REPORT

of

Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by _R. Darwin Gray_ for the degree of _M. S._ They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of _Master of Science_

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May 22 1916.

REACTION BETWEEN CHLOROFORM AND AQUEOUS

POTASSIUM HYDROXIDE

A THESIS

Submitted to the Faculty of the Graduate School of the
University of Minnesota

by

R. DARWIN MAY

In partial fulfillment of the requirements for the
degree of

MASTER OF SCIENCE

June, 1916

THEORETICAL PART

REACTION BETWEEN CHLOROFORM AND AQUEOUS
POTASSIUM HYDROXIDE.

This problem arose during research work on the Reimer-
Tiemann reaction by Dr. Hunter and Miss Ziegler.   Some at-
tempts were made to ascertain the extent of the reaction
between chloroform and aqueous potassium hydroxide, as this
might help interpret their results and possibly give them
corrections to be applied to their data.   For this purpose
a thermostat and an egg-flask with reflux condenser were
used, constant stirring being produced by bubbling air thru
the reaction mixture.   The inorganic chlorine produced was
determined, but the results on check determinations varied
so greatly that no reliable information was obtained.

Our reason for taking up this problem is its direct
bearing upon the study of the Reimer-Tiemann reaction which
is being aarried on by Dr. Hunter.   Possibly we could show
whether it is Nef's carbon bichloride (CCl_2) or the radical
HCOH that is the entering group in this reaction.   In a
typical case of the Reimer-Tiemann reaction there is present
phenol, concentrated potassium hydroxide, and chloroform.
It is evident that the study of any two of the three com-
ponents should thro light upon the changes taking place when
all three are present.

The purpose of this work is to study, as far as possi-
ble, the exact nature of the action between chloroform and

aqueous potassium hydroxide.   Very little satisfactory work

has been done upon this subject.   Chloroform was discovered

at about the same time (1831) by Liebig[1] and Soubeiran[2] by the

action of alcohol on chloride of lime and by chlorine on al-

cohol.   Dumas[3] (1834) states that when chloroform and aqueous

potassium hydroxide are boiled in a closed tube, potassium

chloride and potassium formate are formed.   From this work

he made known the correct molecular arrangement of the sub-

stance and named it "Chloroform".   Later Geuther[4] (1862)

observed that a gas which he identifies as carbon monoxide,

is formed during this reaction with alkalies.   The only

other important reference is of Saunders[5] (1900) who worked

with alcoholic potassium hydroxide and chloroform, thus hav-

ing a homogeneous system.   He assumes that the potassium

chloride and potassium formate are the reaction products

and that carbon monoxide is a decomposition product of the

formate.   The reaction as he expresses it is:

$$CHCl_3 + 4KOH = 3KCl + 2H_2O + HCOOK$$

His object was to determine the order of the reaction, and

in a fair way he shows that it is probably bimolecular.

As one of the disturbing factors he mentions the formation

of water, and quoting from Dumas[6] says that an aqueous

solution of potassium hydroxide has no action on chloroform

[1] Liebig   A. 1, 198 (1832)
[2] Soubeiran   A. Ch. (2) 48, 131 (1831)
[3] Dumas   Ann.Phys.Chim. (2) 56, 115 (1834)
[4] Geuther   Ann. 123, 121 (1862)
[5] Saunders   J.Phy.Chem. 4, 660 (1900)
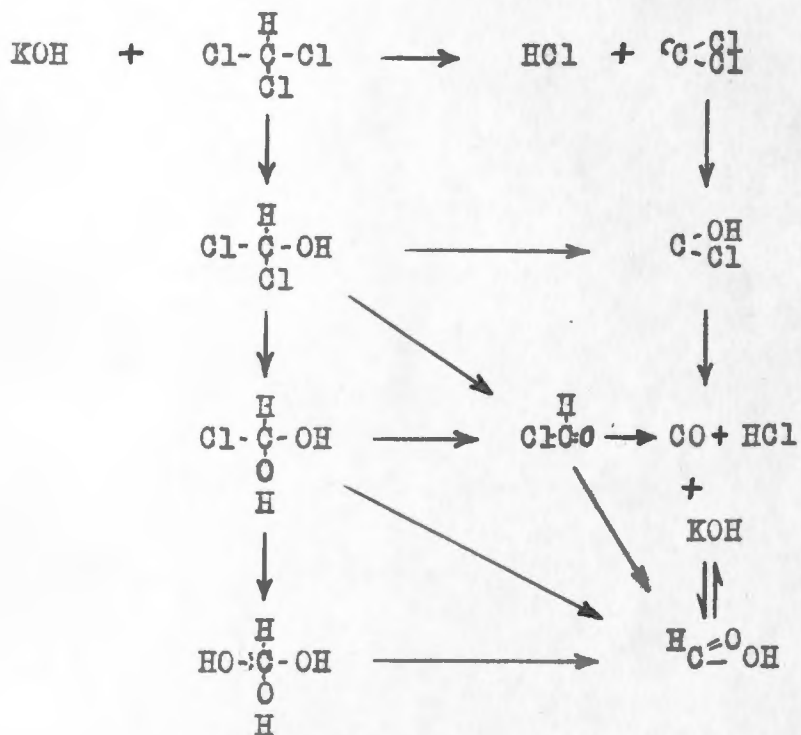[6] Dumas   Ann.Phys.Chim. (2) 56, 115 (1834)

even when boiled.   From this he deduces that the formation
of water would tend to retard his reaction in alcoholic
potassium hydroxide, but adds that so much water is already
present that the amount formed would cause no appreciable
effect.   Referring to the original article by Dumas it will
be noted that Saunders made a mistake in translation.   As
stated before Dumas in this connection states that an aqueous
solution of potassium hydroxide and chloroform when boiled
in a closed tube give the chloride and formate of potassium.

In the meantime, the commercial process of making for-
mates from carbon monoxide made it possible that carbon mon-
oxide might be the first product of the reaction as suggest-
ed by Nef.   This would then give formate with the potassium
hydroxide present.

$$CHCl_3 + KOH = KCl + H_2O + CCl_2$$
$$CCl_2 + 2KOH = CO + 2KCl + H_2O$$
$$CO + KOH = HCOOK$$
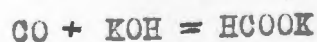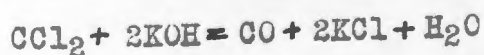
It seemed best then to find out what the relative veloci-
ties of the reactions giving carbon monoxide and formic acid
might be at different concentrations of the hydroxide.   Re-
ferring to diagram on following page, of the possible changes
that may be going on, it is evident that at this time we
were not sure that in our work we would be following out

'Nef   Ann. 298, 366 (1897)

Possible changes that may occur:

$$KOH + Cl-\underset{Cl}{\overset{H}{C}}-Cl \longrightarrow HCl + C\overset{Cl}{\underset{Cl}{:}}$$

$$Cl-\underset{Cl}{\overset{H}{C}}-OH \longrightarrow C\overset{OH}{\underset{Cl}{:}}$$

$$Cl-\underset{\underset{H}{O}}{\overset{H}{C}}-OH \longrightarrow \underset{Cl}{\overset{H}{C}}\hspace{-0.2em}:O \longrightarrow CO + HCl$$

$$+$$

$$KOH$$

$$HO-\underset{\underset{H}{O}}{\overset{H}{C}}-OH \longrightarrow \underset{C}{H}\overset{O}{\underset{OH}{=}}$$

one or two definite reactions.   For this reason kinetic
measurements of the ordinary type, to obtain a "reaction
velocity", with thermostat seemed useless.

