + \log K = C$$

where Q is the thermal exchange of the reaction, p is the pressure, K is the mass law constant, C is the equilibrium constant. (Taken from C.A. 20 2109).

V. Investigations which have sought mainly to obtain experimental data on the general effect of pressure on the progress and results of chemical reactions.

In these, several types of chemical reactions have been studied, including mainly: organic oxidation and reduction; reduction of solid metal oxides; reduction of solid metal halides; and precipitation

of metals from solution of their salts by hydrogen. It is the last of these groups that is of direct interest to the present work.

Nearly all of the recent work along this line has been done by the Russian Chemist, Ipatiev. In order that the results so far obtained may be more briefly presented and more readily examined, they are given in table form in Tables I to V inclusive.

An examination of the data given in these tables brings out the fact that, while there have been a large number of experiments performed and some interesting and valuable data obtained, there has in no case been any systematic study of the effect of varying temperatures and pressures upon precipitation from any one solution. Hence there is little opportunity of using these results in predictions for the future.

There is, however, one thing of importance shown by the experimental data published. That is, that they do not agree either among themselves or with the generally accepted theories.

As noted previously Lewis and Randal (13), as well as several others, have shown that the change of E. M. F. of the hydrogen electrode with pressure

TABLE 1

Salt	Conc.	Temp. in °C	P in Atms	Time	Products	Ref.
Hg NO ₃	Sat	160	130		Yel. Cryst. 2HgO, N ₂ O ₅ , H ₂ O and Hg visible under microscope.	12C
Hg NO ₃	Sat	225	130		Hg only	12C
Hg(NO ₃) ₂		100	120		Cryst. as above and HgO.	12C
Hg(NO ₃) ₂		240- 250	120?		Hg and HgO	12C
Cd(NO ₃) ₂	2N	220	195		White needles of Cd- (NO ₃) ₂ , CdO, 2H ₂ O	12C
Cd(NO ₃) ₂	2N	250- 260	195?		Similar to above and cryst. of Cd.	12C
Cd SO ₄	2N	220	250		CdSO ₄ , H ₂ O and some Cd.	12C
Cd SO ₄	2N	270- 285	250		CdS	12C
Zn(NO ₃) ₂	2N	290	140		Basic salt.	12C
Zn(NO ₃) ₂	2N	320- 330	140		ZnO	12C
Zn(NO ₃) ₂	2N	350	360- 380		Similar and micro. crys. of Zn.	12C
Zn SO ₄	2N	290	250		ZnS	12C
Mg(NO ₃) ₂	2N	340	230		MgO	12C
Mg SO ₄	2N	340	340		Basic sol. of MgS.	12C
HNO ₃	2N	370	300		NH ₃ Completely.	12C
H ₂ SO ₄		350	238		H ₂ S almost completely	12C

TABLE 11

Salt	Conc.	Temp. in °C	P in Atms	Time	Products	Ref.
ZnO	*	380	320		Not reduced	12D
Co SO ₄	2N	103	100	24hr	No precipitates	12D
Co SO ₄	0.2N	103	100	24hr	No precipitates	12D
Co SO ₄	2N	145- 150	100?	24hr	Co and CoSO ₄ , H ₂ O	12D
Co SO ₄	0.2N	145- 150	100?	24hr	Co and CoSO ₄ , H ₂ O	12D
Co (NO ₃) ₂	2N	150	100	24hr	No precipitate	12D
Co (NO ₃) ₂	0.2N	150	100	24hr	No precipitate	12D
Co (NO ₃) ₂	1N	205- 210	100	24hr	Co ₂ O ₃	12D
Co (NO ₃) ₂	0.2N	205- 210	100	24hr	Co ₂ O ₃	12D
Co (NO ₃) ₂	1N				Co ₂ O ₃ and a little Co.	12D

* Freshly precipitated in the presence of H₂O

TABLE 111

Salt	Conc.	Temp. in °C	P in Atms	Time	Products	Ref.
Nitric protoxide of mercury	Sat	160	100	13hr	Bright yellow crystals of $2\text{Hg}_2\text{O}$, N_2O_5 , H_2O & some Hg	12D
	Sat	225	90		Hg completely	12D
$\text{Cd}(\text{NO}_3)_2$	2N	180	110	7hr	No reaction	12D
$\text{Cd}(\text{NO}_3)_2$	2N	220	135		Crystals formed Compound not sure 89.95% CdO , 10.07% NO_3	12D
$\text{Cd}(\text{NO}_3)_2$	2N	270	220	10hrs	Cryst. as above and Cd.	12D
Cd SO_4	2N	260-280	250	6-8hr	Cd-trace and some $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ cryst.	12D
Cd SO_4	2N	270-290			CdS	12D
$\text{Zn}(\text{NO}_3)_2$	2N	290			Basic salt	12D
$\text{Zn}(\text{NO}_3)_2$	2N	330-350	300-340		ZnO and some dark specks of metallic Zn	12D
Zn SO_4	2N	290	250	5hr	ZnS Some Particles of Zn	12D
$\text{Mg}(\text{NO}_3)_2$	2N	340	220-230	6hr	MgO	12D
Mg SO_4	2N	350	330		MgO and H_2S	12D

TABLE LV

Salt	Conc.	Vol in c.c.	Pres. at Beg.	Max Pres.	Final Pres.	Time in Days	Temp	Products	Ref.
Ni(OAc) ₂	N/10	80	120	180		1	200	Complete sep. of Ni, 99.35% Ni.	12A
Ni(OAc) ₂	N/10	75	120	179	174	1	200	Complete sep. of Ni,	12A
NiSO ₄	N/10	80	120			1	188	Not Comp sep. of Ni.	12A
NiSO ₄	N/10	80	123	179	174	2	207	Complete sep. of Ni. 99.74% Ni.	12A
Co(OAc) ₂	N/10	80	125	180	176			Complete sep. of Co.	12A
CoSO ₄	N/10	80	150	215		0.75	202	Not Comp sep. of Co.	12A
Co(NO ₃) ₂	N/10	15	150			1	230	Complete sep. of Co.	12A
NiCl ₂	N/10	50	120	180		1	240	Not Comp sep. of Ni	12A

TABLE V

Salt	Conc.	Vol in c.c.	Pres. at beg.	Max Pres.	Final Pres.	Temp	Time in hrs	Products	Ref.
NiCl_2	N/10	75	120			200	2	Not Comp sep. of Ni.	12A
$\text{Pb}(\text{NO}_3)_2$	N/10	100	150	219	214	209	2	A white precip. of basic salt.	12A
$\text{Pb}(\text{OAc})_2$	N/10	75	123			160	2	A white precip. of basic salt.	12A
$\text{Pb}(\text{OAc})_2$	N/10	64	150	242	239	240	0.75	Complete sep. of Pb (cryst.)	12A
$\text{Bi}(\text{NO}_3)_3$	Sat.	10	150			230	1	Black precipitate of Bi.	12A
$\text{Bi}(\text{NO}_3)_3$	Sat.	100	150	220	212	215	1	Sep. of white ppt. of basic salt."	
$\text{Bi}(\text{NO}_3)_3$	Sat	52	150	252	228	283	1	Bi was separated in form of small coral tree.	12A
$\text{Bi}(\text{NO}_3)_3$	Sat	55	150	242	222	248	0.75	Complete sep. of Bi.	12A

follows the Nernst equation

$$E = \frac{RT}{2F} \ln p$$

where E is the change in E. M. F. of the cell caused by changing the pressure from one to p atmospheres.

In order for a metal in contact with a solution of its ions to be in equilibrium with hydrogen and hydrogen ions, it would be necessary for the pressure of the hydrogen to be such that the electrode potential of the hydrogen was the same as that of the metal.

