ALTERNATING CURRENT ELECTROLYSIS

(Original)

1.

A   THESIS

PRESENTED TO THE FACULTY OF ARTS AND SCIENCE

OF

THE UNIVERSITY OF MANITOBA

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE

DEGREE OF MASTER OF SCIENCE,

By

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March,1927.

CONTENTS.

List of Diagrams and Figures.

Part I   Introduction.
Section 1.

Historical.

An alternating current when passed through an
electrolyte by means of electrodes will, under certain
conditions, produce no visible decomposition of the
electrolyte on these electrodes, while under other con-
ditions, rapid decomposition takes place. The gases
produced are found to be violently explosive, so much
so that the dangers of experimentation were complained
of as early as 1837; at which time some work was done
by De la Rive.

The first work of importance on the subject
of alternating current electrolysis was performed by
Maneuvrier and Chappius (1) in 1888. The following
extract is taken from their work, which was chiefly of
a qualitative nature, "... for every platinum electrode
of a certain size there is a current below which there
is no evolution of gas. On the other hand more and
more gas is evolved as the current strength is increased.
In every case chemical analysis has shown that the gases
at either electrode have the same composition. They are
in fact the gases of water, forming an explosive mixture
but in which oxygen forms less than a third of the total
volume. Moreover, the volume of gas liberated per am-
pere minute is always more or less under the theoretical
quantity of 104 ccs.,# which would under similar conditions

#apparently misprinted for 10.4 ccs.

be evolved by a continuous current." They suggest that
the difference is due to secondary reactions, and note
the presence of ozone in the liberated gases.

Certain work on this subject was also per-
formed by Ayrton and Perry (2) and by Kennelly (3)
but their results were uninterpreted and are of little
value.

The first theoretical discussion of impor-
tance was made by Mengarini (4) in 1891 who was the
first to build up the laws of Maneuvrier and Chappuis
from the consideration of the elemental waves of an
alternating current. It is unfortunate that his work
contains several apparent inaccuracies which affect
the value of his results. He derives an expression
for the electromotive force of polarization which
gives a sine wave in advance of the current wave but
gives it twice the period of the current wave.

Hopkinson, Wilson and Lydall,(5) two years
later give their experimental determinations of the
relation of the potential difference wave to the curr-
ent wave. All their curves show that the current
leads the voltage by a large phase difference, which
fact does not agree with the treatment of Mengarini.

In the same year (1893) Malagoli (6) made
a contribution to the theory of alternating current

electrolysis in which he develops a formulae from which
can be evolved all the laws given by Mengarini. Further
reference will be made to this paper in the theoretical
discussion in this thesis.

Of more recent origin we have the work of
Marsh (7) in 1920. This work is not of importance to
the research of this thesis, being concerned chiefly
with the length of time, under varying conditions,
required for platinum to become sufficiently coated
with platinum black to prevent the evolution of gas.
His results appear to be poorly interpreted.

Reference is also made to the work with lead
electrodes by Sheldon and Waterman (8) and to the
work of Cooper (9) in which he shows the similarity
of the phase difference between the voltage and the
current to a capacity effect such as in condensers.
In a condenser circuit the current leads the voltage
which is as found by Hopkinson, Wilson and Tydall.

It is a noteworthy fact that the early
workers on this subject take little cognizance of
the work done by their co-workers on this subject.

2.   The Origin of the Investigation.

The application of electricity to heating
problems has again brought up the subject of alterna-
ting current electrolysis. In the water-resistor type

of electric boiler, which type is finding wide application because of its simplicity and economy of design, heat is generated by passing the electric current by means of iron electrodes through resistant water. Decomposition of the water means loss of energy, but, that which is of greater importance, the presence of the products of the electrolytic decomposition present an explosion hazard which has exhibited itself on several occasions. The existence of such a danger was at first denied but the work by Shipley and Blackie (10) gave conclusive evidence to show that hydrogen and oxygen are produced in the types of boiler used commercially. Electrolytic gases were found by them to be produced with a large number of types of electrodes and the rate was found to increase near the boiling point.

The present research was commenced with the object of discovering the factors which affect the rate of alternating current electrolysis, whereby these factors could be so controlled as to diminish or to entirely eliminate the decomposition of the electrolyte.

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Part II.   Preliminary Experiments.

1. Experiments with Platinum.

        To arrive at the fundamental reactions of
alternating current electrolysis the investigation was
commenced with platinum electrodes. Two pieces of plat-
inum foil of dimensions, 1 by 2.5 by .0063 cms. were
sealed by means of platinum leads, inside a glass tube.
An air-cooling jacket, a reservoir and a tube for collecting
gases were connected to the electrode tube at the ends;
the whole resembling a miniature hot-water heating system.
The electrolyte was natural water.

        Thirty-five experiments were carried out with
this apparatus of apparent current density varying from
0.03 Amps. per sq. cm. to 0.1 Amps., and at different
temperatures. Hydrogen was found in all the gases that
collected. At low current densities no gas collected.
Gas was first produced on the sharp corners of the elec-
trodes and at higher current densities on the edges. In
no experiment of this series was gas produced on the sides.

        A second series of ten experiments were carr-
ied out with diluted sulphuric acid as the electrolyte.
The apparent current density was successively increased
from 0.1 Amps. to 0.33 Amps. In no case was gas produced .
The platinum became coated with platinum black.

2. Experiments with Carbon.

        A similar apparatus was set up using flat carbon

electrodes. Twenty experiments were carried out at
varying currents and temperatures. As in the series
with platinum gas was first evolved from the corners.
At higher currents it was evolved from the edges and at
still higher currents it was evolved from the sides.
The gases on analysis showed the presence of hydrogen,
oxygen and carbon dioxide.

An apparatus was designed in which ten carbon
rods projected through a rubber stopper into a spherical
glass jar. The usual type of cooling system was installed
but on a larger scale than the above. When the current
was passed through the carbons which were connected
alternately in parallel and the electrolyte, a copious
evolution of gas took place from the projecting ends.

3.   Importance of Current Density.

The above experiments indicate that electrolytic
gases are first produced on projecting points and edges
of electrodes, and in larger quantities than on the sides.
The natural conclusion to be drawn from these observations
is that the current density, given in amperes per square
centimeter, is greater on these projecting points and
edges than on the sides. This is born out by the fact
that although the path of the current between two points
on opposite electrodes may in some cases be longer than
between two sides, the volume of the electrolyte through
which the current may pass is much greater and the resis-
tance along this path will be less than along a path

between the sides. The larger part of the current will take the former path which means a greater current density on the points and edges.

These experiments have indicated that the primary factor in the production of gas by alternating current electrolysis is current density.

Part III.   Uniform Current Density.

1. Introductory.

        The variation of current density over the
surface of the electrodes has been totally neglected
by early experimenters. Values given by some are of
little use, others give no values. Marsh (loc cit)
briefly mentions a variation of current density to
explain an anomaly in his result. The preliminary
experiments of this research, having shown that gas
is first produced at the places of high current den-
sity, showed also that no progress could be made with-
out a design of electrode on which the current density
is as nearly as possible uniform over the surface.

2. Equipotential surfaces and Current Density.

        Imagine two identical spherical electrodes
in a uniformly conducting electrolyte, at a distance
apart great as compared with their diameter and with
a difference of potential between them. This difference
of potential may be continuous or alternating without
influencing the reasoning. The boundaries of the electro-
lyte are at a great distance from the electrodes as com-
pared with their diameter. All points on the plane per-
pendicular to the line joining the centers of the electrodes
and at the point of bisection of this line will be at the
same potential. No work will be done in moving a body
from one point to another, and if any two points are
connected with a conductor no current will flow.

18.

This plane is an equipotential surface. All other equi-potential surfaces will be in the shape of spheres approximately concentric to the electrodes. An analogy is seen in the ordinary text-book example of equi-potential surfaces about a single, charged, spherical conductor in a non, conducting medium. The proximity of the second electrode causes a distortion of the concentric spheres which distortion increases as the distance between the electrodes decreases. The central plane is essentially a sphere of infinite radius.

The current density at any point varies inversely as the distance to the nearest equipotential surface. If the resistance of the electrodes is negligible their sur-faces will be equipotential surfaces. From the above reasoning it is seen that the current density on the surface of the sphere will be uniform if the nearest equi-potential surface is concentric to the sphere, and the uniformity depends on the concentricity.

The above conditions are ideal, and cannot be obtained experimentally, but their consideration is nec-essary in order that necessary deviations from these conditions may be better understood.

3. Uniform Current Density with Circular Electrodes.

Imagine two circular discs fitted tightly in the ends of a cylindrical vessel with insulating walls the space between the electrodes being filled with a uniformly conducting electrolyte. The discs are parallel and have

a difference of potential. The equi-potential surfaces
are parallel planes and the conditions for uniform current
density are satisfied. No po$\overset{s}{\wedge}$tulation is necessary as to
relative dimensions, as in the case of the spheres.

An apparatus was constructed using this principle
on the design shown in figure 1. A and B are the two
platinum electrodes, to which connection is made by the
mercury filled arms. The gas collecting trap with a
thermometer, is shown above the electrodes. The electrolyte
flows through the trap to a water cooled tube and back into
the base of the electrode chamber. Any gases that are pro-
duced collect in the tube C.

The experiments performed with this apparatus
will be given presently. The opposing factors to uniform
current density were, the inlet and outlet, the impossibility
of obtaining perfect fitting electrodes and the temperature
variations. The latter defect, which causes a violation of
the condition given above of a uniformly conducting electrolyte
and the limited range of its use, caused the eventual discard-
ment of this type of apparatus.