Some trouble was also expected from the different
equilibria.set up by these two immiscible liquids.   Nernst
says that the velocity of reaction in heterogeneous systems
is largely dependent upon the extent and nature of the
separating surface between the reacting phases, and on other
circumstances such as the diffusion capacity and velocity
of stirring.   With sufficiently vigorous stirring, which
is kept constant thruout the experiment, it may be assumed
that the water solution has a homogeneous composition.   It
is highly probable, that at every boundry between two phases,
equilibrium is established with practically infinite velocity
(compared to the rate of diffusion).   In final analysis,
if the reaction is more rapid than the diffusion into the
water, it is probably the diffusion constant (for a thin
film) which regulates the rate of reaction rather than the
concentration; while, if diffusion, aided by stirring and
communition of the phases, is more rapid than the reaction,
the velocity of the reaction will be measured.   It is the
latter set of conditions that we think we have reached in
our work.

Our first step was to devise a method by which the
desired results could be obtained.   A few experiments were
carried out with thermostat and egg-flask, but in duplicate
experiments the results would vary as much as 100%.   This

could be expected from what has just been stated on the possible changes and conditions in this system.

To see what kind of stirring is produced by passing vapor of chloroform thru a solution of potassium hydroxide, an apparatus of the Landsberger type was tried out. This consisted of a round bottom flask for boiling the chloroform; a Dewar tube with cork stopper holding a thermometer, outlet tube, and an inlet tube reaching to the bottom; and a condenser the top of which was connected with the outlet tube of the Dewar. The inlet tube reaching to the bottom of the Dewar was bent at the end into the shape of a ring which fitted the bottom of the Dewar and thru which were twelve or fifteen small holes. It was discovered in using this apparatus that a definite temperature equilibrium is established in the reaction mixture, which depended upon the potassium hydroxide concentration. Also it was shown that with this multiple hole inlet thru which vapor of chloroform is passed, that very good stirring is obtained. It seemed advisable to use this means of stirring in our work on the reaction between chloroform and potassium hydroxide, and several forms of apparatus involving it were tried out.

First, the apparatus described above was used, the chloroform after passing thru the hydroxide solution in the Dewar being condensed and collected externally, but the amount of water carried with the chloroform (in twenty minutes) increased the concentration of the hydroxide producing a corresponding increase in temperature. A longer Dewar tube was then made use of and the chloroform after

condensing was delivered back into the Dewar.   In this
case the liquid level would rise from six to eight centi-
meters,and the increased pressure under which the chloroform
vapor must enter caused an appreciable rise in temperature;
also poorer stirring was obtained due to the large amount of
liquid chloroform present.   Another modification of the
apparatus was tried out.   A long air-condenser and water-
condenser were connected by a short "U" tube, the two con-
densers making up the sides of an inverted large letter "U".
The air-condenser was now connected with the Dewar tube,
with the idea that the water vapor would condense first and
return to the Dewar while most of the chloroform vapor
would pass into the second condenser and the liquid chloro-
form be caught in a separate vessel.   In this way the objec-
tions to the two former modifications would be done away
with.   It was not satisfactory, however, and was given up.

The exact data of a sample experiment as taken with this discarded apparatus is as follows:

November 10, 1915.

25ccKOH (75%) used   B.P. 731.9mm

Time	Temperature
1:17	
1:18	57.20° C
1:19	57.20
1:20	57.44
1:21	57.51
1:22	57.58
1:23	57.62
1:24	57.63
1:25	57.64
1:26	57.66
1:27	57.70
1:28	57.70
1:29	57.73
1:30	57.78
1:31	57.79
1:32	57.79
1:33	57.79
1:34	57.78
1:35	57.79
1:36	57.80

Only 50% or 60% of $CHCl_3$ passed thru, condensed in second condenser and was collected in separate vessel. One or two c.c. of H_2O separated from this $CHCl_3$ also.

These facts with the gradual rise in temperature obtained make this type of apparatus undesirable.

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The next form of apparatus tried out proved satisfactory and was used thruout our work. It consists of a Dewar tube A (see plate I), flask B, condenser C, and trap E. The latter delivers the entrained water back into the Dewar while the condensed chloroform is received in another vessel L. The vapor of chloroform passes up thru the potassium hydroxide solution and then thru tube D, to the water condenser C, entering by way of the two holes marked J; and the condensation then falls to a common reservoir E where the chloroform and entrained water naturally separate. By keeping the meniscus K, formed by the two liquids, at a certain height in the reservoir the chloroform and water are antomatically, by overflowing, cared for just as fast as the vapor might come over. The whole apparatus is made of glass. For dimensions see experimental part.

Briefly the procedure during a typical determination is as follows: A solution of potassium hydroxide is placed in the Dewar tube, heated by a platinum heating element to the temperature equilibrium corresponding to the hydroxide concentration, and the vapor of chloroform passed thru for twenty minutes. The contents of the Dewar are then transferred as quickly as possible to ice-cold nitric acid solution; and the inorganic chlorine and alkali present determined. Considering the carbon of each chloroform molecule attacked going either to carbon monoxide or formic acid, we can now with the data at hand calculate the amount of each present at the end of any determination.

The results obtained with varying concentrations of

of potassium hydroxide and equal time (twenty minutes) are
seen in the curves on plates II, III, and IV.   Curve A
expresses total chlorine found in milligrams, while B and C
are in terms of chlorine equivalent to formic acid and car-
bon monoxide respectively.   A summation of the curves B
and C necessarily give the values of curve A.   It is be-
lieved that we get a true measurement of the formic acid
present, from the calculation based upon the excess acidity
after neutralization.   Evidently a molecule of potassium
hydroxide is used for each chlorine atom replaced and for
each molecule of formic acid formed.   After allowing the
reaction to take place, the contents of the Dewar tube is
neutralized with nitric acid equivalent to the hydroxide
started with.   It can be supposed that the remaining hy-
droxide after the reaction occurs, reacts with the nitric
acid; and then the nitric acid being the stronger replaces
the formic acid in the formate.   We now have free the
formic acid and whatever nitric acid there may be in excess.
If this is true and also our belief that the carbon in the
chloroform goes either to carbon monoxide or formic acid,
then our curves are truthful expressions of the amounts of
the substance present.