The above work is reported as having caused the precipitation of several metals from solution by hydrogen pressure. Let us consider cadmium for example. The electrode potential for this metal is given 0.3976-0.420 Volts. If we take the lower value 0.3976 and calculate from the Nernst equation the pressure necessary to give a hydrogen electrode this potential, we obtain the following

$$E = \frac{RT}{2F} \ln \frac{p_2}{p_1}$$

assuming $p_1 =$ one atmosphere, temperature = 18°C

and transposing, we have

$$\ln p_2 = E \frac{2F}{RT}$$

substituting and changing to common logarithms

$$\log p_2 = 0.598 \frac{2 \cdot 96500 \cdot 0.434}{8.32 \cdot 291} = \frac{2 \cdot 0.298}{0.058} =$$

13.742

from this $p = 5.30 \times 10^{13}$.

Similar calculation for zinc gives 5.01×10^{25}

It is obvious that somewhere there is a discrepancy between the theory and the published data and, while I did not hope to solve the problem I thought that I might help in its ultimate solution by obtaining more experimental evidence.

In view of the fact, mentioned above, that the experiments so far performed are so scattered it seemed that one of the things that was needed was a systematic study of the effect of changes of temperature and pressure upon the precipitation of some metal from a single salt solution and this I have attempted to do.

Silver acetate was selected for this work because it seemed desirable to have a reaction that

took place readily at room temperature and atmospheric pressure and also one in which there were as few complicating side reactions as possible. Some earlier experiments were made using solutions of silver nitrate but this was given up because of the fact, already known, that the hydrogen under pressure will act upon the nitric acid which is liberated during the precipitation of the metal.

EXPERIMENTAL

EFFECT OF VARIATIONS OF TEMPERATURE ON THE PRECIPITATION OF SILVER FROM A SATURATED SOLUTION OF SILVER ACETATE BY HYDROGEN.

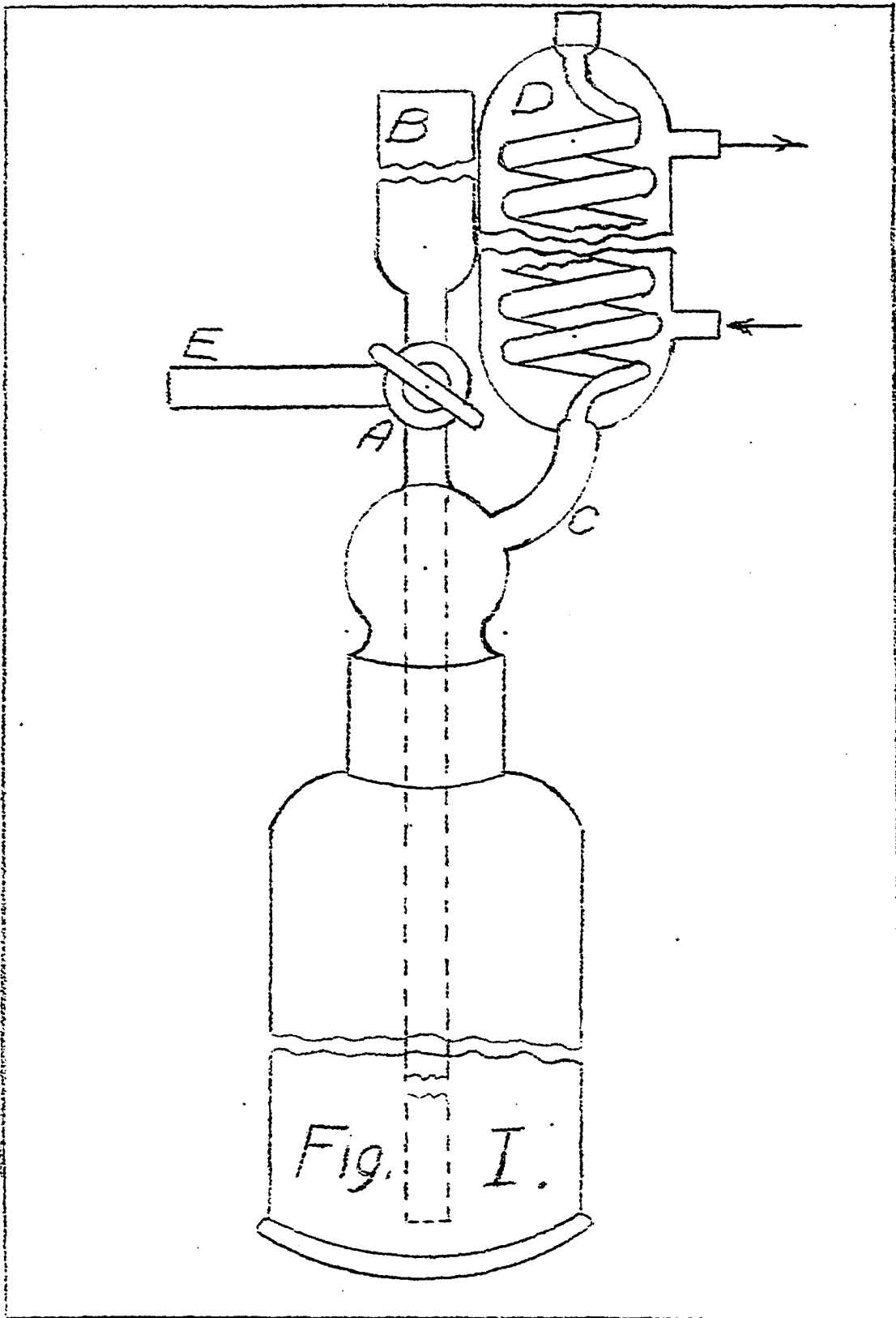
MATERIALS:- Hydrogen was made from ordinary stockroom C. P. HCl and mossy Zn. It was washed through solutions of NaOH, $Pb(OAc)_2$, $KMnO_4$, a saturated solution of $AgOAc$, the same as was used for the reductions, and a strongly alkaline solution of pyrogallic acid in KOH.

Silver acetate was C. P. reagent most of which was from Mallinckrodt's.

SET UP:- The reaction tubes used were made from Dreschel wash bottles of about 400 c. c. capacity; Fig. 1. To the inlet tube of each of these was sealed a three way stopcock A. On one arm of the stopcock was a cup B, of about 20c.c. capacity, to be used as a sampling cup. On the outlet tube of the wash bottle C was sealed a condenser D. Since the head

of the wash bottle was fitted by ground glass joint and the attachments mentioned were all sealed on, there was no chance of the liquid coming in contact with anything but glass.

The complete set up is illustrated in Fig. 11. A is an ordinary Kip generator for the preparation of the hydrogen. The top of this was connected by a rubber stopper and glass tube to a six liter aspirator bottle B. This was placed about three feet above the top of the Kip and not only served as an extra acid reservoir but also made it possible to obtain an extra pressure head which was necessary to force the hydrogen through the several solutions used. C, D, E, and F are four 250 c. c. wash bottles which contained respectively NaOH, $Pb(CAc)_2$, $KMnO_4$ and saturated AgOAc. A bunson valve G was inserted to prevent the solutions from backing up in the tubes in case a leak should occur in the apparatus back of this point. The U tube H was filled with glass beads and a strongly alkaline solution of pyrogallic acid in KOH. Four reaction tubes, K, I, J and L are made as described above and illustrated in Fig. 1. Of the four reaction bottles used, I was a conditioning bottle and its contents were not used, J and K were the reaction tubes used for the run and each was analysed from time to time. L was a blank to which no hydrogen was added. These were set in a De Khotinsky constant temperature bath.