4. Equi-potential Lines and Current Density with Rod Electrodes.

Returning to the experiments given in Part II. section
2, with carbon rods as electrodes, it was found that gas evol-
ution took place on the ends of the electrodes, where it is
assumed the current density was greater. The simpler case of
two rod electordes projecting into an electrolyte through an
insulating substance, and a cross-section of the equi-potential
lines that would exist with a difference of potential across
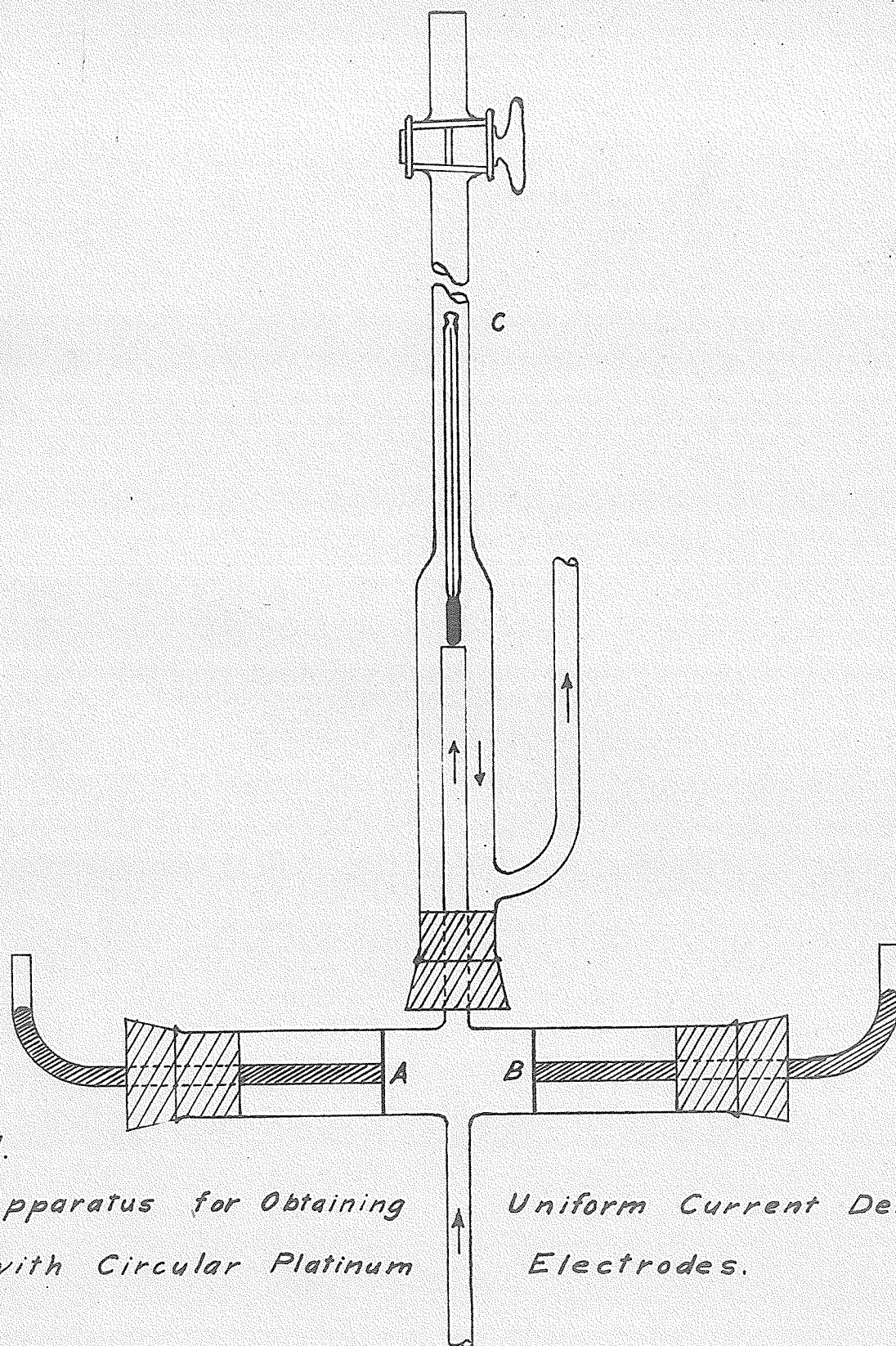
Fig. 1.

Apparatus for Obtaining Uniform Current Density
with Circular Platinum Electrodes.

the electrodes, is shown in figure 2a. Except for upper boundary A B, the bounds of the electrolyte are not shown, and are considered to be infinite. The rods are parallel and the ends of the electrodes are hemispherical. This is similar to the one which occurs in the commercial type of electric boiler in use at the time of writing.

The resistances from the projecting ends C and D of the electrodes are less than on the sides, and the equi-potential lines are therefore much closer together on these ends. High current density is the result.

The evaluation of the absolute current density on such a point, rounded for simplicity, would be a difficult matter, and could only be obtained by means of complicated integrations. There is no doubt but that it would be found to be related to the curvature, the greater the curvature the greater the current density, and the current density would be a minimum when the curvature is zero, that is on a flat surface. It is estimated that the current density on a sharp point may amount to many hundred times that on the flat surface. It is necessary to note here that the direction of the point makes no difference to the current density as the current will travel through all possible paths from one electrode to the other.

5. Shielded Electrodes to Obtain Uniform Current Density.

From the above experimental work and consideration of the equi-potential lines about electrodes, the final
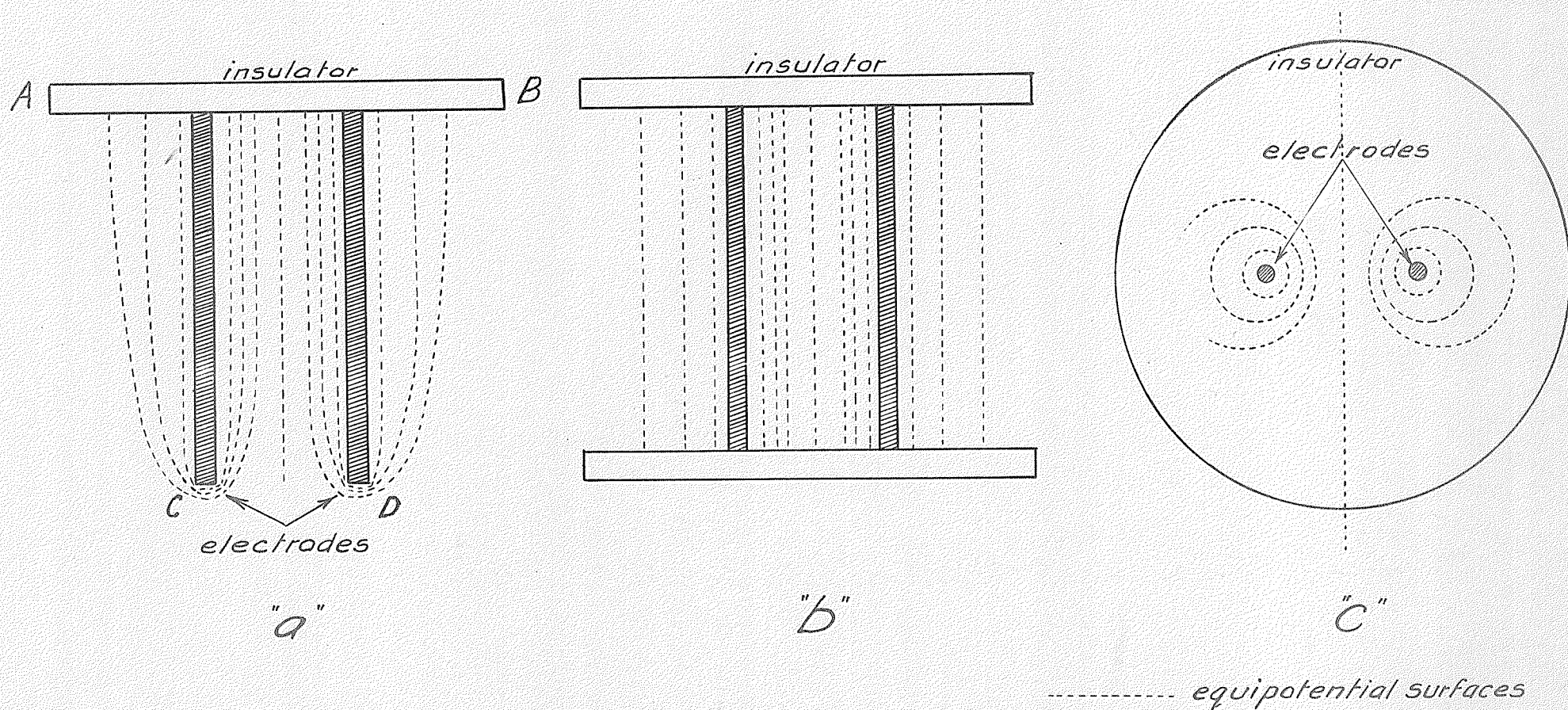
Fig. 2. Equipotential Surfaces about Unprotected and Protected Electrodes.

design of electrode, which was used with modifications,
throughout the remainder of this research, was developed.
A combination of the two theoretical cases given in
sections 2 and 3 of this part was designed as shown in
figure 2 b. In this design two identical cylindrical rod
(or tube) electrodes are projected from one flat insulator
to another, at a distance apart great as compared with
their diameter. The cylinders may be of any convenient
diameter and are parallel to one another. The insulating
plates are also parallel and their boundaries are at a
great distance as compared with the diameter of the electrodes.
No part of the electrodes except that between the plates is in
contact with the electrolyte.

The equi-potential surfaces will be approximately
concentric cylinders as shown in the figure. These sur-
faces are shown again in cross-section in figure 2c. This
cross-sectional view is identical to a cross-section of
the case of the spherical electrodes of
section 2 of this part .

Confirmation of the production of uniform current
density by this method was not forthcoming until a later
date, but will be included here to complete this part.
Using a type of apparatus of the above design of electrodes
it was found that on increasing the current density from
zero, gas was (generally) first evolved from certain points.
These points were not particularily located but seemed to
be due to local metallic differences on the surface. In all

cases these traces of gas were followed on a slight increase
of current by a general evolution over the surface.

A quantitative proof of the uniformity of current
density lay in the corrosion of the electrodes. The rate
of corrosion was found to increase with an increase of
current density and to be roughly proportional to it. When
one part of the rod electrodes for some reason corroded
away more than other parts, the current density was increased
on this narrower part, causing greater corrosion and eventu-
ally cutting it in two. In the experiments with apparatus
using the above design, the corrosion was found to be very
uniform, and in one case the electrode, although 86 per
cent corroded away, did not vary in diameter more than
two-thousandths of a centimetre over its entire surface.

Part IV.   Experiments at Low Current Density.

1.   Platinum electrodes.

Using natural water in the apparatus as
described in Part III. section 3, and shown in figure 1.,
five experiments were performed at the boiling point and
at current densities from 0.05 to 0.13 amps. per sq.cm.
The duration of each experiment varied, the aggregate of
the five being 185 hours. The residual gases were analyzed
by an apparatus consisting of a eudiometer, a Hempel's
pipette with sodium pyrogallate to remove the oxygen, and
a palladium tube to remove the hydrogen.