Curve D, Plate III, is total chlorine in milligrams –
for the purpose of comparison.   Curves E and F show the per-
cent of total chlorine which is equivalent to the formic
acid and carbon monoxide respectively.   Curve G shows tem-
perature variation and is quite irregular due to barometric
changes.   If these values are corrected for disturbances

in pressure, using the coefficient for chloroform', a smooth curve very similar in shape results. The irregular curve is shown instead of the corrected one because a true comparison of our results with temperature actually present is desired. Curve H, plate IV, is again total chlorine --- for comparison; I and J express milligrams of carbon monoxide and formic acid respectively. The change in specific gravity of the potassium hydroxide solution at 15°C is shown by K, and gives only relatively an idea of the changes at the temperature used by us.

On plate V are curves from data of experiments run on the same hydroxide concentration (40%) and varying time. Curve L is from total chlorine found and is a measure of the reaction velocity. Curves M and N are per cent of chlorine equivalent to carbon monoxide and formic acid.

Complete data of the two series of experiments is to be found in Tables I and II. The columns of data are under the following headings:

1. Arbitrary number of the experiment.
2. Percent of potassium hydroxide used.
3. Time reaction goes on, in minutes.
4. Chlorine found in milligrams.
5. Formic acid found in milligrams.
6. Carbon monoxide found in milligrams.
7. Percent of total chlorine equivalent to formic acid found.
8. Percent of total chlorine equivalent to carbon monoxide found.
9. Free hydroxide after running experiment, in percent of that present at beginning of reaction.

'Timmerman J.   C.A. 4 (2) 2896 (1910)
ᴸLunge   Chemiker Kalender

10. Average equilibrium temperature of
system.
11. Barometric pressure at time of experiment.

It will be noticed in the chlorine curve A, that up to
60% potassium hydroxide it is practically a straight line and
at an angle of 45° meaning that the change in total reaction
velocity is directly proportional (up to 60%) to the increase
of hydroxide concentration. This fact is also shown by re-
ferring to column "% KOH left" in Table I, where the potassium
hydroxide remaining after the reaction is allowed to take
place, is expressed in percent of that present at the begin-
ning of the determination. The decided change in the direc-
tion of the chlorine curve is probably due to several things.
First, the slight rise in temperature may be taking effect
here, causing a decrease in the solubility of the chloroform
in the hydroxide, which would necessarily slow the reaction
velocity. Second, it is known that some organic liquids,
chloroform included, behave differently in acid and alkali
solutions. In the latter a globule of chloroform, other-
wise spherical, becomes flattened and more inert physically.
Absorption of the alkali on the chloroform is given as an
explanation, which means that the alkali immediately sur-
rounding the chloroform is of a higher concentration than
the rest of the solution. At the potassium hydroxide con-
centration in question, this phenomenon might easily be sup-
posed to have an inhibiting effect on the reaction. The
larger amounts of formic acid at this place would also de-

crease slightly the hydroxide concentration and retard the
reaction.   Another important factor is the stirring.
With the increasing viscosity and specific gravity of the
hydroxide solution, it is questionable whether at this point
our stirring is sufficient and we are measuring the diffu-
sion of the chloroform into the hydroxide; or whether inef-
ficient stirring is obtained and thus sets the reaction
velocity.   This much is true, that with a smaller appara-
tus of the same form (which was used first) and with which
poorer stirring was obtained due to chloroform vapor pas-
sing thru more slowly, that the change in direction of the
curve was similar, but started at 45% instead of at 60%.
This in the writer's view is proof that inefficient stir-
ring is being obtained from 60% on.   This, however, may
not be the main disturbing factor for it is right here(at
60%) that the percent of carbon going to formic acid starts
to rapidly decrease, and the percent of carbon going to
carbon monoxide rapidly increase.   Inefficient stirring
alone should not produce this change.   It will be noticed
at this time that the results at 60% and 70% vary much more
even than at 85% and 100%.   In a reaction of this kind
(with a heterogeneous system) where the maximum effect in
each case is desired, and where by decreasing the rate of
chloroform vapor, the results can be made to fall anywhere
below the curve shown, it is plain that the curve in gen-
eral should not pass thru an average of the points, but
nearer the maximum.

Satisfactory explanation of the formic acid and carbon monoxide curves is quite difficult. As has been stated there are four possible causes for the reaction products as they appear.

First, formic acid alone may be formed which, after changing to the formate, partly decomposes to potassium hydroxide and carbon monoxide.

Secondly, carbon monoxide alone may be formed which in turn with the hydroxide partly goes over to the formate.

Thirdly, both formic acid and carbon monoxide may be formed and in exactly the proportion which we find them, or

Fourthly, both may be formed in the reaction, but changes from one into the other may take place.

Saunders states, "Owing to the partial and variable decomposition of the formate it is impossible to prepare solutions which shall remain equivalent after the reaction has begun, ..." It might be imagined that the carbon monoxide results when the potassium hydroxide acts to split off hydrochloric acid, and the formic acid resulting when the chlorine is replaced by a hydroxyl group. Evidently there is more dissociated hydroxide in the dilute solutions, but this in turn would not be expected to split off hydrochloric acid thus giving a very high percent of carbon monoxide.

If formic acid is formed at all, it would immediately change to potassium formate which in solutions such as we have from 30% on, would not be expected to break down into

carbon monoxide and the hydroxide.   On the other hand the
reverse of this action might naturally be expected.   It is
quite striking that the formic acid by weight (curve J)
after reaching its maximum rapidly decreases to practically
nothing.   It will also be noticed (curve E) that the per-
cent of carbon going to formic acid decreases rapidly to
nothing.   The radical changes taking place at about 60% in
all the curves may be due largely to the hydroxide concentra-
tion which the reaction mixture approaches.   Referring to
column of "% KOH left" in Table I, it is seen that the per-
cent of hydroxide left after running experiment, is very
constant up to 60% when a continual rise sets in.   To clear
up these points, if possible, a series of experiments were
run on the same hydroxide concentration, but varying the
time of reaction.   For this series 40% hydroxide was chosen
as our results with it in the twenty minute series, were quite
high and uniform.

Referring now to plate V and Table II, it is seen that
the percent of chlorine equivalent to formic acid (curve N)
decreases and then increases as time of reaction is made
longer.   Also from Table II that the actual weight of for-
mic acid present first decreases and then increases as the
time is extended.   That the actual weight of carbon monoxide
found varies correspondingly is seen.   The only explanation
for this is that the supposed reaction:

$$HCOOK \rightleftharpoons CO + KOH$$

does take place and is reversible.   As some evidence of the
reaction going from right to left we mention here some

work by Thiele. Using chloroform and sodium hydroxide equivalent to our 35% solution, he found 21.14% chloroform had changed to formic acid, the reacting mixture being at an equilibrium at 25°C. By increasing the temperature the amount of formic acid is increased somewhat.