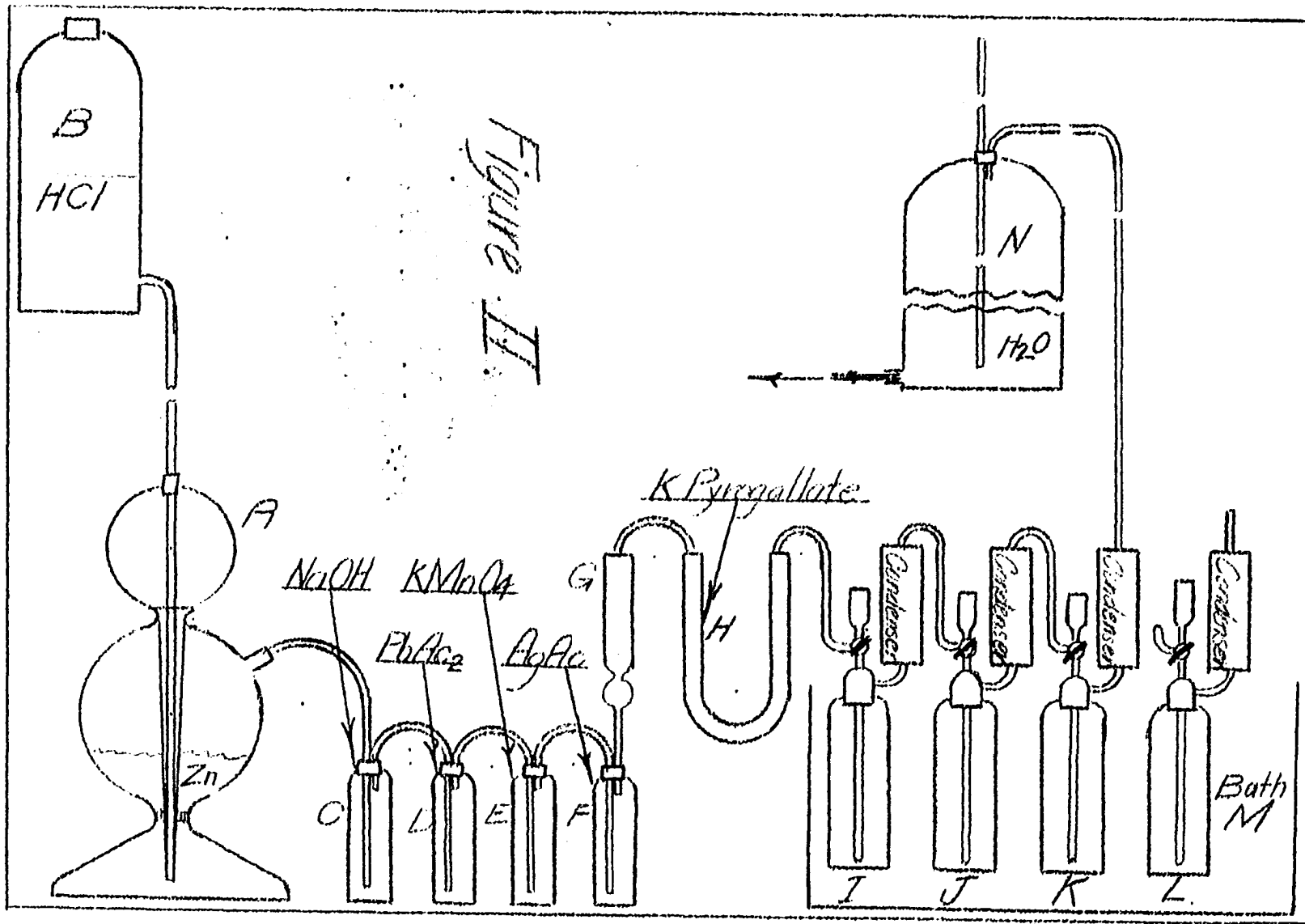


Figure II.

Four twelve liter aspirator bottles N were used to control the rate of flow. This was done by connecting these four bottles in series both top and bottom and then connecting all with an outlet through a small glass nozzle. The bottles were filled with water and the escape of the water through the nozzle gave a fairly constant rate of flow. The pressure was kept slightly above atmospheric.

METHOD:- The solutions were put into the reaction bottles in a De Khotinski constant temperature bath, connected up and allowed sufficient time to come to the temperature of the bath. Hydrogen was then turned on and allowed to bubble slowly through the solutions for fifteen minutes to allow them to become saturated with the gas. The outlet from the last reaction bottle was then connected to the aspirator bottles and the rate of flow controlled as indicated above. The average rate was about $\frac{1}{2}$ l. per hours.

A preliminary run was made with varying rates of flow to determine whether or not this had any effect. The indication was that so long as there was sufficient flow to stir the liquid the rate was not important.

After the run was started samples were removed from the bottles at appropriate intervals and analysed for silver by titrating with NaCl solution, one C. C. of which was equivalent to one c. c. of the original AgOAc solution. Na_2CrO_4 was used

as an indicator. The titration was made by measuring out 10.00 c. c. of sample from a pipette, then running in an excess of NaCl solution from a burette and titrating the excess of NaCl with AgOAc. This gave directly the amount of Ag that had been removed from the solution by the reduction. This amount of silver, calculated as percent of the amount originally present was plotted against time.

The temperatures used varied from 35° to 90°C. Lower temperatures were not used because the rate of reaction was so slow.

At the close of most of the runs the precipitate was analysed to determine whether or not it was metallic silver or some other reduction or hydrolysis product. To make this analysis the solution remaining in the reaction bottle was transferred to an especially prepared filtering apparatus. This was so made that the residues could be transferred to it, washed, dried and weighed without being exposed to the air. After this was done the residue was dissolved in concentrated HNO₃ and the Ag precipitated and weighed as AgCl.

RESULTS:- The results of the above experiments are given by the curves in Fig. III and IV and the analyses of the precepitates are in Table VI.

On these curves the percent decrease in concentration of silver is plotted as ordinates against time as abscissas.

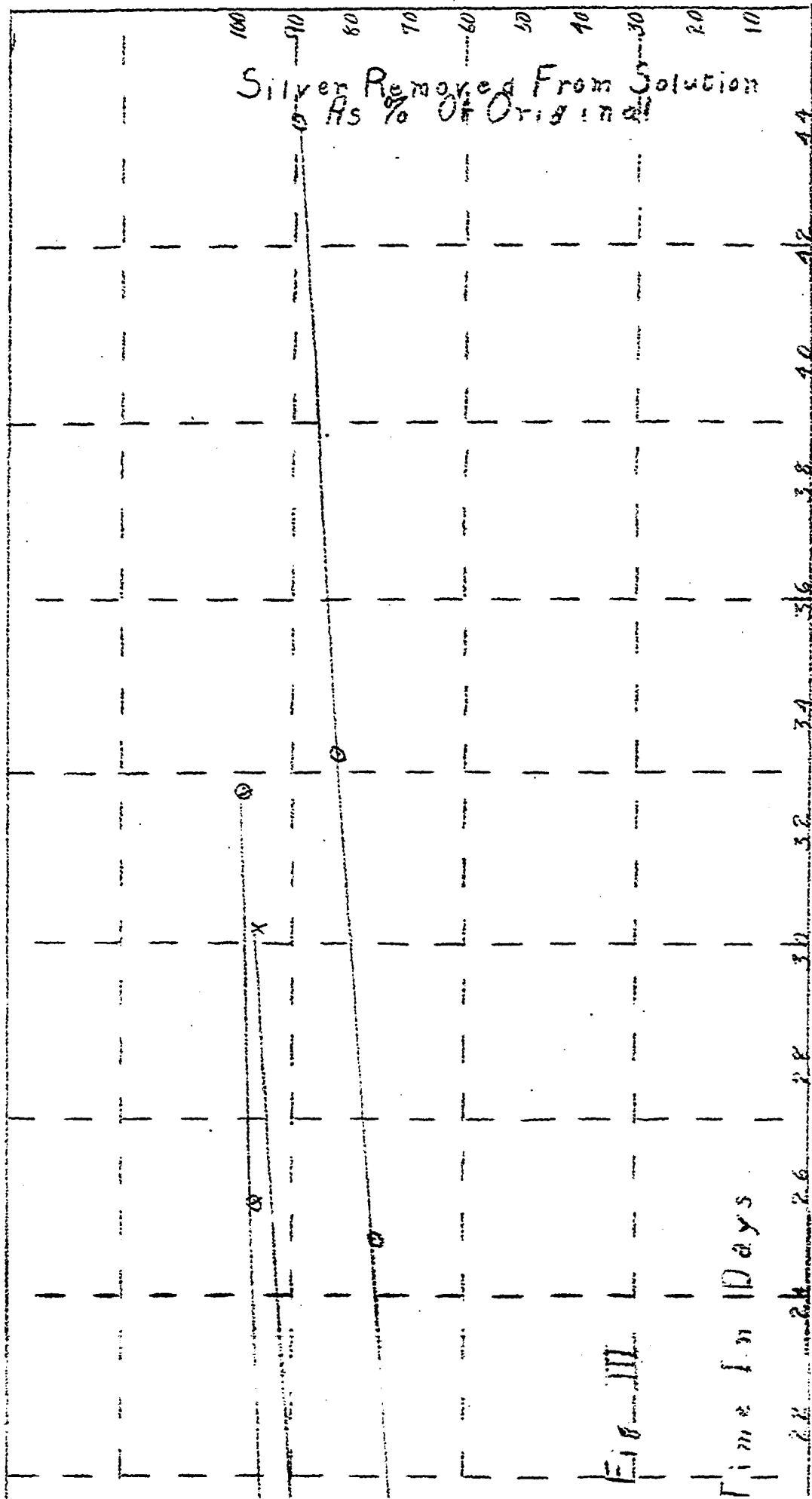
Curves A, B, C, D and E shown on Fig. III represent, respectively, temperatures of 35, 45, 50, 60 and 65 degrees centigrade. They are plotted to a scale in which one small square on the ordinate equals one percent and one large square on the abscissa equals one day. Curves E, F, G, and H shown on Fig. IV represent, respectively, temperatures of 65, 75, 81 and 90 degrees centigrade. They are plotted to a scale in which $1\frac{1}{2}$ small squares on the ordinate equal one percent and 2 small squares on the abscissa equal one hour.