In all of these experiments the analyses
indicated the presence of traces of hydrogen. The oxygen
content was low.

With an electrolyte of approximately 0.0003 N,
Calcium sulphate a series of twelve experiments at gradually
decreasing current density of from 0.1 to 0.016 amps. per
sq. cm. In all cases evidence of the production of hydrogen
was obtained, although in the lower current densities the
rate was very low. The final experiment operated at a
current density of 0.016 for 150 hours and produced 0.7 ccs
of hydrogen as found by analysis.

The production of hydrogen on platinum at such
low current densities was found to be in distinct disagree-
ment with subsequent results with platinum in which it

was found that a current density of 0.75 amps per sq. cm. was necessary to produce any decomposition. Lack of uniform current density in the above apparatus might partly account for the difference, but the disagreement is too great. The more probable error lies in the gas analysis.

2. Iron Electrodes - Apparatus.

The above apparatus had a very limited range and its experimental usefulness was limited. An apparatus on a much larger scale was eventually developed, after considerable experimental difficulties had been overcome . The final apparatus is shown in Plate I. (see frontispiece). Uniform current density was obtained using the principle outlined in Part III. section 4,. The electrode chamber was a glass bulb and contained six electrodes of mild steel (carbon content 0.174%). Each electrode was exposed to the electrolyte for a distance of 19 cms, and their diameter was 0.68 cms. The electrodes were placed in a circle and the ends of each were protected by a large rubber stopper at the top and bottom. Large bore connections to the electrode chamber for the flow of the electrolyte were provided. Each electrode was connected to a switch on the distributing board, by which any combination of electrodes could be connected

through the ammeters and resistances (not shown) to
the switch-board. A voltmeter, pilot lamps, cut-outs,
etc. were included in the electrical set-up.

Above the electrode chamber was placed a
specially designed gas trap. The electrolyte on enter-
ing the trap was given a circular motion, by which
the gas was centrifugally forced away from the elec-
trolyte outlet to the gas collecting apparatus. The
gas collected in a pipette and could be drawn off into
a gas bulb for analysis.

The heat developed in the electrode chamber
was used up by passing the electrolyte through water-
jacketted brass tubes connected in parallel. The flow
of tap water in the jackets could be accurately controlled.
The electrolyte flowed, as in a hot water heating system
by convection. A reservoir took care of the expansion
and formation of steam. A small thermometer was placed
in the electrode chamber and in the gas trap above.

To maintain the high temperature at lower
currents the whole apparatus was encased in a heat-
proof box and auxiliary heaters in the box prevented
radiation.

With this apparatus readings were sometimes
taken over a considerable period, which necessitated

it being operated unattended. A certain element of danger existed in the possibility of explosive gases collecting in the electrode chamber and causing an explosion. A more immediate danger lay in over-heating. An over-night increase in the line voltage, a change in the room temperature, or, as happened several times a slow leak in the rubber connections which would lower the electrolyte to such an extent as to prevent its flow, would unbalance the conditions which gave steady boiling, and cause a violent and dangerous boiling which would damage the apparatus.

These difficulties were eventually overcome by a glass float in the reservoir, by which any elevation or depression of the level caused the permanent cutting off of the current. A dangerous collection of gas would raise the level and disconnect the power. Although lessening the danger this automatic control was inconvenient as on innumerable occasions experiments were incompleted owing to the action of the cut-off.

The gases were analyzed by a Burrell Precision Gas Analysis Apparatus. The oxygen was absorbed by potassium pyrogallate until a constant volume was obtained in the compensated burette. Hydrogen was removed by passing the gas over copper oxide at $280^{\circ}C.$, until no further decrease in volume was observed.

3. Iron Electrodes - Experimental.

The above apparatus was filled with 0.001 N. sodium hydroxide, and electrodes 1,3, and 5 were connected against 2.4 and 6 electrodes, the electrodes being numbered around the apparatus. The resultant gases, after operating at the boiling point, at a current density of 0.037 amps. per sq. cm. for 54 hours, contained less than two ccs. of hydrogen. The electrodes at the start had a metallic luster but soon became dark with corrosion.

Despite numerous accidents, fifteen complete experiments were carried out at current densities starting from 0.025 and increasing successively at intervals of 0.01 up to 0.2 amperes per sq. cm. The strength of the electrolyte was increased to 0.005 N in the latter part of the series. The number of electrodes used was decreased. Steady boiling was maintained throughout, an experiment and the duration of each experiment averaged about twenty hours. The gases that collected were residues from the steam and in no case was hydrogen detected. The analyses averaged about 90% nitrogen and 10% oxygen. This is evidently due to air having brought into the system and part of the oxygen having been combined with the iron.

These experiments indicated that electrolyte decomposition by alternating currents does not take place at a current density of 0.2 amperes per square centimeter and below.

Part V.   Experiments at High Current Densities.

1. Apparatus.

The apparatus described in the last chapter was very efficient in the collection of gases. The chance for escape of gases produced in the system was small and the only air which entered was that which diffused through the pipe to the reservoir. On the other hand the range of current densities at which it could be operated was limited, and the temperature, an important factor in the production of gas, was difficult to control. These led eventually to its abandonment.

An apparatus was developed, after repeated trials, by which the temperature could be accurately controlled, and which was capable of being adapted to an almost unlimited range of current densities. The apparatus in its final form only, will be described. This is shown, except for a few minor alterations in Plate II. (see frontispiece)

The same method of obtaining uniform current density was used with the exception that the electrodes were on separate pairs of insulators and situated some distance apart. Observations were made on each separately. A four litre Pyrex beaker acted as the electrode chamber, and the gases , when produced, were

-LEGEND-

A — AMMETER
B — BATTERY
C — GAS COLLECTING FUNNEL
D — D.P.D.T. SWITCH
E — ELECTROLYTE CHAMBER
F — FUSE
G — STORAGE AND OVERFLOW
H — D.P. CONTACT SWITCH
I — FLOW REGULATOR
J — S.P.S.T. SWITCH
K — S.P.D.T. SWITCH
L — LAMPS
M — MOTOR
N — COOLING COIL
O — RELAY
P — POTENTIOMETER
Q — ELECTRODES
R — RHEOSTAT
S — SERIES-PARALLEL WIRE-BOX
T — MERCURY THERMOSTAT
U — ELECTROLYTIC CELL
V — VOLTMETER
W — EUDIOMETER
X — MERCURY CONTACT CUP
Y — SOLENOID
Z — RUBBER CORK
a — STIRRING PADDLE

WATER

BUS

A.C.

GAS

Fig. 3. Complete wiring diagram and assembly of electrical apparatus in determining rate of a.c. electrolysis.