It is our belief that the fourth possible cause mentioned above explains the changes taking place. That is, both carbon monoxide and formic acid are formed,

$$CHCl_3 + 4KOH = 3 KCl + 2H_2O + HCOOK$$

$$CHCl_3 + 3KOH = 3KCl + 3H_2O + CO$$

but an equilibrium is then set up and determined largely by the potassium hydroxide concentration and carbon monoxide pressure. That the main reaction is producing mainly formic acid up to 60% and then mostly carbon monoxide according-ing as to whether chlorine is replaced by a hydroxyl group or hydrochloric acid is split off. Also that the equilibrium reaction between formic acid and carbon monoxide up to 40% is largely in this direction:

$$HCOOK \longrightarrow CO + KOH$$

but from 40% on the reaction appears to be in the opposite direction due to hydroxide concentration.

We have proven that following reaction:

$$HCOOK \rightleftharpoons CO + KOH$$

takes place and is reversible depending upon conditions present. It has always been supposed the formic acid was a true reaction product and the carbon monoxide occurs from subsequent decomposition. From the way the above theory

Thiele   Ann. 302, 275

can be applied and from the following facts we believe that the carbon monoxide is also a true reaction product.

W. Löb Joist' states that with electrical heating and water being present, bromoform gives formic acid and no carbon monoxide; while under the same conditions chloroform gives carbon monoxide and no formic acid. The fact is important also, that the maximum points in our chlorine, formic acid, and carbon monoxide curves do not appear at the same hydroxide concentration, but in the order of carbon monoxide, chlorine and then formic acid.
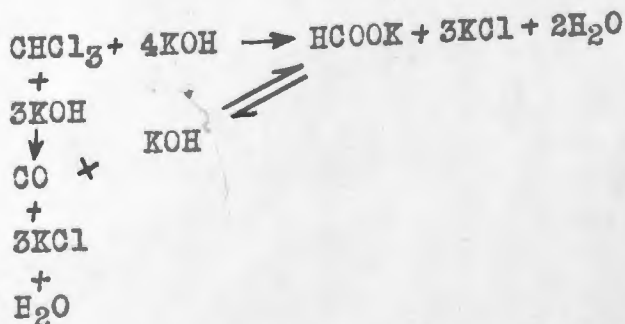
In conclusion, we can say that the supposed reaction between chloroform and aqueous potassium hydroxide expressed as:

$$CHCl_3 + 4KOH = 3KCl + 2H_2O + HCOOK$$

is probably untrue, and that the following reaction expresses the true changes:

$$(a+b)CHCl_3 + [3(a+b) + a] \; KOH \longrightarrow 3(a+b)KCl$$
$$2(a+b)H_2O + (a)HCOOK + (b)CO$$
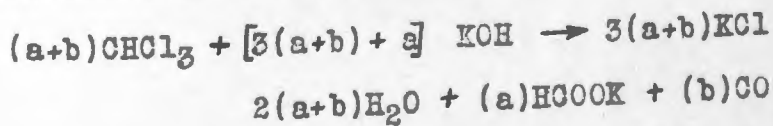
the exact coefficients depending upon existing conditions. The equation is simply a statement of the equilibria following:

$$CHCl_3 + 4KOH \longrightarrow HCOOK + 3KCl + 2H_2O$$

$$
\begin{array}{l}
+ \\
3KOH \\
\downarrow \quad\quad KOH \\
CO \quad \times \\
+ \\
3KCl \\
+ \\
H_2O
\end{array}
$$

This means that both formic acid and carbon monoxide are

reaction products of chloroform and aqueous potassium hydroxide, the amount of each depending upon the character of the hyårpxide; and that then an equilibrium:

$$HCOOK \rightleftharpoons CO + KOH$$

tends to take place, which is governed largely by the hydroxide concentration present and the partial pressure of the carboh monoxide.
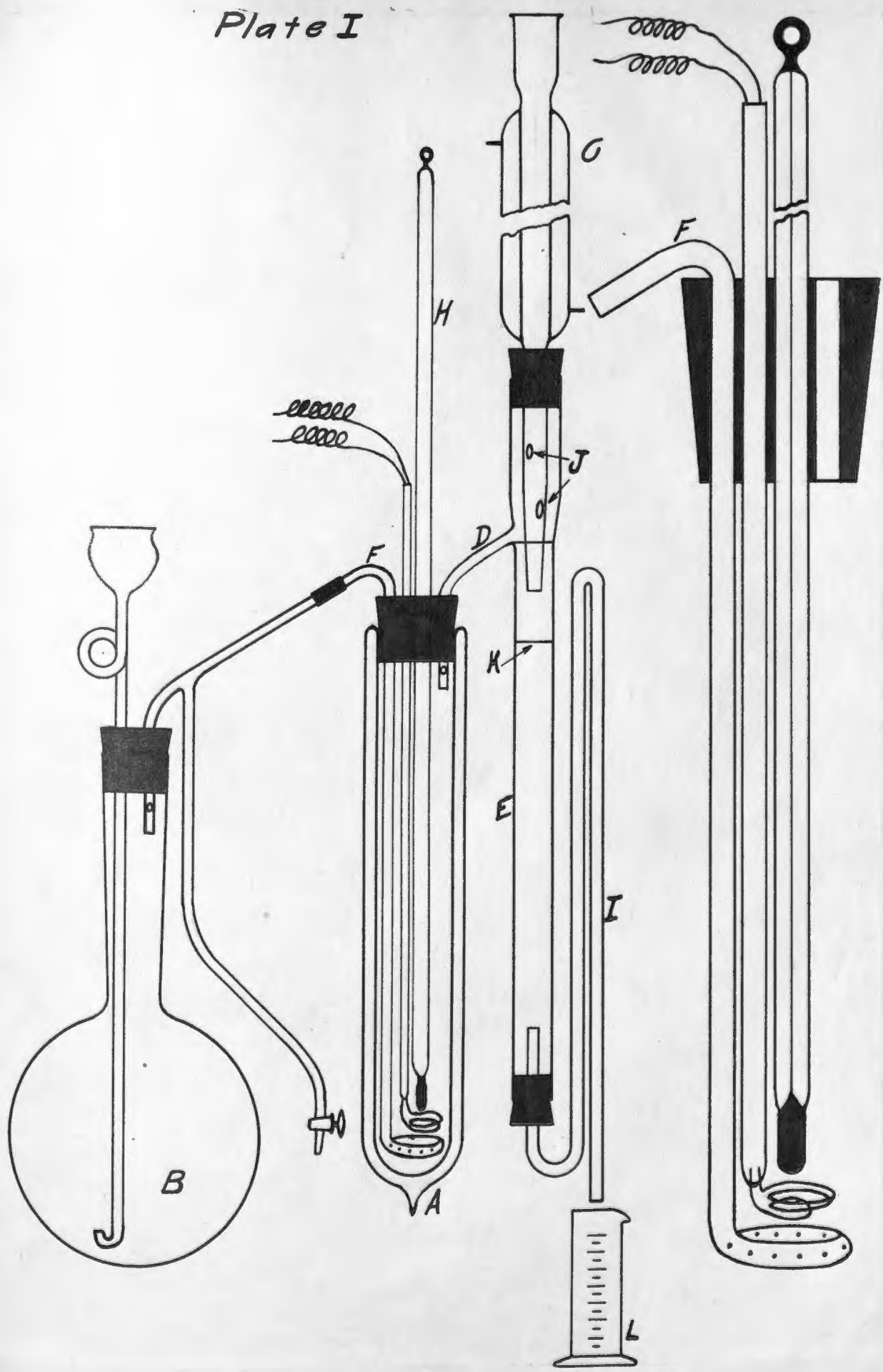
Plate I