Since the scales had to be different for the two sets of curves, E was put on both sets so that comparisons could be more readily made.

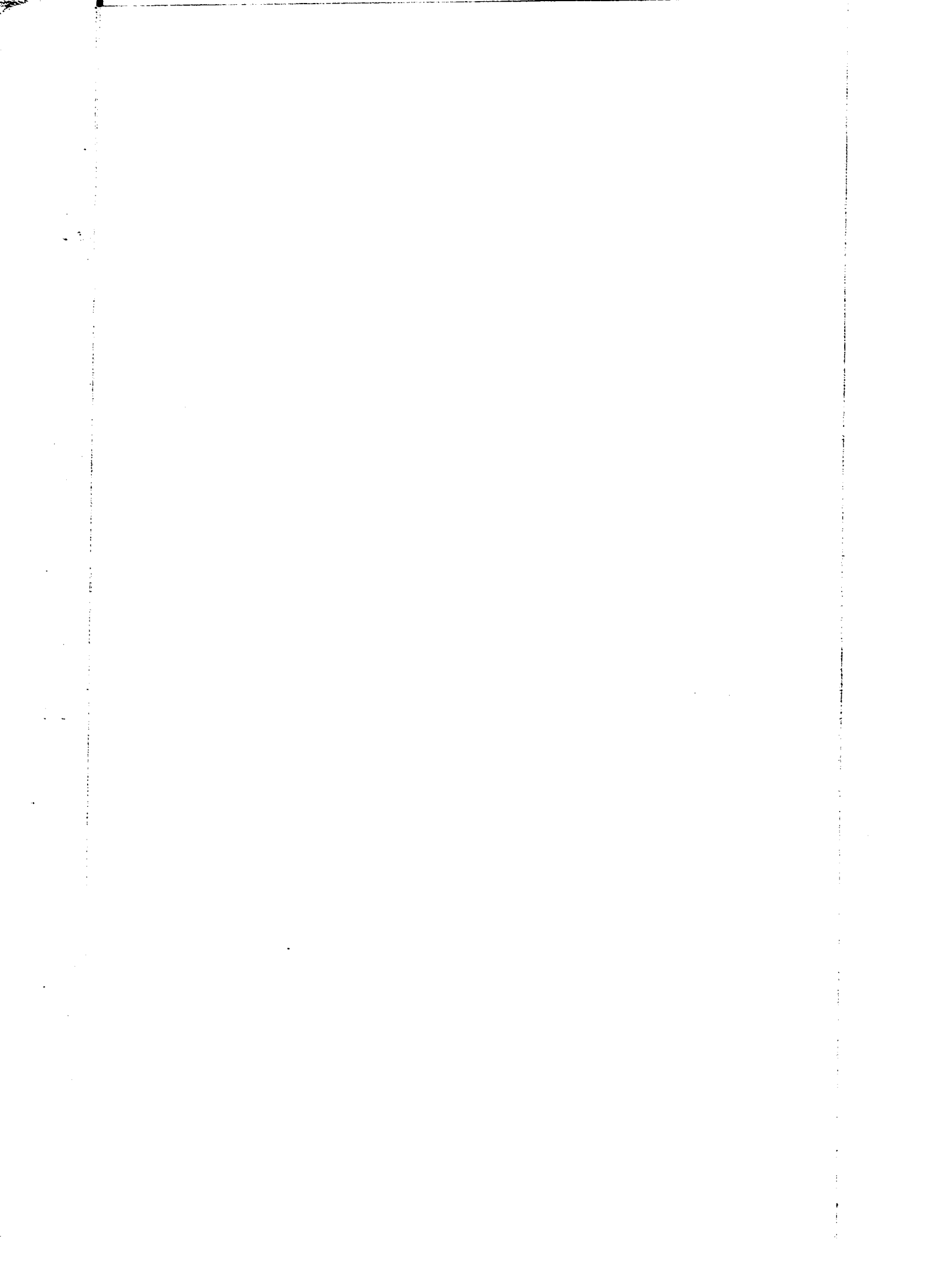
The analyses given in Table VI show that the precipitate was nearly pure silver.