D.C. BUS

V

V

J

J

A

A

A

J

J

E

J

J

SWITCH

BOARD

A.C. BUS

G

U

Z

Z

Y

q

C

Z

Z

T

M

W

E

H

D

D

D

S

S

R

K
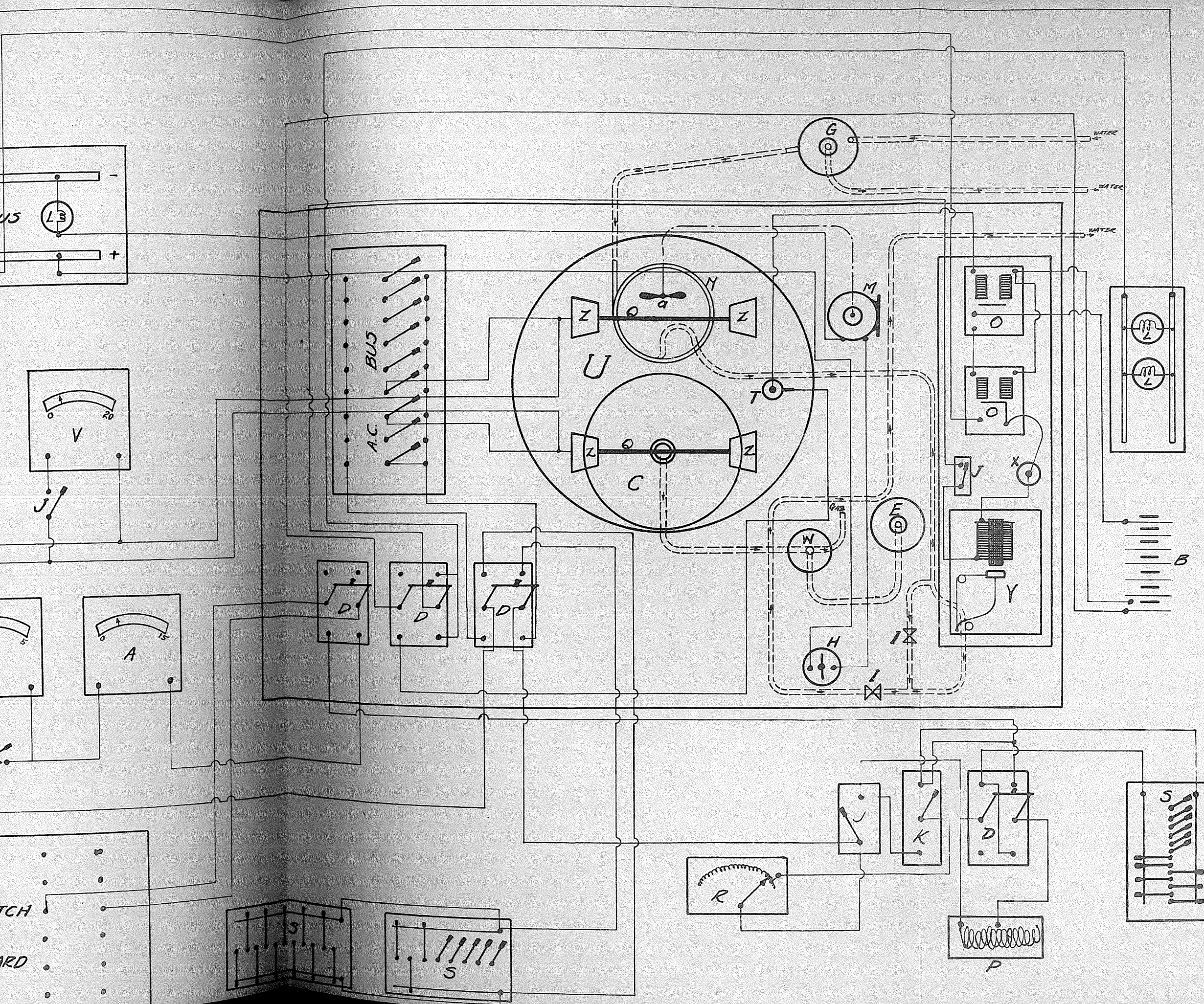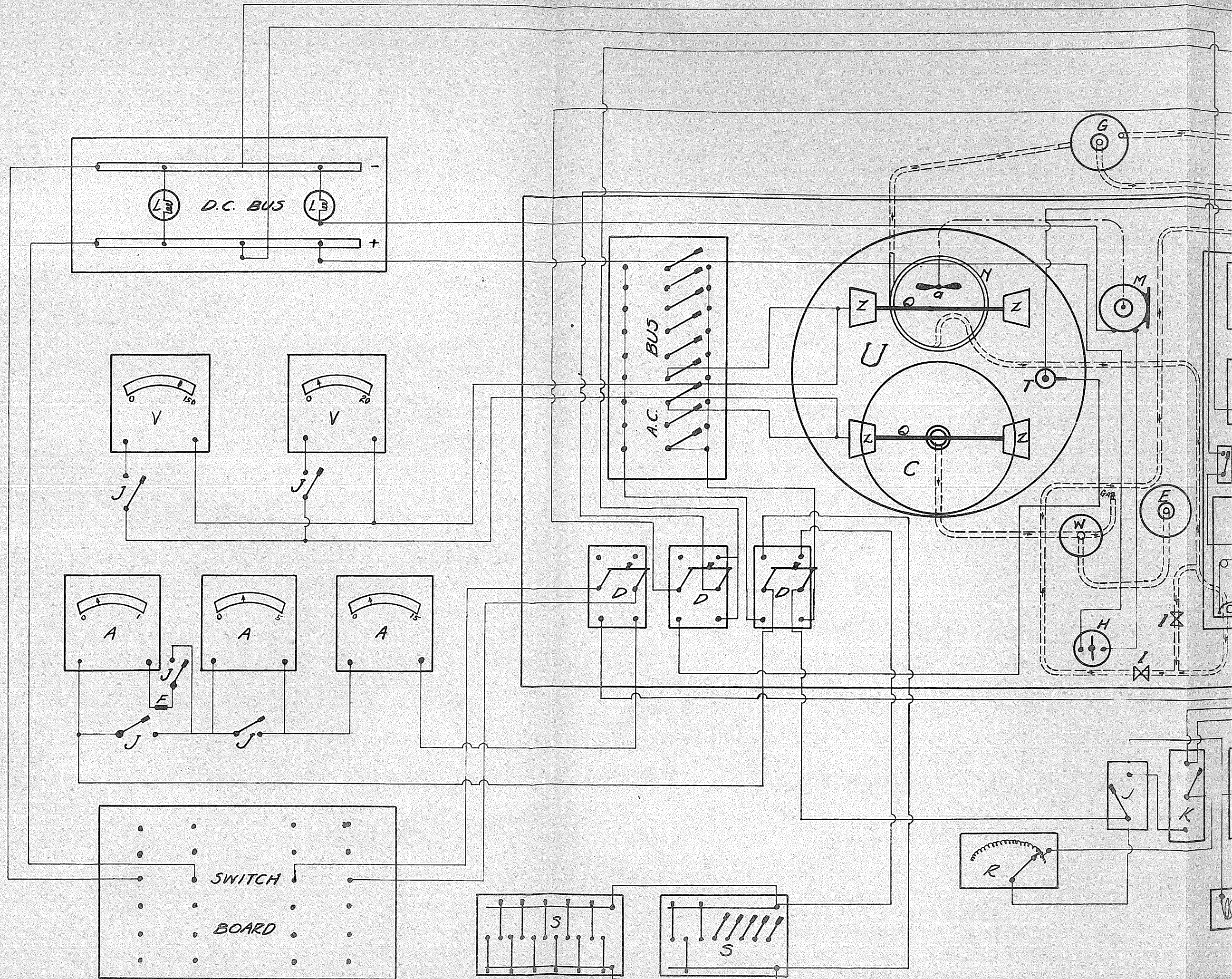
collected by a pair of cones and a bulb, and were drawn off into a eudiometer tube, situated at some distance from the heater to keep it at room temperature. The whole gas collecting apparatus was filled with the electrolyte. The volume of gas produced was measured in the eudiometer. These parts of the apparatus are shown in figure 3.

The heat generated in the electrolyte was removed by water circulating in a copper cooling coil (wound at an angle to save space). An elaborate set up was required to maintain the temperature constant or to rapidly change it. A mercury filled thermostat control of the usual design, was built to give a range of from $0^{o}C$ to $100^{o}C$ but to still have a high degree of accuracy. This control operated a reversing relay, of a special design to overcome the effects of arcing. The relay controlled the current to a solenoid which in turn controlled the water supply from the constant pressure reservoir to the cooling coil, except for a thumb-screw controlled by-pass. The whole temperature controlling system was easily adjusted to meet the conditions in the electrode chamber. The Pyrex-beaker rested on an air-blast gas furnace, by which the temperature could be rapidly raised or the furnace could act

as an auxiliary heater to maintain high temperatures.
An auxiliary electric heater of commercial use was
immersed in the electrolyte. Thermometers were inserted
at several points. The electrolyte was maintained at
a uniform temperature by a motor stirrer. Some diff-
iculty was experienced in controlling the speed of
the stirrer, owing to the under-load on the motor.
Uniform speed was very essential. This difficulty
was eventually overcome by the use of an adjustable
brake-band load and a governor of the centrifugal
braking type. The resultant heating of the motor
necessitated cooling by an air blast.

One of the distinct features of the apparatus
was the ease with which the electrodes could be re-
moved, despite their crowded quarters, for examination
and measurement. The entire temperature controlling
and heating system connected with the electrode
chamber, were clamped together in such a way that
they could be removed clear of the apparatus and
replaced in exactly the same position in one motion.

Electrical connection was made to the
electrodes by copper wires through glass tubes and
soldered to the electrodes inside the insulating
rubber ends. To avoid differences in current den-
sity due to the resistance of the electrodes,

connection was made to one electrode at both ends.
Tests showed that the error introduced without
this double connection was inappreciable. These
connections can be seen in figure 3 .

The wiring diagram of the apparatus is
shown in figure 4 . The electrodes were connected
to switches on the distributing board the power
on which was controlled by a timing switch. The
power could be controlled by hand or by electric
relay, and its duration was timed by a stop-watch
to an accuracy, in experiments of short duration,
of one-tenth second.

Three ammeters of ranges 0.2 to 1.0, 1.0
to 5.0, and 3.0 to 15.0 amperes were connected in
series, with shorting switches across the lower
range ammeters. This gave accurate readings over
a wide range of current. The strength of the
current was controlled by a series of three var-
iable rheostats of maximum resistances 4.5, 60,
and 600 ohms. respectively. These were conn-
ected to an arrangement of switches whereby all
possible combinations of the resistances could
be connected into the circuit. The resistance
of the total bank could be varied from 0.03 ohms.
to 664.5 ohms. rapidly or in very small steps

capillary tube

collecting
bulb

electrical
connections

collecting cones

electrodes

insulators

eudiometer tube

gas heater
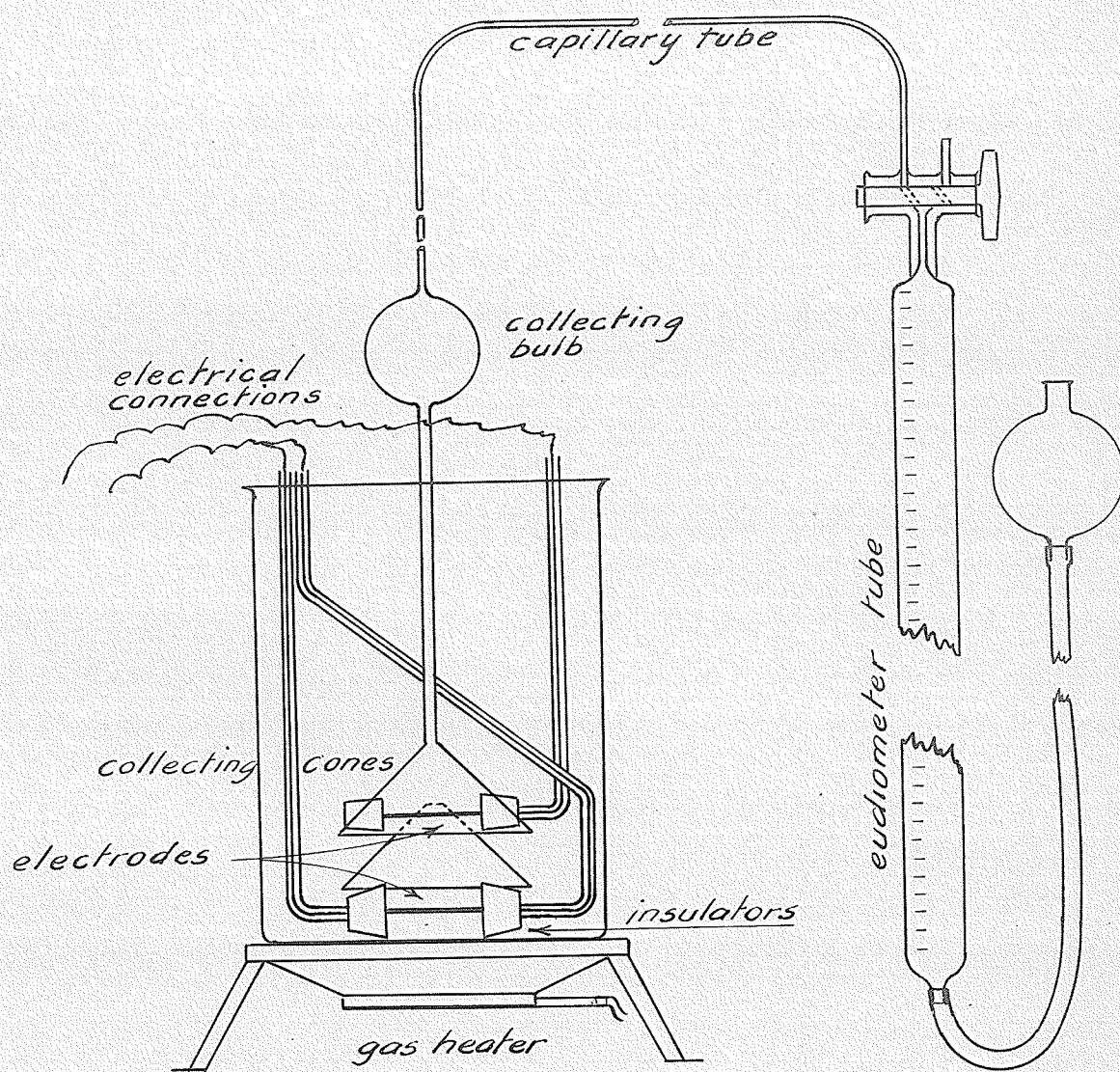
Fig. 4. Apparatus for Determining Rate of
Electrolysis by Alternating Currents, Showing
Electrodes and Gas Collecting Apparatus.

as desired. A voltmeter was connected to the
electrode leads to give the difference of poten-
tial. The remainder of the circuit consisted
of pilot lamps, cut-outs, switch-board, etc.
Suitable lighting arrangements were provided
for observation of the electrodes.