Plate II

A = Total Cl
B = Cl → HCOOH
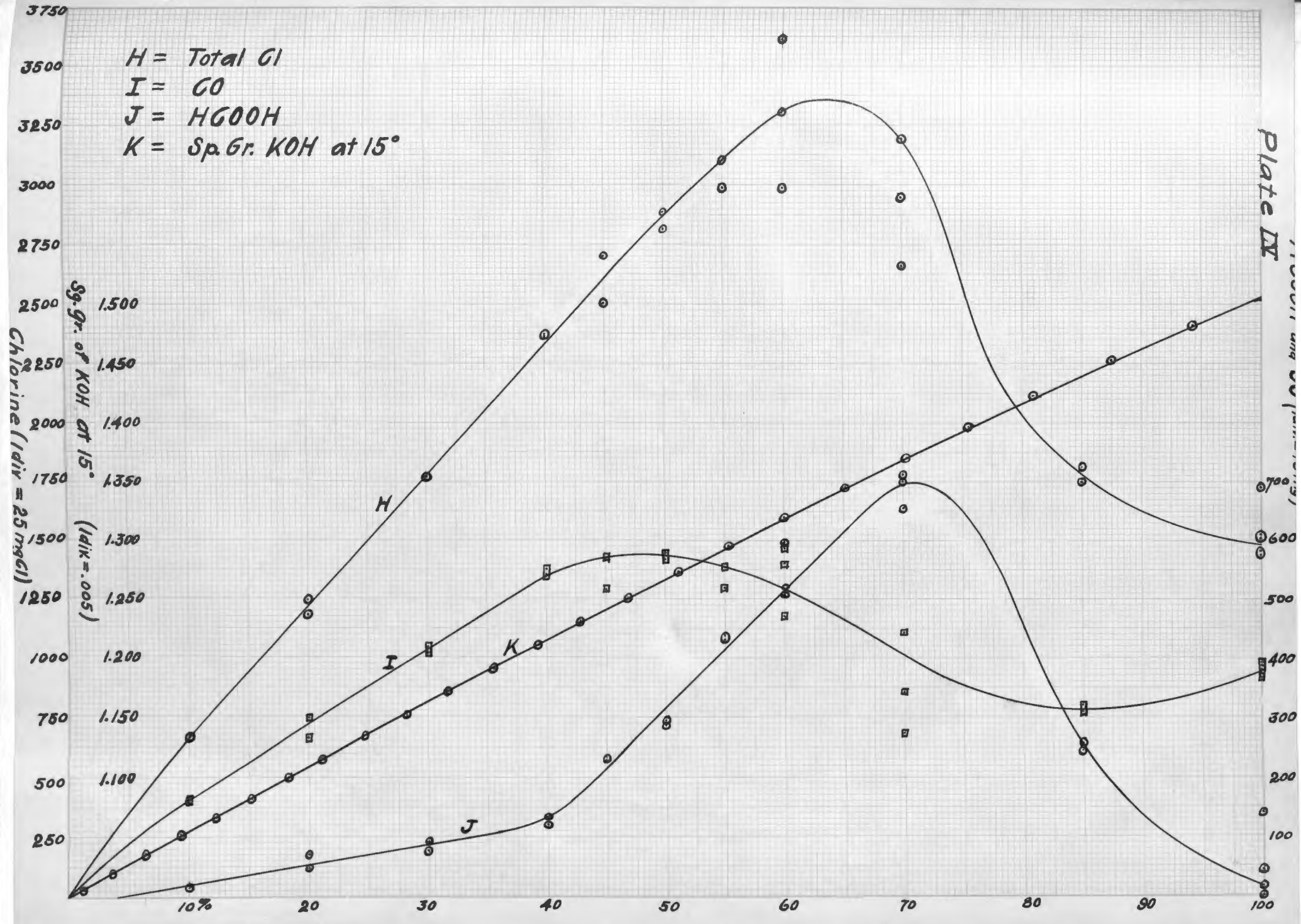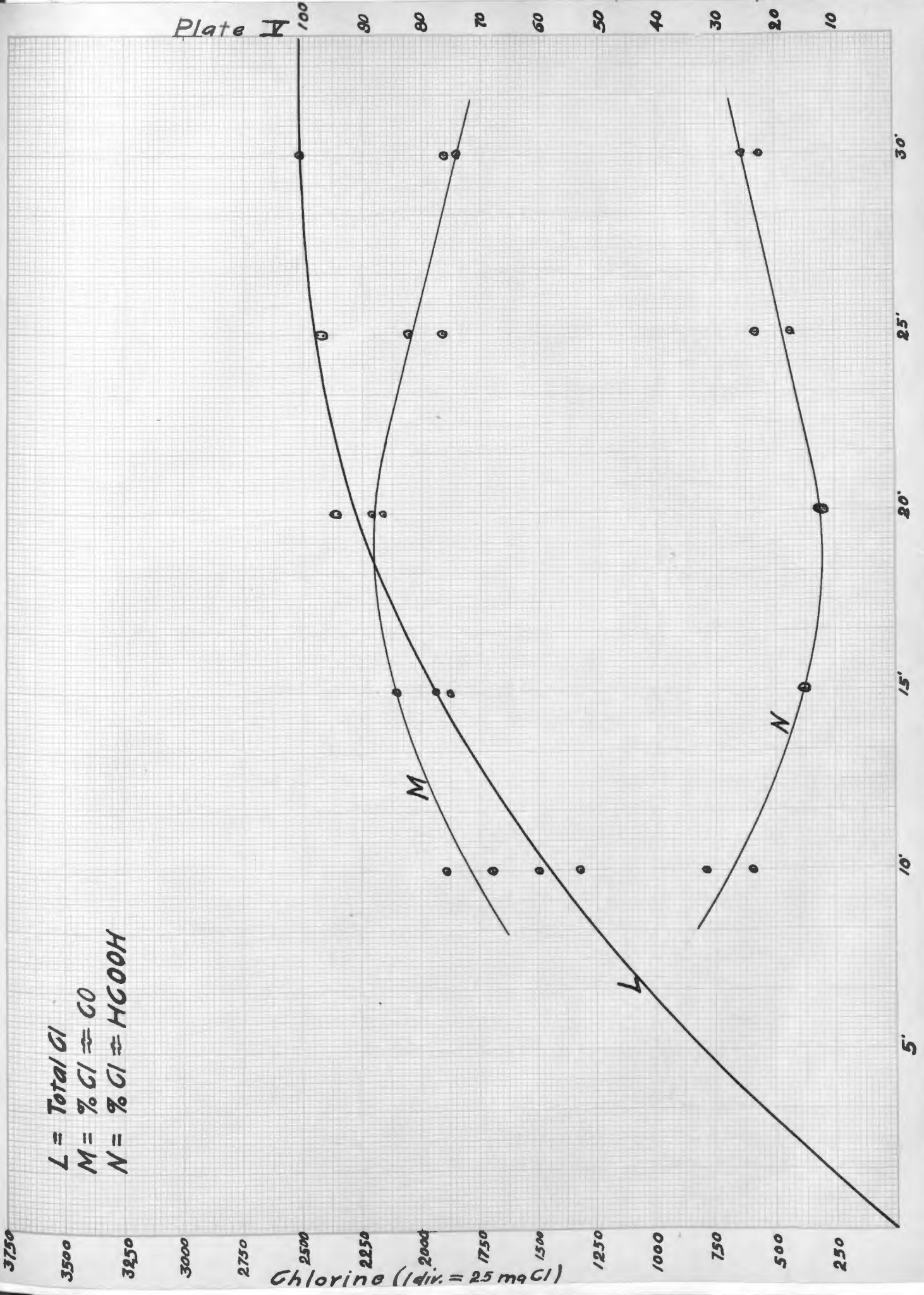C = Cl → CO