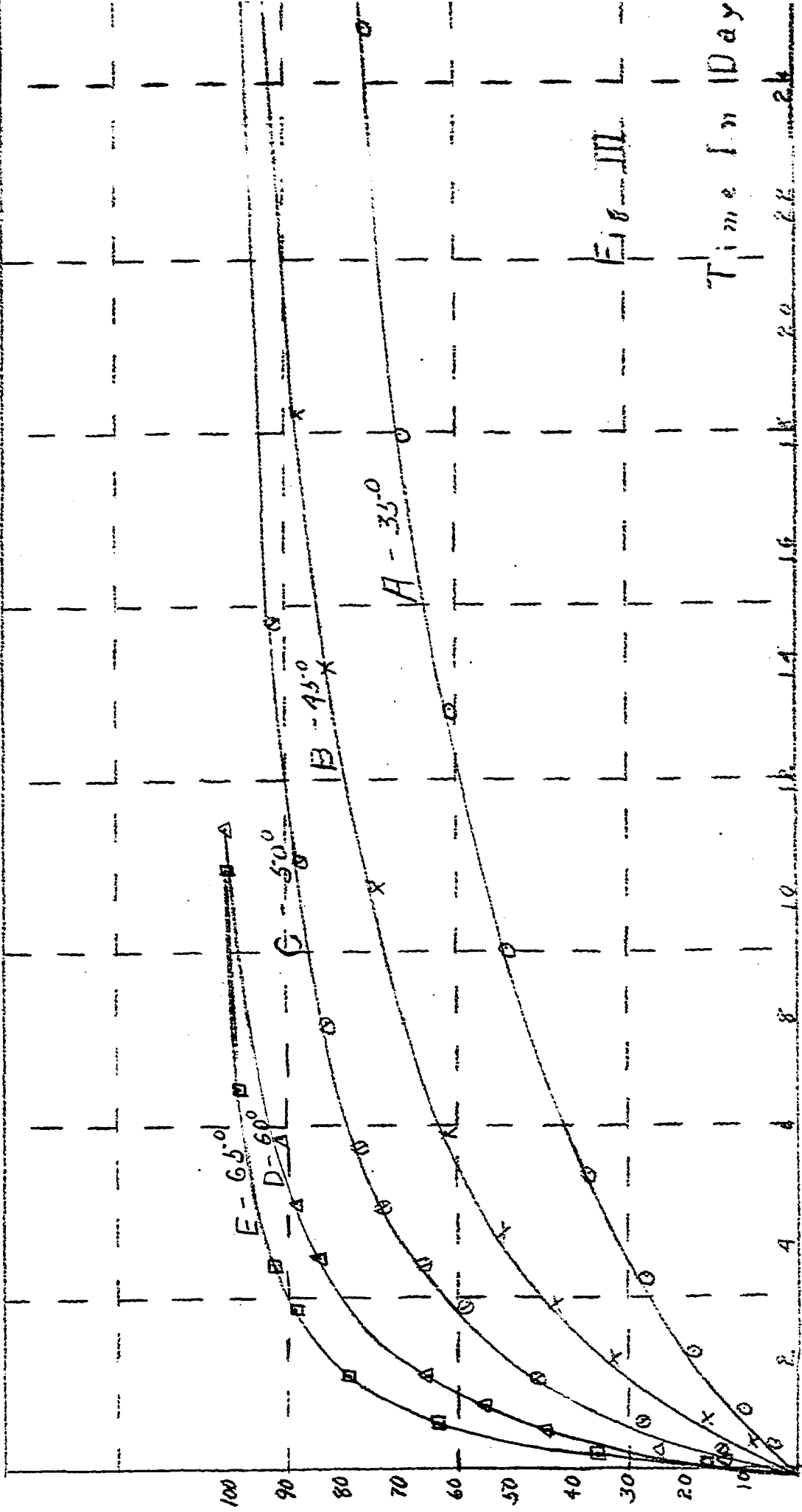
TABLE VI

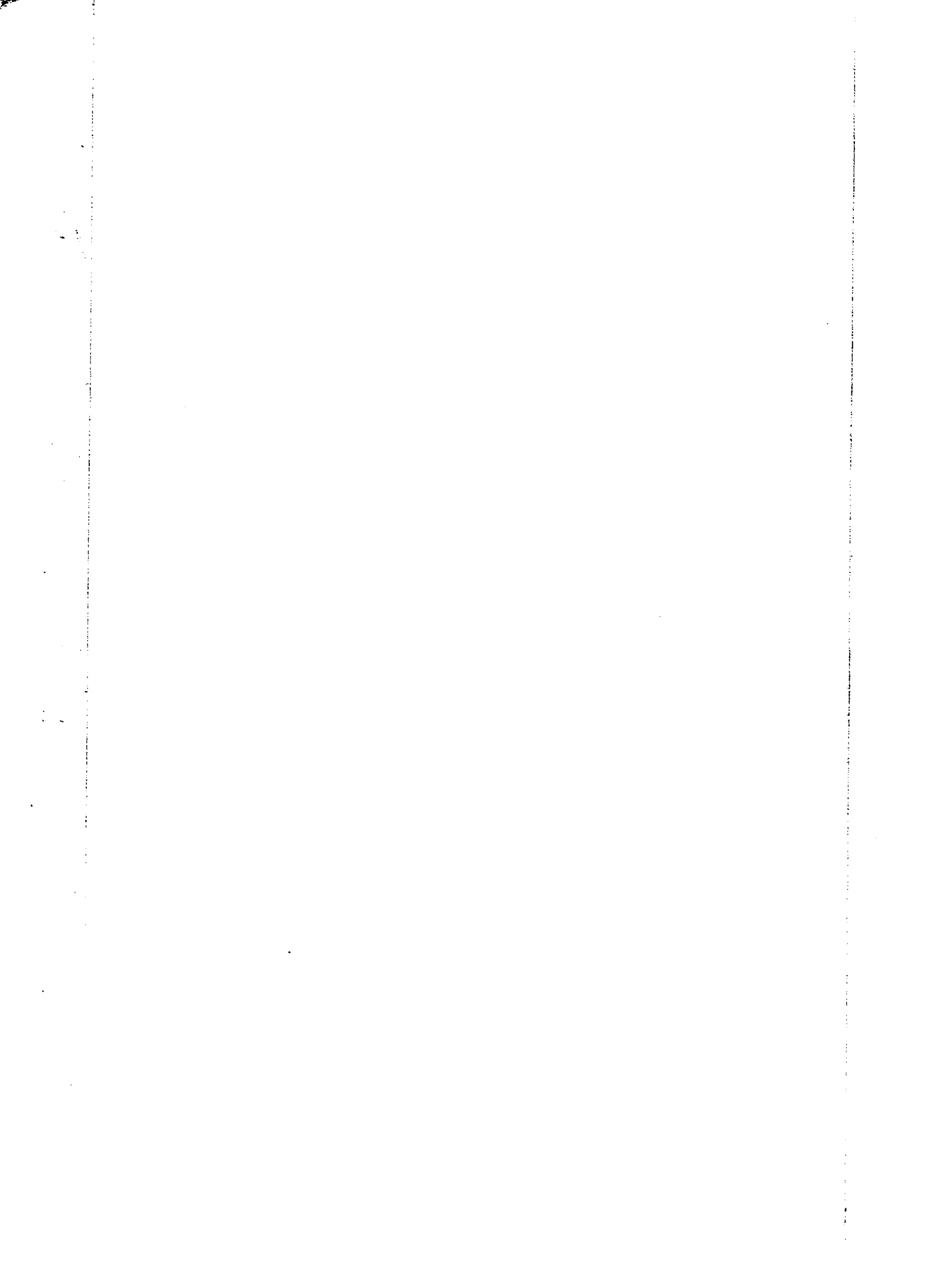
Analysis of Precipitates			
Run No.	Temp.	Pres	% Ag
18	35°	1 at	98.9
17	60°	1 at	98.9
16	90°	1 at	98.4
15	81°	1 at	98.7
14	75°	1 at	98.4