Experiments carried out at low temper-
atures required an ice-brine mixture for cooling.
A temperature of $-12^\circ C$ was obtained with
crushed ice, salt, and a saturated salt solution
in a porcelain container. To maintain this
temperature it was necessary to place the ice
in a wire basket to keep it at the bottom of the
mixture. The liquid was passed through a strainer
and siphoned through an insulated tube to the
cooling coil. The brine was kept saturated by
passing it through a funnel of solid salt.

2.   Experimental. - First Series.

Two electrodes of the same steel as used
previously, (Part IV. section 3) of dimensions
3.3 cms by 0.671 cms. were constructed and placed
in the above type of apparatus. Tenth normal
sodium hydroxide was the elctrolyte.

Twelve experiments at a current density of 0.86, were conducted at gradually increasing temperatures to a maximum of $77^\circ C$. Traces of gas were evolved with the fresh electrode, but the electrodes darkened and no further gas was produced. The same was repeated at 0.91 amperes current density and no trace of gas was produced. The current density was gradually raised and evolution of gas commenced at a current density of 2.0. On raising the temperature to the boiling point (from 80°) the rate was found to increase at constant current density, but at all times it was very low. In the last set of this series, at a current density of 2.0 and at the boiling point, four experiments were carried out, their time aggregating twenty hours, and in all analyses of the gases that collected no indication of the presence of hydrogen was obtained.

These results lead to the following conclusions.

1. Fresh polished steel electrodes give off gas at low current densities.

2. Oxide coated steel electrodes do not produce decomposition of the electrolyte at current densities of below 2.0.

3. Observations indicate that steam formation aids the production of gas.

3. Experimental - Second Series.

Using shorter electrodes a similar series of
forty experiments were carried out. The results
of the last series were confirmed and in addition
the following were obtained. Operating at a
temperature between 50^0 and 70^0 no evolution of
gas was observed at a current density of 3.75 amps.
per sq. cm., or below. Operating at the boiling
point very slight traces of hydrogen were found
after six hours at a current density of 3.0 amps.,
while at 3.75 the rate was appreciable. No hydrogen
was produced below a current density of 3.0.

With still shorter electrodes, a series
of twelve experiments showed that no gas was pro-
duced at a current density of 5.0 and at a temper-
ature of 70^0 during a period of twelve hours.

4. Experimental - Third Series.

The first part of this series was carried
out at 50^0C. and with 0.2 N. sodium hydroxide. The
electrodes were of the same steel turned to a
smaller diameter. At all values of current density
below 6.0 no sign of decomposition was observed. Gas
was evolved in quantity at a current density of 7.3
but the rate, small at first, increased rapidly to a

limiting value at constant current density.

The same was observed while operating at a temperature of 60°. Below a current density of 6.0 no gas was produced, above, the rate increased with increased current density. An attempt was made to find the relation of the rate to the current density but consistent readings could not be obtained. A total of eighty-five experiments were performed which showed, in a qualitative way, that electrolytic decomposition commences at a definite current density, that the rate increases rapidly at this current density as the action proceeds until it reaches a limiting value, and that above this point the rate increases, with increasing current density. In all these experiments the gases collected were from both electrodes, and the complication introduced by a difference in the corrosion of the two necessitated the study of the electrodes individually. This will be outlined in the next section. The gases on analysis were shown to contain two parts of hydrogen to one part of oxygen by volume.

5. Experimental - Fourth Series.

The mild steel electrodes were replaced by piano wire steel as it was impossible to turn

the steel to a finer diameter, and the electrodes were placed on separate pairs of insulators as shown in figure. 5.   Accurate determination were made of the quantity of gas evolved from one electrode, while qualitative observations were made on the other.

Each determination was designated by the time of day at the commencement of the experiment. The time of the current was measured by a stopwatch.   The ammeter and temperature readings were taken at least twice during each determination. The gas evolved was drawn over into the eudiometer tube and allowed to come to room temperature. The barometric pressure was taken. Measurements of the diameter of the electrode before and after each series was performed, were taken and the area was calculated and interpolated throughout the series. The possible error introduced by this interpolation was much less than the limits of error of the experiment. From the current and this area the current density was determined, and from the gas evolved and the time interval the rate was determined. This rate was multiplied by a factor which corrected for temperature, atmospheric pressure and the vapor pressure of the sodium hydroxide solution. The rate

was divided by the area to bring to 1 sq. cm.

The data for the first twenty-five experiments are shown in Table I. This table is copied directly from the notebook and is included as a sample of the method of tabulation and calculation used in the fifteen hundred experiments in this research, the results of which are given graphically in subsequent pages. The consistency of duplicate readings is seen from the Table.

6.   Experimental - Fifth Series.

With the same electrodes in a more corroded condition, fifty determinations were made at 50° C. The corrosion became very great and the readings very irregular. No appreciable gas was evolved until a current density of 8.0 was reached. Above 13.0 it rose rapidly until at 17.0 the rate lay on the curve (extended) of the series above. Arcing was exhibited at current densities above 14.0.

With the same electrodes in a still more corroded condition, thirty determinations were made at 30°C. A similar curve to the above was obtained but the readings were more consistent. The curve had the same slope for its lower part but the slope increased from a current density of 18.0 to 22.1

T A B L E I.

Sample and Method of Recording Results
and
Calculations in Laboratory Notebook.

Date
17/6/26

Barometer 29.3 - 744 mm.
Temperature 17°C - 290° A.
Vapor Pressure   -   14 mm.

Gas Pressure.   730 mm.

S. T. P. Correction Factor 0.904

Time of Day of Reading	Current	Area	Current Density	Temp.	Rate R	Rate at S.T.P.= R X.904	Rate per Cm^2.
1142	3.5	1.0	3.5	30°	0	0	0
1215	3.5	1.0	3.5	30°	.6	.54	.54
1228	4.0	1.0	4.0	34°	4.0	.35	3.5
1431	4.0	1.0	4.0	30°	4.25	3.84	3.8
1444	4.5	.99	4.55	28°	6.4	5.8	5.9
1505	5.0	.99	5.05	28°	8.6	7.78	7.9
1514	5.0	.98	5.1	30°	8.0	7.24	7.4
1523	5.0	.98	5.1	30°	8.1	7.33	7.5
1532	5.5	.97	5.67	30°	9.3	8.41	8.7
1541	5.5	.97	5.67	30°	9.2	8.32	8.6
1554	6.0	.96	6.25	29°	10.9	9.85	10.2
1558	6.0	.96	6.25	30°	11.3	10.2	10.6
1602	6.0	.95	6.32	30°	11.1	10.02	10.6
1609	6.5	.95	6.84	30°	13.7	12.4	13.1
1612	6.5	.94	6.92	30°	13.7	12.4	13.2
1616	7.0	.94	7.45	31°	15.9	14.4	15.3

TABLE I. Cont'd.

Time of Day of Reading	Current	Area	Current Density	Temp.	Rate	Rate at S.t.p.= R X.904	Rate per cm^2.
1620	7.0	.93	7.53	31^0	15.8	14.3	15.4
1626	7.5	.93	8.06	30^0	17.6	15.9	17.1
1630	7.5	.92	8.15	30^0	17.5	15.8	17.2
1637	8.0	.92	8.7	30^0	21.0	19.0	20.7
1643	8.0	.91	8.78	30^0	21.0	19.0	20.9
1649	8.6	.91	9.45	30^0	24.0	21.6	23.7
1653	8.5	.90	9.45	30^0	23.5	21.2	23.5
1703	9.0	.90	10.0	30^0	26.1	23.6	26.2
1708	9.0	.89	10.1	30^0	26.3	23.8	26.7

amperes per sq.cm.   At all points it was lower
than the curve with morderately corroded electrodes.

7.   Critical Current Density.

        The existence of a "critical current
density," below which no decomposition takes place
and above which there is rapid decomposition, has
been definitely established in the course of this
research. Over thirty series of experiments of
from ten to fifty observations in each, using steel
electrodes under varying conditions, gave a value
of current density above which electrolytic decom-
position suddenly commences. In the preliminary
experiments, in which the current density was
not uniform, the critical point was gradual, while
in later experiments it's position could be found
to one-tenth of an ampere. This position was found
to vary as conditions were varied , such as corrosion
temperature, etc. These factors will be discussed
presently.

        Twelve series of experiments, similar to
the above, indicated a very definite critical current
density for platinum which was lower than iron and depended
on such factors as temperature and coating of the
electrodes.

8.   Experiments at Lower Temperatures.

          Operating at a temperature of 30° Centigrade
the current density was successively increased from
zero to 10.0 amperes per square centimetre. Piano
wire steel was used for the electrodes and half-normal
sodium hydroxide for the electrolyte. No decomposition
took place until a current density of 3.5 was reached.
The rate at which electrolytic gases were produced from
one electrode in cubic centimetres per minute per
square centimetre, corrected to standard conditions
is shown, plotted against the current density by the
curves A and B, (taken under the same conditions but
at different times), in figure 5, Readings were
taken at half-ampere intervals above a current density
of 4.0 and at one-tenth-ampere intervals near the
critical point, and each reading was verified by three
to four duplicates. These duplicates are not shown
in the graph.