Plate III
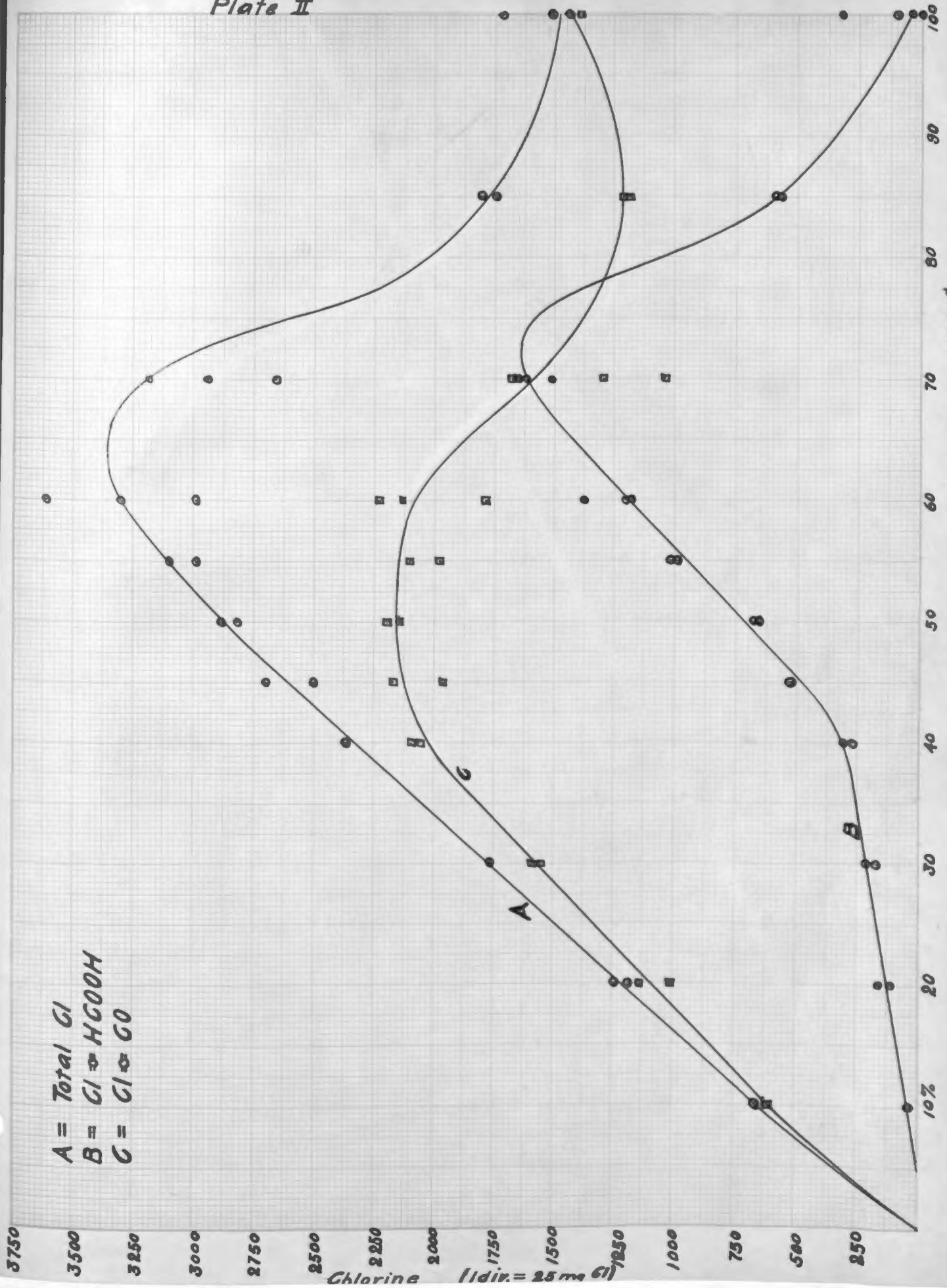
D = Total Cl
E = % Cl ⇌ HCOOH
F = % Cl ⇌ CO
G = Temperature