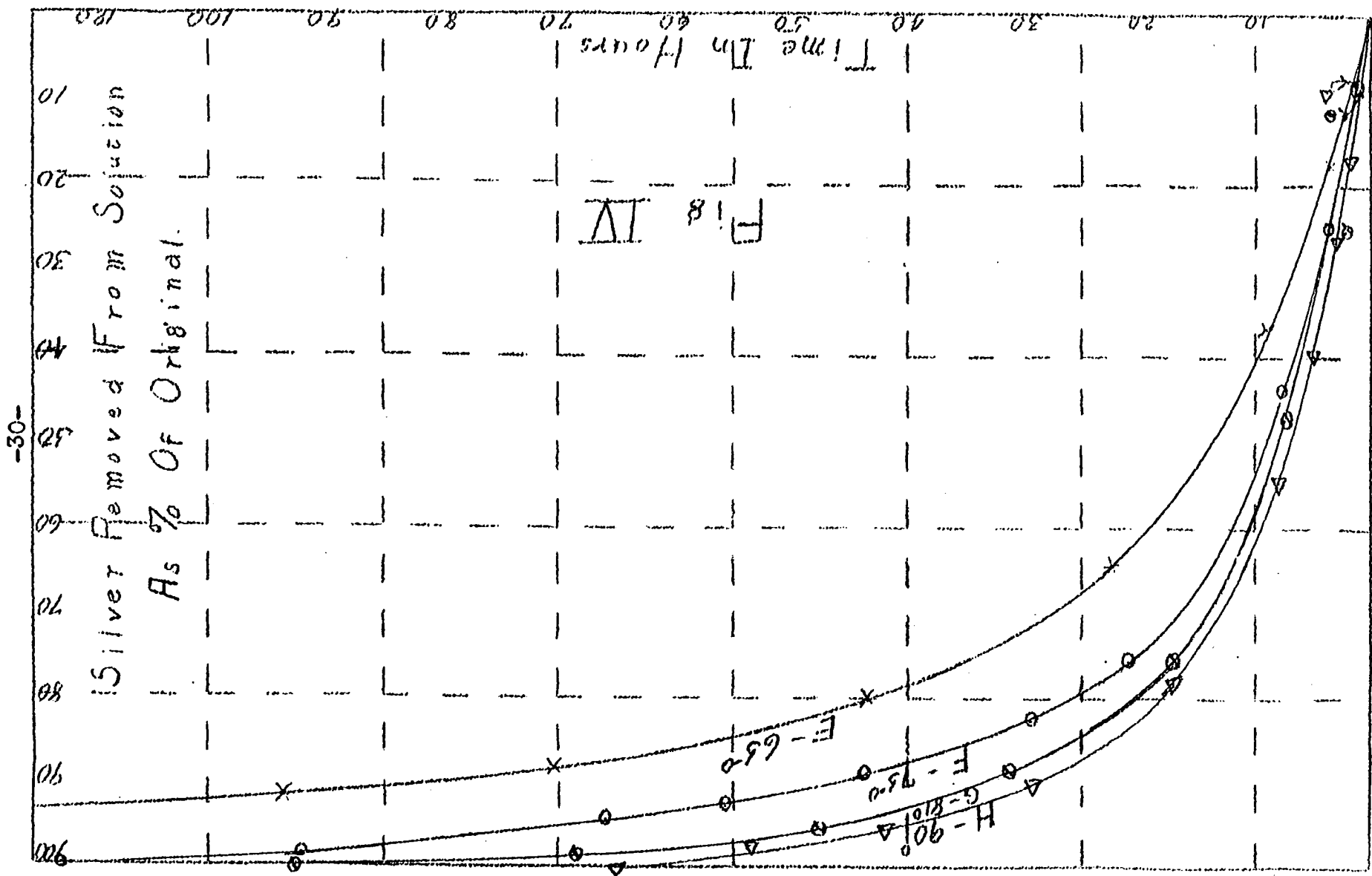


Feb III









EFFECT OF VARIATIONS OF PRESSURE ON THE PRECIPITATION OF SILVER FROM A SATURATED SOLUTION OF SILVER ACETATE BY HYDROGEN.

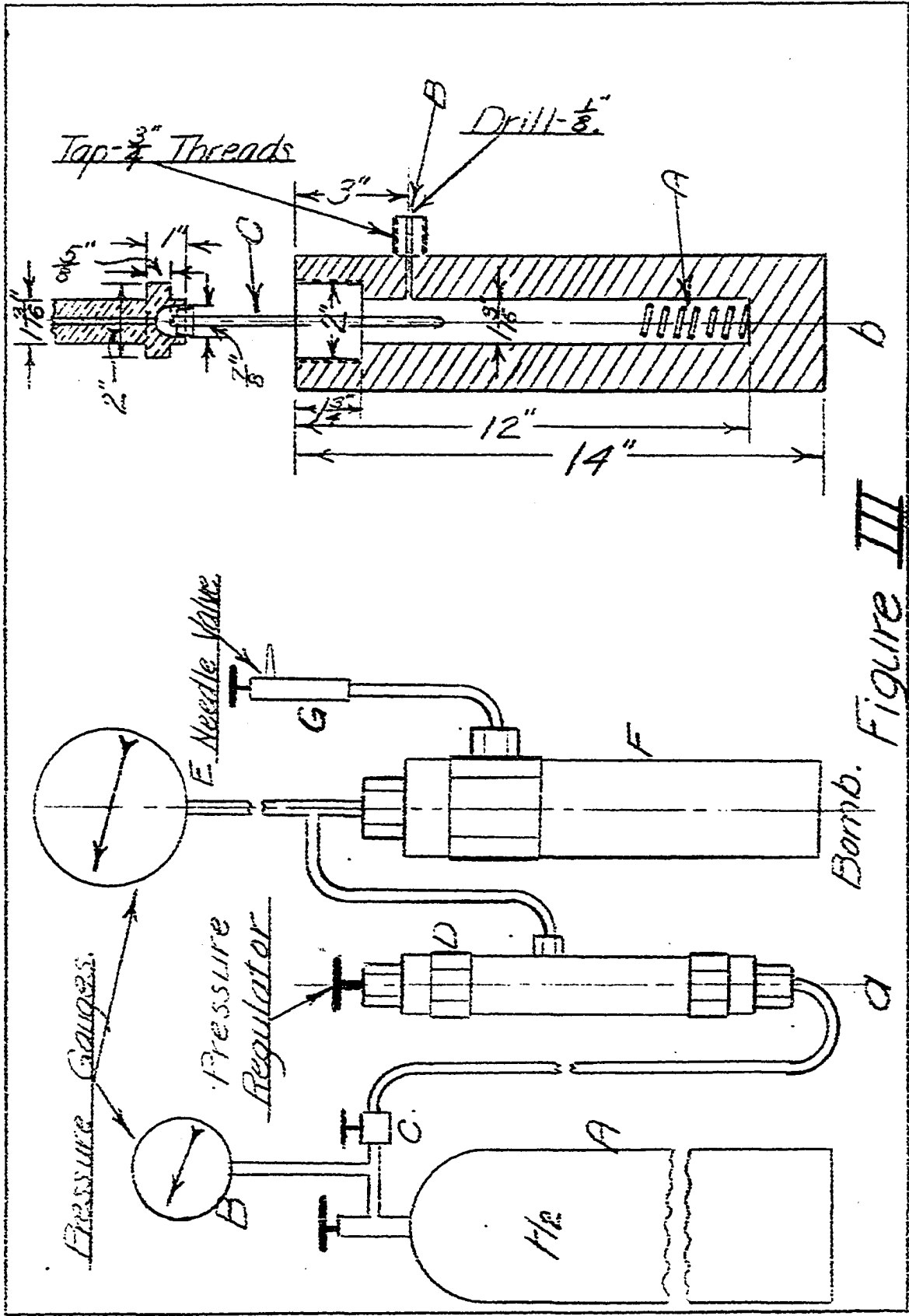
MATERIALS:- The H₂ used in this part of the work was cylinder H₂ obtained from Betendorf Oxygen and Hydrogen Co., Betendorf, Iowa.

The AgOAc was the same as that mentioned above.

SET UP:- The set up of the apparatus used is illustrated in Fig. V in which A is an ordinary commercial high pressure hydrogen tank, B is pressure gauge and C a cut off valve. An automatic pressure regulating valve D was operated by electrical contact in the pressure gauge E*. The reactions were carried out in a steel bomb F, illustrated somewhat more in detail in Fig V b. A Parr needle valve G was provided for releasing the pressure.

METHOD:- Twenty-five c. c. of the silver acetate solution were put into a 7" x 1" pyrex test tube; this was brought to the desired temperature--45°C--and inserted in the bomb F, Fig. V a. The tube rested on a spiral spring A Fig. V b and

*This valve was made in the machine shop of the Chemistry Department at Iowa State College according to the description given by Larson and Karrer. J. Ind. and Eng. Chemistry. 14 1013 (1922).



the bomb contained sufficient water to raise the level to outlet B when the tube was in place. The cap of the bomb was fitted with a removable glass inlet tube C which reached to within one half inch of the bottom of the test tube.