          Similar curves were obtained at different
temperatures and different states of corrosion. These
were of the same slope as A and B, but were displaced
to one side or the other.

9.   Relation of A.C. Electrolysis to Faraday's Law.

          One ampere of direct current in one minute would
produce, in accordance with Faraday's Law, 10.4 cubic centi-
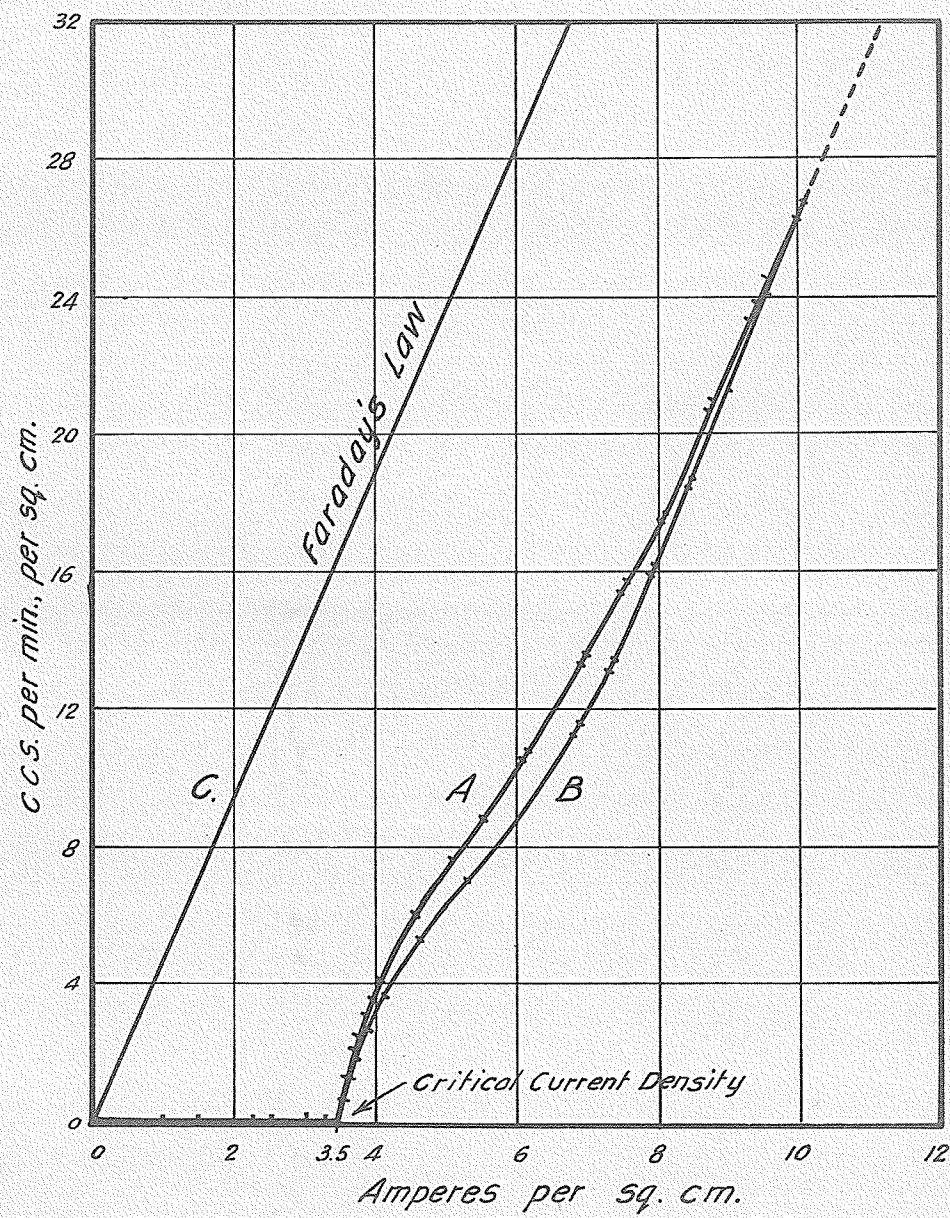
Fig. 5. Relation of Rate of Electrolytic Gases to Current Density.

meters of electrolytic gas at standard conditions.
As the ammeter reading of an alternating current is
1.11 times the average current for each wave, and
as the average current is the electrochemical curr-
ent, one ampere of alternating current should theo-
retically produce 9.42 cubic centimetres per minute.
One electrode should produce 4.71 cubic centimetres
of electrolytic gas per minute. This is shown by
curve C in figure 5.

It was found that above the critical point
an increase of one ampere increased the rate of gas
production by 4.71 cubic centimetres per minute,
within the limits of experimental error. (There is
a small discrepancy close to the critical point.)
This is shown in the graph by the curves A, B and C,
the upper part of A and B having the same slope as
that of C. Above the critical current density alter-
nating current electrolysis follows the law of direct
current electrolysis, provided that the critical current
density is subtracted from the current density used.
When the critical current density is reached, all the
current above that point generated electrolytic gases,
which are freed from the electrode. This law for
alternating current electrolysis was developed from
over one thousand observations on the rate of gas
production with iron and platinum electrodes.

Part VI.   Other Factors in A.C. Electrolysis.

1. Influence of Temperature on Critical Current Density.

The initial point at which gas is evolved was
determined over the range of temperature $0^{\circ}C$ to $100^{\circ}C$.
It was found that the critical point rose rapidly to a
maximum at about $80^{\circ}C$ and fell off to a value of 3.0
amperes at the boiling point. This is shown in figure 6.

The rise in the first part of this curve
indicates that gas was first evolved at a continuously-
increasing current density, as the temperature was
raised. On the formation of steam on the electrodes
the critical current density was lowered, the extent
of the lowering increasing with the increase of steam
formation. The rise is due, we believe, to an increase
in the velocity of the secondary reactions with a rise
in temperature. The catalytic activity of the surface,
which, it seems probable, is largely responsible for
the secondary reactions, evidently increases with the
temperature. Further reference to these secondary
reactions will be made later. The formation of steam
on the electrodes probably has a washing effect where-
by recombination is partly prevented by the removal
of some of the products of electrolysis. The part
played by temperature in this phenomenon is being
further investigated.
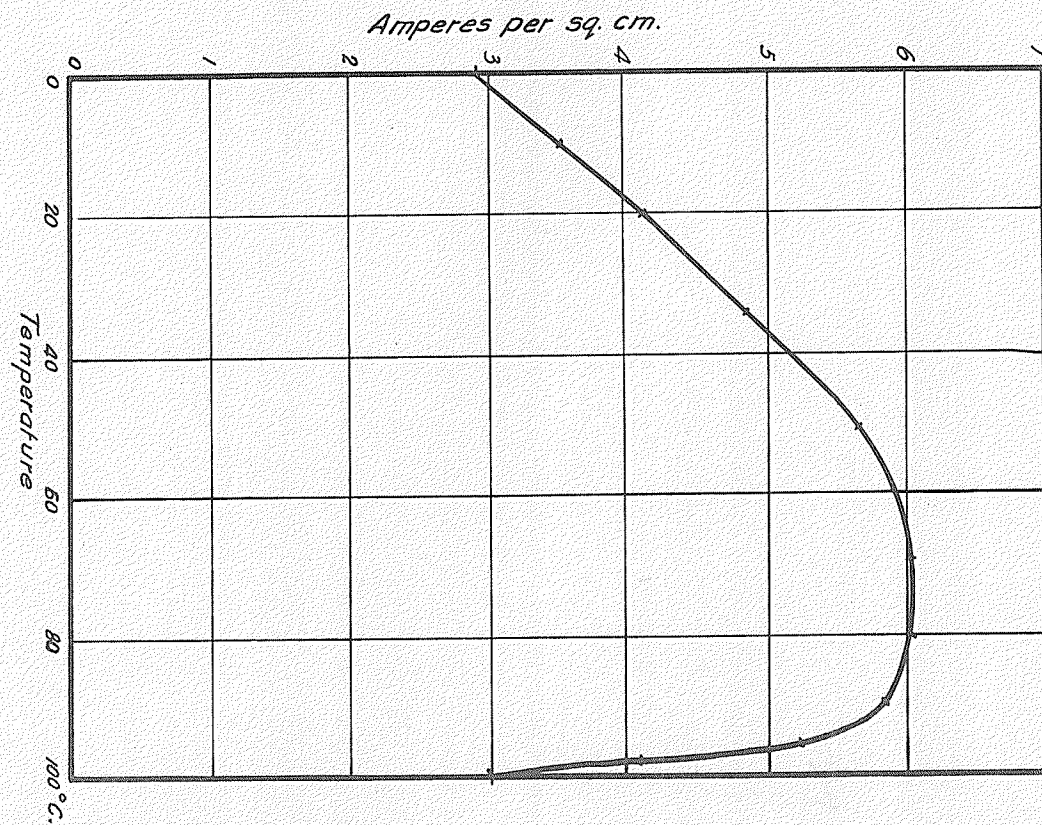
Fig. 6. Relation of Critical Current Density to Temperature at Atmospheric Pressure and with Iron Electrodes.

49.

All of the experiments of this research were
carried out at atmospheric pressure. Increasing the
pressure would increase the temperature at which
boiling takes place, and the drop in the curve would
take place near the new boiling point.

2. Other Factors which Affect Critical Current Density.

Fresh metallic electrodes produce gas at a
lower current density than corroded electrodes. The
extent of the corrosion is very important. At constant
temperature moderately corroded electrodes gave a crit-
ical point at 3.5 amperes per square centimetre, whereas
heavily corroded electrodes were found to produce no
decomposition at a current density of as high as 9.5
amperes. It is to be remembered in this connection
that the current densities given are the apparent
current densities. No allowance can be made for pitt-
ing of the electrodes, which would thereby increase
the actual surface. Apparent current density is all
that is necessary for practical considerations.

No marked difference in the position of the
critical current density was observed when the electro-
lyte was prepared from an acid or a salt. The corrosion
of the iron in the normal salt solution and the acid
solution was much greater than in the sodium hydroxide
solution. Alkaline solutions have thus a practical
advantage.

Mild steel was found to have normally a higher value for its critical current density than hard steel, such as piano wire. This will be investigated further. The critical current density using platinum electrodes was very sharp at 0.75 amperes per square centimetre at $30^{\circ}C$.