Plate IV

H = Total Cl
I = CO
J = HCOOH
K = Sp. Gr. KOH at 15°

Plate V

L = Total Cl
M = % Cl ⇌ CO
N = % Cl ⇌ HCOOH

Chlorine (1 div. = 25 mg Cl)
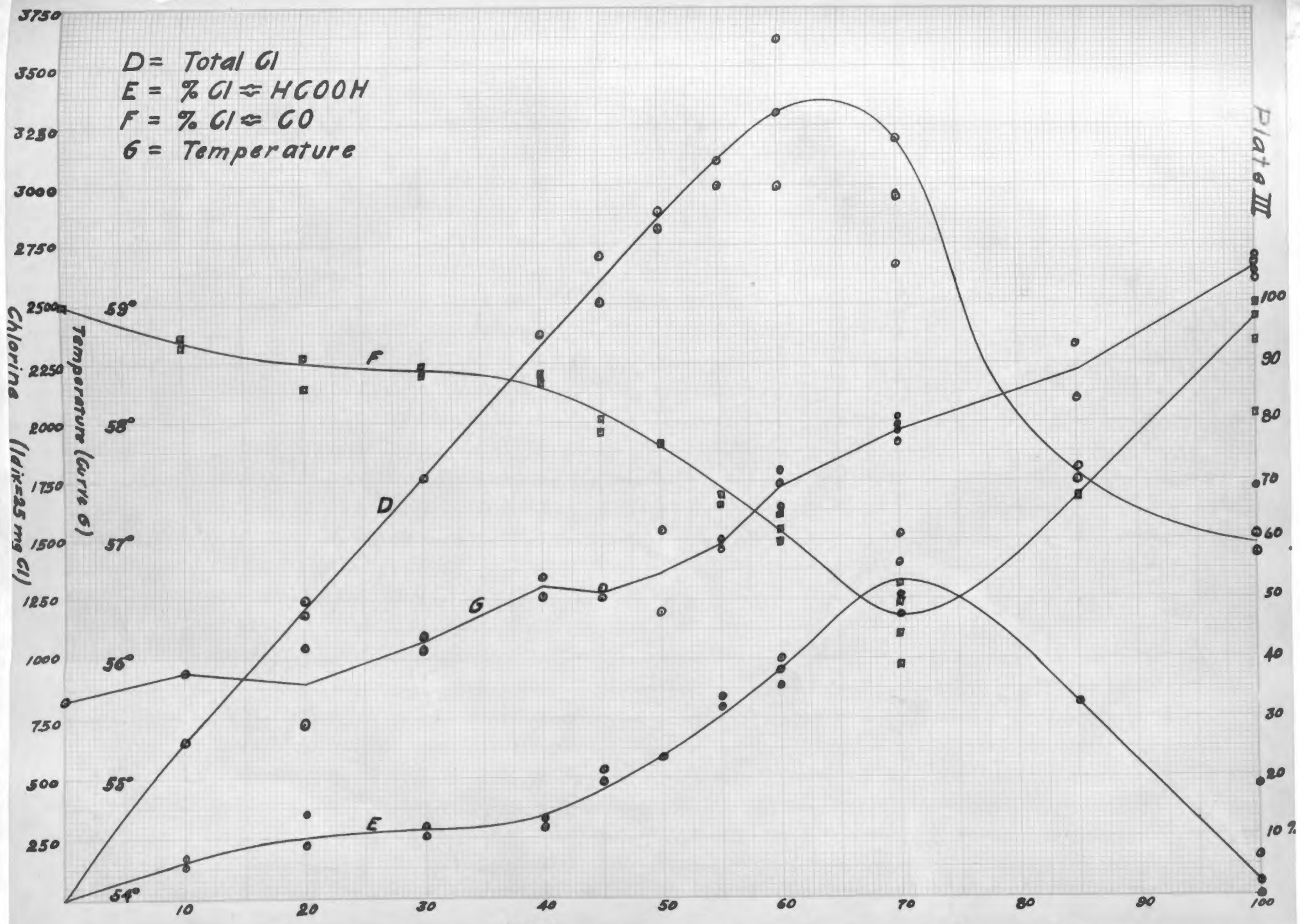
EXPERIMENTAL PART

The chemicals used for this work were of the best obtainable. The chloroform was part Merk's and part Eimer and Amend's, and contained between $\frac{3}{4}$ to 1% alcohol. It was purified by shaking twice with con. sulphuric acid, twice with potassium hydroxide solution, twice with water, dried over calcium chloride and distilled, coming over between 60° and 61° C at 740mm. Kahlbaum's potassium hydroxide was used, the solution being made up by adding about 2400 grams of hydroxide to 1800 cubic centimeters of water. This gave a 12.83 N solution which thruout our work we considered as 100%. No particular effort was made to exclude carbon dioxide so that a small amount of carbonate was present. The silver nitrate and potassium thiocyanate solutions were approximately N/20 and were standardized both by metallic silver and gravemetrically standardized hydrochloric acid solution. The nitric acid solution used for neutralizing contents of Dewar tube, was close to 3N; while the potassium hydroxide and nitric acid solutions used in titrating acidity after neutralization, were about N/3. All acid and alkali solutions were standardized against succinic acid as a standard and checked by the gravimetrically standardized hydrochloric acid.

Checks experiments were made where errors may occur. For instance, the amount of nitric acid 3N necessary to exactly neutralize the hydroxide started with in each determination was calculated. Trying this out on the 50% and 100% hydroxide solutions, it was learned that a slight correction had to be made. Phenolphthaliene was used as

indicator in all acid-alkali titrations. All vessels used, such as flasks, burretters, etc., were calibrated to true cubic centimeters at room temperature. The temperature readings were made with a normal 100° calibtrated thermometer. Distilled water boiled to free it from carbon dioxide was used in all our work.

The apparatus as shown on plate I consists of a liter round bottom flask, a Dewar tube 3 cm.X25 cm. in size, an ordinary water condenser 25 cm. in length, and a trap as shown, which is 25 cm. in total length. Most of the glass tubing used was .7 cm. in diameter. These dimensions are mentioned because it is probable that exact checks on the separate determinations would not be obtainable in an apparatus very different.

In preparation for running a determination, it is necessary to make sure the chloroform is free of phosgen as this may occur. It is also important that the apparatus be clean. Exactly 25cc of potassium hydroxide in each case is measured by burrette, run into Dewar tube and the cork stopper with thermometer, heating element and multiple-hole inlet is now put in place. Before connecting with rest of apparatus it is essential that the tube "D", plate I, which connects the Dewar tube with the trap, is well moistened on the inside with water. If this is not done drops of chloroform adhere to the tube thus blocking the free passage of the vapor one way and the return flow of the water to the Dewar. This being done the apparatus is assembled

and the alkali solution heated to the equilibrium temperature corresponding to the hydroxide concentration as read from curve. No electrolysis was apparent as the fall of potential thru the platinum wire was made small. With the right temperature of the hydroxide, boiling chloroform in flask B, and cold water running thru condenser, one is ready to start the reaction. With watch, note book, and lens at hand, the flask B is connected with inlet to Dewar. At the time when fair stirring is obtained, the time is noted to the second. Temperature readings should be made every minute and the apparatus continually watched. The boiling of the chloroform should be constant and as rapid as contents in Dewar will allow. The return flow of the water to the Dewar should be uniform as possible, otherwise several drops together in tube D will cause intermittent passage of the vapor and serious trouble - to be done away with only by slowing the boiling of the chloroform.

During the reaction potassium chloride crystallizes out, - the time depending upon the hydroxide concentration - and usually causes a slight increase in temperature. Also appreciable water is formed during the experiment and if not carried away fast enough by saturating the chloroform in the reservoir, the meniscus K must be lowered by pulling down tube I, in order that the hydroxide solution is not appreciably diluted - causing a corresponding drop in temperature. This lowering of the meniscus is very important if the temperature is to remain constant. During the

whole experiment the electrical heating is continued in order to reduce the amount of condensed chloroform in the Dewar tube. The initial condensation of chloroform while the apparatus is warming up, is enough so that at all times there is sufficient liquid chloroform present to assure saturation of the aqueous phase.