After the tube was inserted in the bomb the top was screwed on and the connections completed as shown in Fig. V a. The H_2 was then turned on and the pressure within the bomb gradually raised to that desired for the run. This required from 2 to 5 minutes, depending upon the pressure used. After the desired pressure was reached the release valve G was opened slightly so that there was a slight flow through the solution for 5 minutes after which the valve was closed. The pressure was maintained for a given length of time usually with a maximum variation of ± 5 pounds. At the end of the run the valve G was opened so that the pressure returned to atmospheric in about the same time as was taken to build it up. Time was counted from the time the H_2 was turned on until the release valve was opened.

When the pressure was back to atmospheric the bomb was opened and the tube and solution cooled in water as soon as possible. This usually took from 3 to 5 minutes from the time the pressure reached atmospheric. The solution was then filtered and analysed in the same manner as described for the experiments at atmospheric pressure.

Runs were made in this manner for time durations of 1, 2, 4, 8, and 12 hours and for pressures of 150, 300, 600 and 1000 pounds. Each run was made at least twice and some of them four or five times.

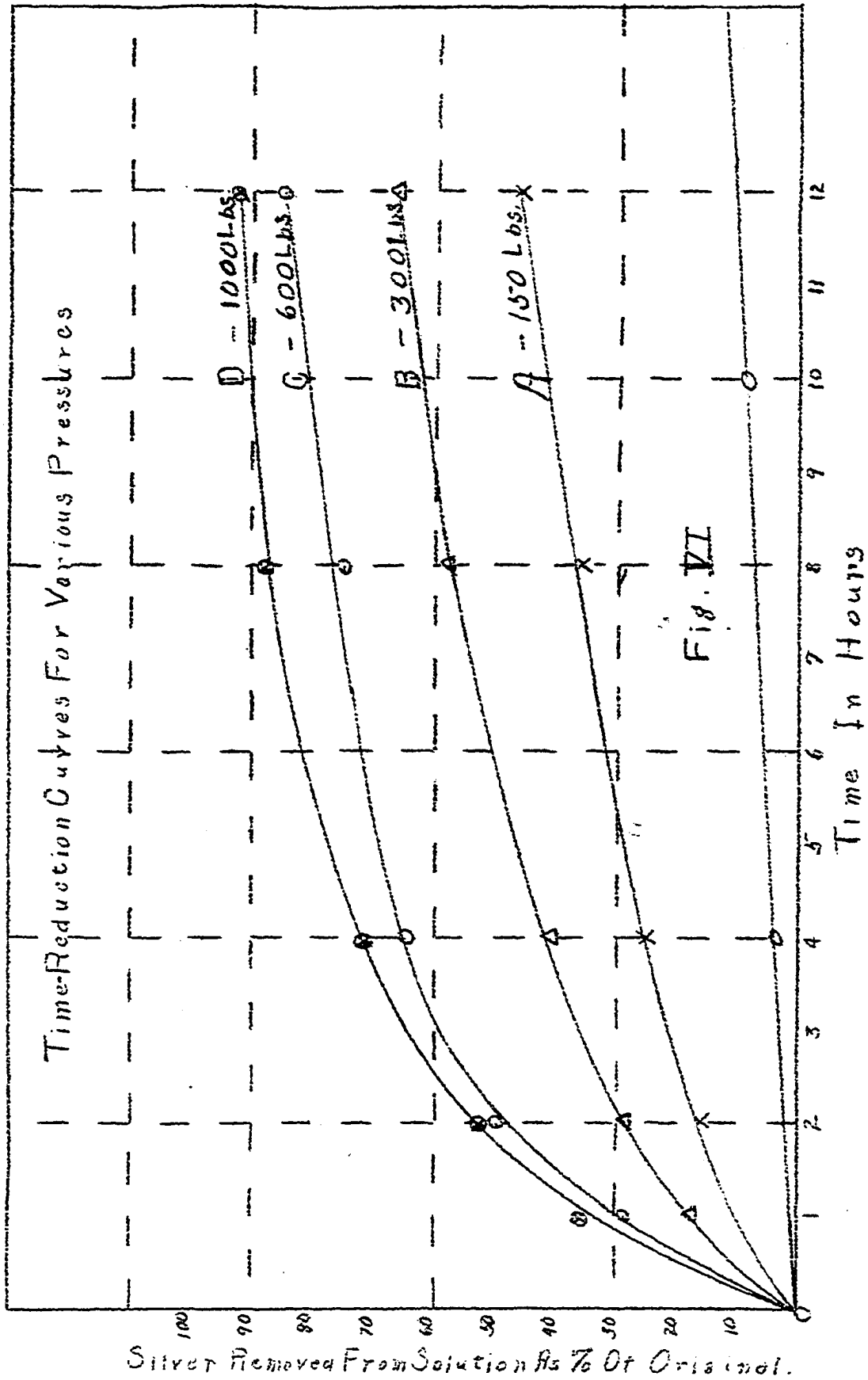
For a number of these runs the precipitates were analysed as described for the runs at atmospheric pressure.

RESULTS:- The results of the analyses described here are given by the curves shown on Fig. VI and in Table VII

The curves are plotted the same as those above, percentage reduction in concentration of silver against time. One small square on the ordinate represents the removal of 1% of the total amount of silver originally present and 1 1/2 large squares on the abscissa represent 1 hour of time.

TABLE VII

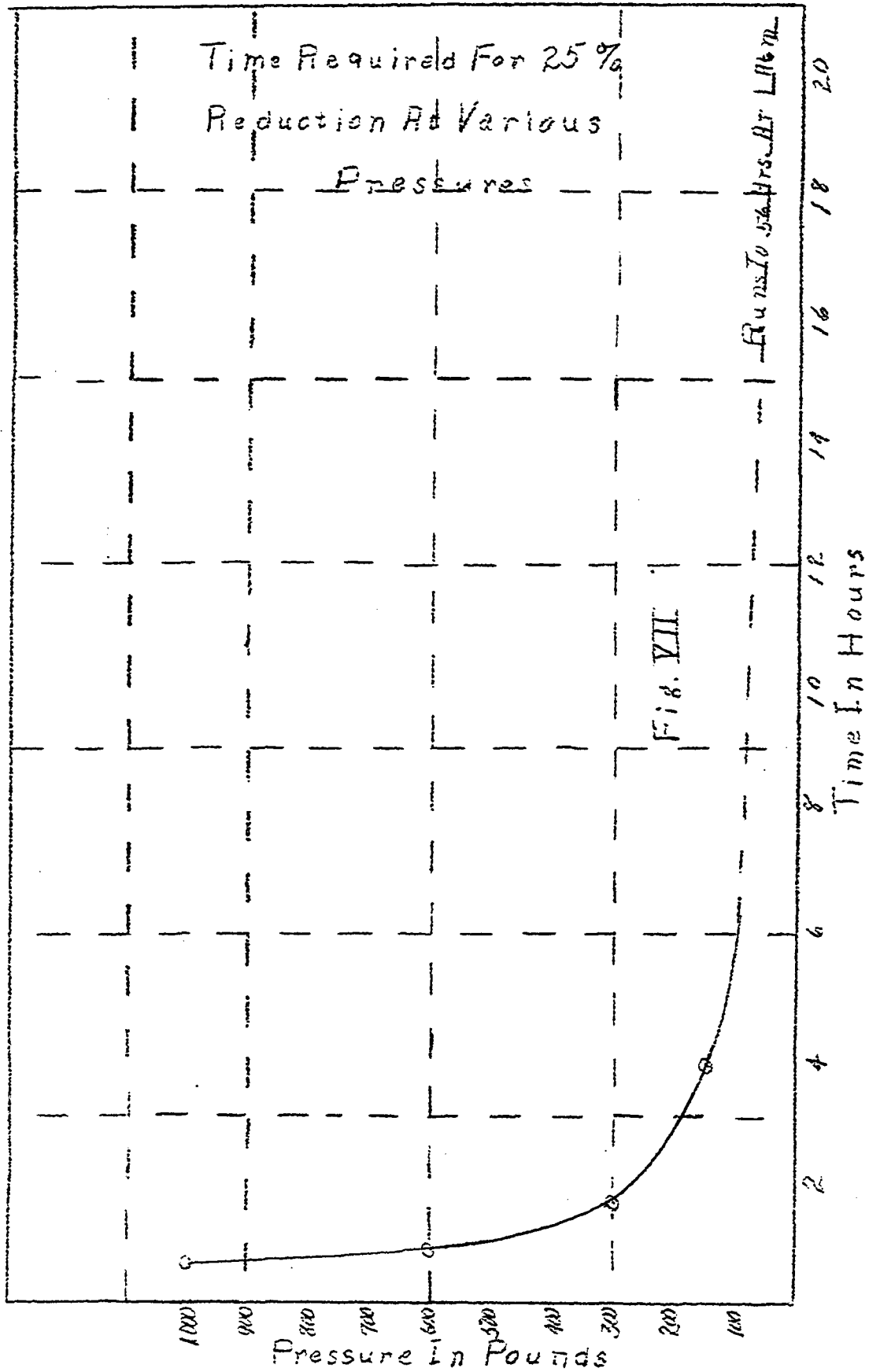
Run No.	Temp.	Pres.	% Ag.
35i	45°	1000	92.9
34b	45°	300	95.0
34c	45°	300	92.5
34d	45°	300	100.6
34e	45°	300	100.6
34f	45°	300	98.5
34g	45°	300	103.2
35k	45°	1000	97.9
35c	45°	600	97.9