3. Effect of Temperature on the Rate of Electrolysis.

Typical curves for steel electrodes, in which the rates of evolution of gas at constant current densities are plotted against the temperature, are shown in figure 7. Numerous curves representing different states of corrosion to that of those shown were obtained. They were all of the same form, but were above and below the position of those in the figure. The rate drops rapidly with rising temperature to a minimum at $80^{\circ}C$ and rises again at the boiling point. These curves are related to the critical current density curves by the relation to Faraday's Law given above.

4.   Effect of Arcing.

Arcing took place to some considerable extent at high current densities and temperatures, and was associated with vigorous boiling. A slight increase in the rate occurred along with the arcing,
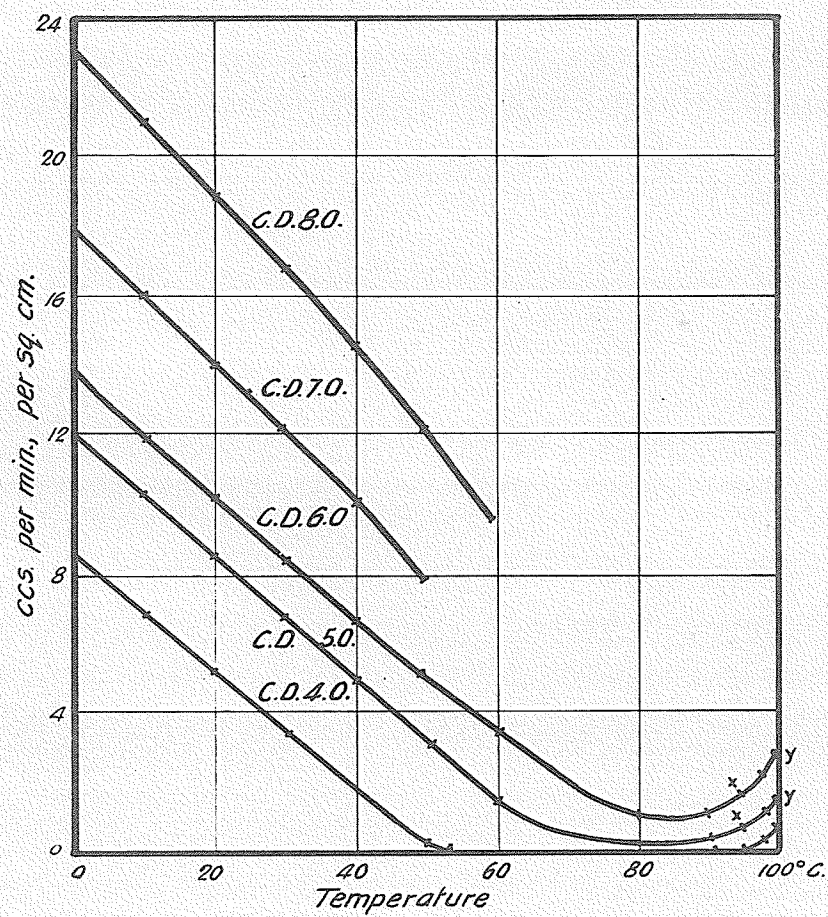
Fig. 7 Relation of Rate of Generation of Electrolytic Gases to Temperature, with Iron Electrodes.

but this increase was no greater than the normal
increase at the boiling point without arcing. In
figure 7. the parts of the curves for current den-
sities 5.0 and 6.0 marked "xy" indicate where arcing
took place. The rise in these parts is no greater
than the rise in the curve below, in which there
was no arcing.

A large number of experiments were per-
formed in which arcing took place, and in no case
was it found that arcing made any appreciable diff-
erence in the rate of electrolysis. Actual obser-
vations showed a decided drop in the rate with
arcing, but when the rate was corrected for the
change in area due to steam coating, (calculated
from the change of resistance), the curve shows
the normal rise.

The results are not in agreement with
the statement made by Kaelin and Matheson[1], who
assume that no decomposition takes place except
thermal decomposition in arcs on the electrode
surface.

5.   Other Factors Affecting the Rate of Electrolysis.

All of the above experiments were carried

[1] F.T. Kaelin and J.W. Matheson, Eng. Jour.IX. No.2,
p. 198, 1926.

out using 60-cycle alternating current. The effect
of changing the frequency has been experimented with
by Maneuvrier and Chappuis, (loc. cit.), who found
that increasing the frequency decreases the rate of
gas formation. The relation is not simple.

Our experiments were carried out at voltages
below 110. Electrostatic effects and an increase
in arcing might be expected at high voltages. Whether
these factors have any appreciable effect or not on
the evolution of gas is being investigated.

Part VII.   The Influence of the Metallic Nature
of the Electrodes.

1.   Steel and Iron Electrodes.

Experiments were conducted in which the
current density was successively increased by small
intervals from zero to 10 amperes per square centi-
metre, the volume of electrolytic gas produced per
minute for each current density being measured.
Piano wire steel was used for the electrodes.   No
measureable decomposition took place until a curr-
ent density of 4.5 was reached, above which the
rate rose rapidly.   This point is the critical
current density of this particular steel.   Visible
but negligible, traces of gas were evolved slightly
below the critical point.   The rate at which elec-
trolytic gases were produced from one electrode in
ccs. per minute, per sq. cm., corrected to standard
conditions, plotted against the current density is
shown by the Curve A in Figure 8.   All points on
the curve were verified by a duplicate reading.
This curve is parallel to that required by Faraday's
Law, and if the critical current density is subtracted
from the current densities in the curve it will be-
come coincident with the curve of Faraday's Law.

The surface of the electrodes previously
polished, tarnished at a current density of about
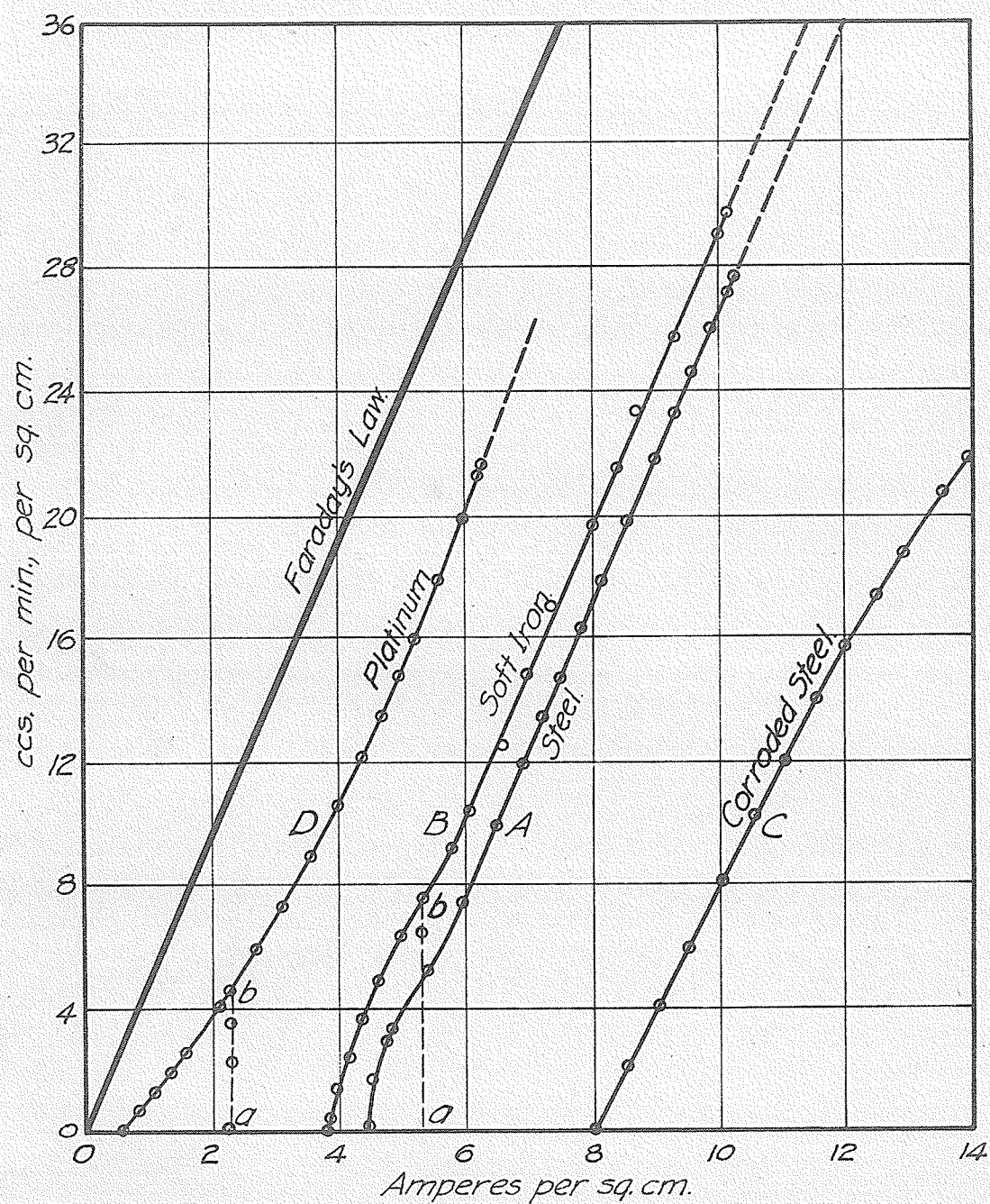
Fig. 8. Relation of rate of generation of Electrolytic Gases to Current Density with Platinum, Iron and Steel electrodes. The change in the rate agrees with Faraday's Law above the critical current density.

2.0 and soon became and remained a deep brown color throughout the duration of their use. This coating was probably due to hydrated oxides of iron and its thickness as shown by micrometer measurements was less than two-thousandths of a millimetre. Piano wire steel electrodes, which were operated at higher current densities and temperatures for some time, became heavily corroded and pitted. The critical point of these electrodes was displaced to the right. An increase in actual surface due to pitting, might account for a part of this increase in the critical current density, but the increase is too great to be entirely accounted for in this way[I].

The relation of the rate of gas evolution to current density with soft iron electrodes is shown by Curve B in Figure 8. The critical current density was found to be at about 3.8 amperes per sq. c.m., which is slightly lower than with the steel electrodes. As above, a constant difference is observed between the rate of alternating current electrolysis and of direct current electrolysis at the same current density.