After the reaction has continued for exactly twenty minutes it is stopped and contents transferred quickly as possible to a beaker containing nitric acid 3N equivalent to alkali started out with. This acid is always diluted so is never 3N at this time, and is cooled with ice so the resulting temperature is between 20° and 25°C. Care in taking the apparatus apart is necessary as pressure changes take place and some of the reaction products may be lost. The thermometer etc. and Dewar tube are carefully washed and most of the aqueous solution decanted into a 1000 cc graduated flask. The rest with the small amount of liquid chloroform is placed in a separatory funnel and the chloroform washed in the usual way. The wash water is added to the contents of the graduated flask, and solution made up to the mark; aliquot parts then being titrated for inorganic chlorine and acidity. Check titrations were made in each case. In the titration for acidity it is necessary to run past the end point and come back till the pink barely shows.

Our methods of calculations may be easily understood by referring to the equations used, as shown in the exact copy of a page of our notes.

The following is an exact copy of the data from our notes on a typical determination:

#45   January 21, 1916

25 cc KOH(50%) used.   B.P. 731.7 mm   Time, 20 minutes

cc HNO_3 3N(   ) used in neutralizing

Continual heating by 2-32 c.p. and 2-16 c.p. globes.

Time	Temperature
9:30	
1	56.30
2	.38
3	.39
4	.40
5	.42
6	.40
7	.38
8	.36
9	.34
10	.30
11	.30
12	.34
13	.32
14	.33
15	.36
16	.37
17	.38
18	.38
19	.37
20	.

Vol. $CHCl_3$ sep. by trap 165 cc

$CHCl_3$ in Dewar   35 cc

Meniscus dropped about   2 cc

Titrations (Cl) (25cc)

	$AgNO_3$	KCNS
I	43.60 cc	4.65 cc

$$40[43.60 - (.962 \times 4.65)]1.797 = 2812 \text{ mgCl}$$

II	43.75 cc	4.71 cc

$$40[43.75 - (.962 \times 4.71)]1.797 = 2819 \text{ mgCl}$$

Average   2816 mgCl

HCOOH

			KOH actually needed
I	13.58 cc	.37 cc	. 13.19 cc
II	13.47 cc	.19 cc	. 13.27 cc
	Average		13.23 cc
	correction		.12
			13.35

$$20\left[(13.35 \times 18.01) - (1.583 \times \tfrac{2816}{20})\right].819 = 286 \text{ mg.HCOOH}$$

CO

$$[2816 - (2.311 \times 286)] .2632 = 567 \text{ mgCO}$$

HCOOH $\leftrightarrows$ 23.5% of Cl
CO $\leftrightarrows$ 76.5% of Cl

The method used running the experiments on the variable time series is exactly the same as that already given except the reaction is allowed to proceed for different periods of time and that the same strength potassium hydroxide was used to start each experiment.

Necessarily there are some errors in this method due to mechanical control and differences in conditions; but in order to get as fair results as we have obtained, it takes practise until the work becomes routine even to a practised manipulator.

VARIABLE CONCENTRATION SERIES

TABLE I

# of Exp.	% KOH	Time	MgCl	Mg HCOOK	Mg CO	%Cl HCOOK	%Cl CO	%KOH left	Temp.	B.Press.
56	10%	20	660	15	165	5.3	94.7	40.9	55.90	745.9
55	10	20	662	20	162	7.0	93.0	40.4	55.88	745.0
54	20	20	1245	48	298	8.9	91.1	43.6	56.10	744.4
53	20	20	1178	72	266	14.1	85.9	45.7	55.46	727.9
52	30	20	1768	77	418	10.1	89.9	46.4	56.20	750.3
51	30	20	1768	92	409	12.0	88.0	46.0	56.10	746.7
49	40	20	2373	121	551	11.8	88.2	45.8	56.52	747.4
50	40	20	2368	134	542	13.1	86.9	45.6	56.68	747.7
48	45	20	2703	231	571	19.7	80.3	43.7	56.60	741.1
47	45	20	2504	234	517	21.6	78.4	47.5	56.52	741.1
45	50	20	2816	286	567	23.5	76.5	46.6	56.40	731.7
46	50	20	2884	293	581	23.5	76.5	45.3	57.08	748.9
44	55	20	3104	432	554	32.1	67.9	45.0	56.93	739.8
43	55	20	2991	439	520	33.9	66.1	46.7	57.00	742.1
65	60	20	3307	509	561	35.6	64.4	45.7	57.48	740.7
61	60	20	3616	596	589	38.1	61.9	40.2	57.46	739.1
57	60	20	2986	519	470	40.2	59.8	50.3	57.60	748.2
58	60	20	2629	518	377	45.5	54.5	55.6	57.28	739.2
62	70	20	3192	655	442	47.4	52.6	53.5	57.83	737.6
66	70	20	2145	470	279	50.6	49.4	68.5	58.04	740.6
60	70	20	2946	714	341	56.0	44.0	56.0	57.92	738.9
59	70	20	2665	704	273	61.0	39.0	59.7	57.94	739.2
67	85	20	1750	247	310	32.6	67.4	79.9	58.20	726.6
68	85	20	1808	257	320	32.8	67.2	79.2	58.65	741.0
42	100	20	1728	141	369	18.8	81.2	83.8	59.20	740.0
63	100	20	1512	43	372	6.6	93.4	86.4	59.26	741.3
70	100	20	1522	15	391	2.3	97.7	86.4	59.24	739.4
69	100	20	1437	-2	378	0	100.	87.3	59.26	741.1
64	100	20	1456	-38	383	0	100.	87.2	59.32	742.3

VARIABLE TIME SERIES

TABLE II

#of Exp.	% KOH	Time	MgCl	Mg HCOOH	Mg CO	%Cl HCOOH	%Cl CO	%KOH left	Temp.	B.Press.
75	40	10	1506	157	301	24.1	75.9	64.2	56.24	732.1
76	40	10	1320	182	237	31.8	68.2	67.9	56.30	741.8
74	40	15	1873	129	415	15.9	84.1	56.6	56.24	740.0
73	40	15	1940	129	432	15.4	84.6	55.2	56.10	740.0
49	40	20	2373	121	551	11.8	88.2	45.8	56.52	747.4
50	40	20	2368	134	542	13.1	86.9	45.6	56.68	747.7
71	40	25	2432	187	526	17.6	82.2	43.4	56.31	741.4
72	40	25	2409	244	486	23.4	76.6	42.9	56.36	741.1
78	40	30	2538	256	512	23.3	76.7	39.9	55.68	728.1
77	40	30	2535	282	495	25.7	74.3	39.5	.55.80	730.0

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