In some of these runs considerable difficulty was experienced in obtaining uniform results. This was particularly true if there was any leak in the apparatus or if gas was allowed to bubble through the liquid. In some of the runs a rubber tube was attached to the release valve. This was run into a beaker of water and the valve opened enough to allow a very slow bubbling in the water. When this was done the results were very inconsistent. The same was true if there was any leak in the apparatus so that hydrogen had to be added in any appreciable amount during the run. The results used in obtaining the curves shown here were obtained, therefore, from series of runs in which no gas was allowed to pass through the apparatus after the first 5 minutes and in which there was practically no leak. They show that pressure does have a marked effect upon the rate at which the reaction takes place. No definite quantitative relationship has been determined.

A curve of some interest is obtained by plotting the time required to obtain a definite percentage reduction for different pressures. Such a curve is shown in Fig. VII in which the pressures are plotted against the time required to obtain 25% reduction. Curves plotted in the same way for other percentages of reduction have the same form.

This curve shows a very great decrease in the time required up to about 300 pounds pressure. After that a fur-

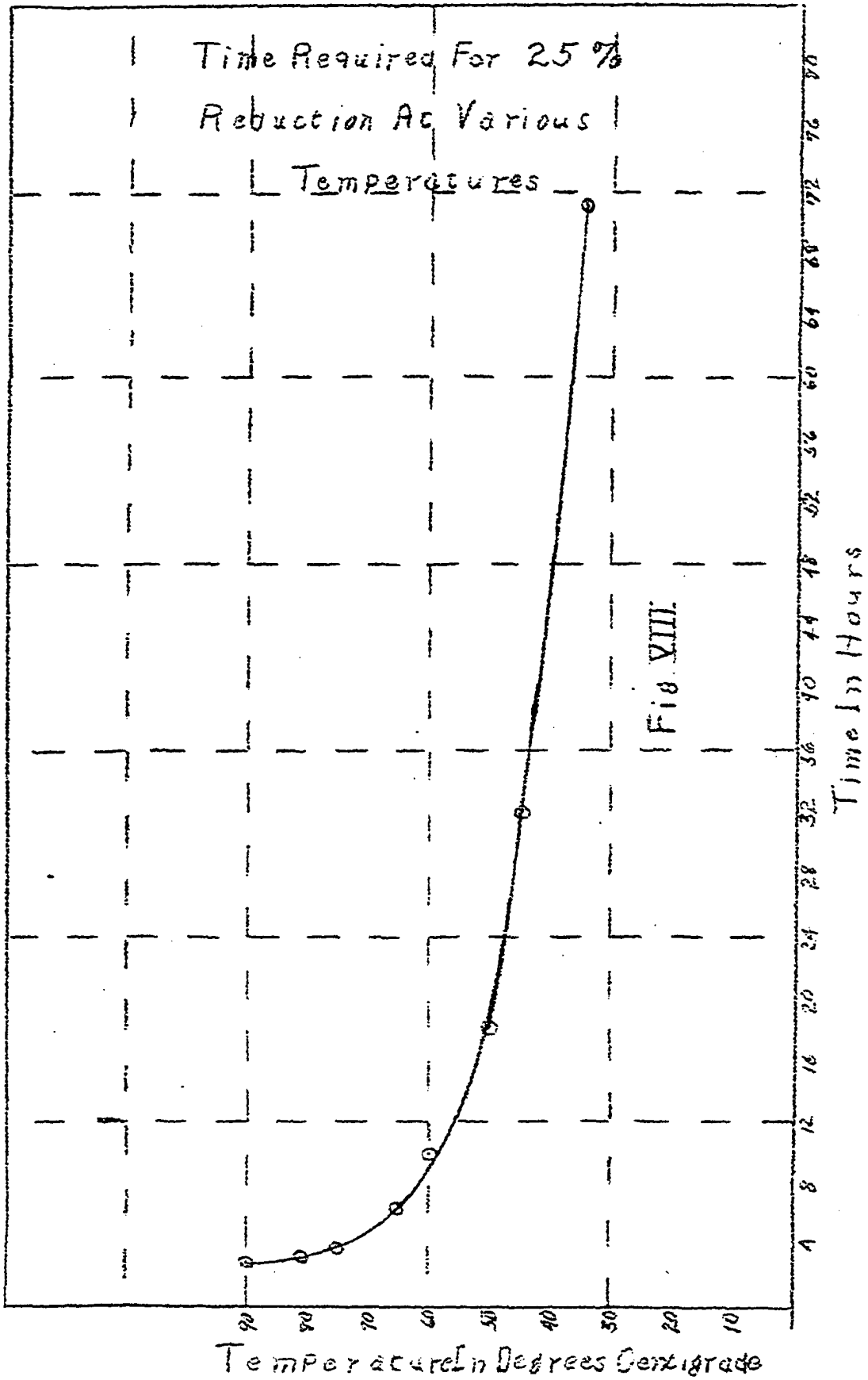


ther increase in the pressure adds little to the rate of the reaction. These results do not agree with the most of those which have been discussed here except that Cohen and Valetton (8) found that the velocity coefficient for the esterification of ethyl acetate decreased above 1000 atmospheres. It maybe that the difference is due to a slow rate of diffusion or some other such factor. Prehaps, if the solution could be actively stirred or a bubbling method could be so controlled as to give uniform results, we would find that there was less change in the velocity coefficient at the higher pressures.

In Fig. VIII a curve is shown in which temperature is plotted in a manner similar to that in which pressure is plotted in Fig. VII. That is, temperature is plotted against the time required to obtain 25% reduction.

It is interesting to note that, in a manner similar to that noted above, increase in temperature causes a very rapid decrease in the time required for a given percentage reduction up to about 65° to 75° and then the effect becomes very small and furthermore that this change comes when the curve has the the same slope as does that one shown in Fig. VII. This again would seem to indicate that there is probably some factor other than temperature and pressure that plays an important role in governing the speed of the reaction.

CONCLUSIONS:- A systematic study has been made of the



effect of variations of temperature upon the reduction of a saturated solution of AgOAc by H₂ for temperatures from 35° to 90° and of the effect of variations of pressure upon the same reaction from atmospheric pressure to 1000 pounds. The results indicate that both temperature and pressure have a marked effect upon the reaction velocity but very little, if any, over the range studied, upon the product which is nearly pure silver; that the coefficient of velocity change with both temperature and pressure is large for the lower temperatures and pressures studied and that, under the conditions of the experiments, these coefficients decrease rapidly for the higher temperatures and pressures studied.

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