On increasing the current density by small intervals from zero, it was found that the current density could be increased above the usual critical

I. The corrosion of steel by an alternating current is is discussed by A.J. Allmand and R.H.D. Barklie, Trans. Faraday Soc. 22,34, (1926).

point without evolution of gas, the electrodes
becoming darker than usual. On the commencement
of gas production the rate increased rapidly at
constant current density until it reached the nor-
mal curve. This is shown by the dotted line "ab"
of Curve B in Figure 8. This elevation of the
critical point was followed by a visible throwing
off of part of the dark surface material, the
electrodes resuming their normal brown color.

On reducing the current density the evo-
lution of gas was not regular close to the critical
point, but was produced in sudden bursts, each
burst being accompanied by a color change on the
electrode similar to that observed with the ele-
vation of the critical point. The intervals of no
gas production between the bursts increased as the
critical current density was approached.

2. Platinum Electrodes.

The relation of the rate of alternating
current electrolysis to current density with plat-
inum electrodes, is shown by Curve D in Figure 8.
The critical point was found to be at 0.70 amperes
and could be reproduced with accuracy. As with
the soft iron an elevation of the critical point

was frequently observed. In the particular
case shown in the figure this elevation amounted
to 1.6 amperes above the critical point, but it
was found that the current density could, with
care, be raised to 5.0 amperes without evolution
of gas. The metallic surface became coated with
a deep gray substance,which was subsequently re-
moved by the evolution of gas. The rate of
evolution of gas coincided with the normal curve
only after the coating had been completely removed.
This coating was unlike platinum black but is pro-
bably composed of finely divided platinum. The
diameter of the electrodes decreased with use.

Although the curve with platinum could
be readily reproduced with great accuracy, its
lower part shows a decided departure from a straight
line. The significance of this will be dealt with
in a subsequent paragraph.

3.   Silver Electrodes.

Like platinum, silver electrodes show a
departure from a straight line near the critical
current density(Curve A., Figure 9), but unlike
platinum, this departure is small. The rate foll-
ows the law of alternating current electrolysis
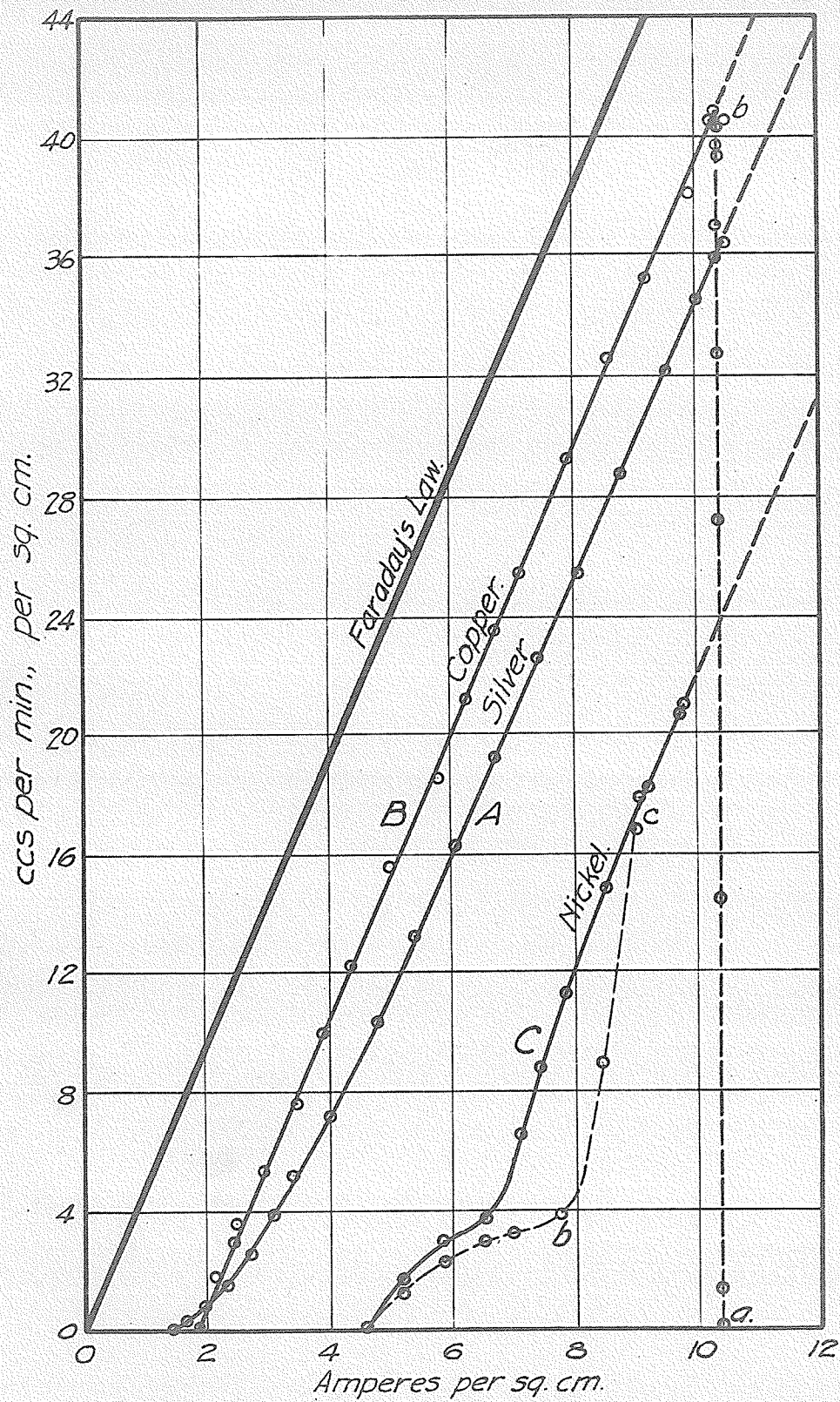
Fig. 9   Relation of rate of generation of
Electrolytic gases to Current Density with
Copper, Silver and Nickel electrodes.

over a wide range. The critical current density
required to be subtracted in this law is obtained
by extrapolation from the curve. The actual crit-
ical current density was 1.6 amperes, while the
extrapolated density was 2.3. No elevation of the
critical current density was observed and the
corrosion was negligible. The electrode surface
became frosted in appearance and remained the same
throughout.

4.   Copper Electrodes.

        Copper gave a sharp critical point at
1.9 amperes per sq. cm. and a perfectly straight
line curve throughout the range (Curve B, Figure 9).
On raising the current density from zero by small
steps the usual critical point was passed without
evolution of gas, the electrodes becoming spotted
with orange and black patches and finally completely
black. The orange substance was likely cuprous
oxide and the the black, cupric oxide. The critical
current density was elevated to 10.2 amperes before
evolution commenced. The black coating was rapidly
removed by the gas and the rate of evolution rose
at constant current density as shown by the part
"ab" of the Curve B in Figure 9. The point "b"

was reached only when the black copper oxide
was completely removed after which the curve
B was obtained with the clear copper surface.
The presence of oxides of copper evidently has
a more marked influence on the critical current
density than the oxides of other metals.

5.   Nickel Electrodes.

The rate of alternating current electro-
lysis for nickel electrodes does not follow the
law at low current densities (Curve C, Figure 9).
On increasing the current density above the crit-
ical point the rate followed the dotted line "abc",
the normal Curve C being obtained with decreasing
current density. This may be a type of elevation
of the critical current density. The departures
from the straight line in the lower part of the
curve may be accounted for by a variation in the
thickness of the surface oxide-coating with the
rate of approximately 3.5 ccs. per minute. The
corrosion of the electrodes was appreciable, but
they remained a deep black throughout the measure-
ments.

6.   Aluminum Electrodes.

A point below which no gas was evolved for
aluminum electrodes could not be found and a

critical current density if existing, must lie
below 0.01 amperes per sq. c.m. It was found
impossible to obtain rate-current density curves
owing to the large changes of resistance and to
the corrosion of the electrodes. Due to the
chemical action of sodium hydroxide on aluminum,
half normal sulphuric acid was substituted as the
electrolyte.

Part VIII. The Theory of A.C. Electrolysis of Water.

The establishment of the law for A.C. electro-
lysis by relating the rate of evolution of electrolytic
gas (2 volumes of hydrogen to 1 of oxygen) to current
density above the critical point led to the consider-
ation of the mechanism of the electrolysis. No con-
tribution of importance to the theory of this mechanism
appears to have been made with the exception of that
of Malagoli.[1] His theoretical considerations were
not based on quantitative evidence but nevertheless
have proven to be surprisingly in accordance with the
above results. Apparently no notice has been taken
of his contribution. Attempts were made by Mengarini[2]
to develop a theory to account for the difference
between a.c. and d.c. electrolysis but his conclusions
do not seem compatible with the above results.

An alternating current being a series of equal
and opposite direct currents should liberate on the
electrodes its equivalent of hydrogen and oxygen acc-
ording to Faraday's Law. One ampere of direct current
in one minute produces, 10.4 ccs. of electrolytic gas
at standard conditions in accordance with Faraday's
Law. As the ammeter reading of an alternating current
is 1.11 times the average current, and as the average
current is the electrochemical current, one ampere

of an alternating current as read from the ammeter,
should theoretically produce 9.42 ccs. per minute.
One electrode should produce 4.71 ccs. of electrolytic
gas per minute. This can be represented by the equation,

$$R = 4.71 \ I_F, \ - - - - \ (1)$$

and by the Curve shown in Figures 8 and 9. In all cases
in this research it was found that the alternating curr-
ent produced less gas than required by Faraday's Law.
The rate of evolution was found (a) to be a function
of the current density, when the current density was
maintained uniform over the surface of the electrode,
(b) to increase with increasing current density above
the critical point, and (c) to follow with few depart-
ures a straight line curve, parallel to Faraday's Law.
The critical point was found to depend on the metall-
ic nature of the electrode, the coating on the surface
and the temperature (Part VI. section 1).

Consider a metallic electrode *with a surface area of 1 sq. cm.* immersed
in an alkaline solution and an alternating current
(Figure 10) passing through the electrode, the
solution, and a second electrode. The current comm-
ences at the point A, and decreases to zero at O.
(If the current commences at any other point an equil-
ibrium, in which the current may be considered as
starting at the point A, is shortly reached as in
ordinary alternating current theory.) Part of the
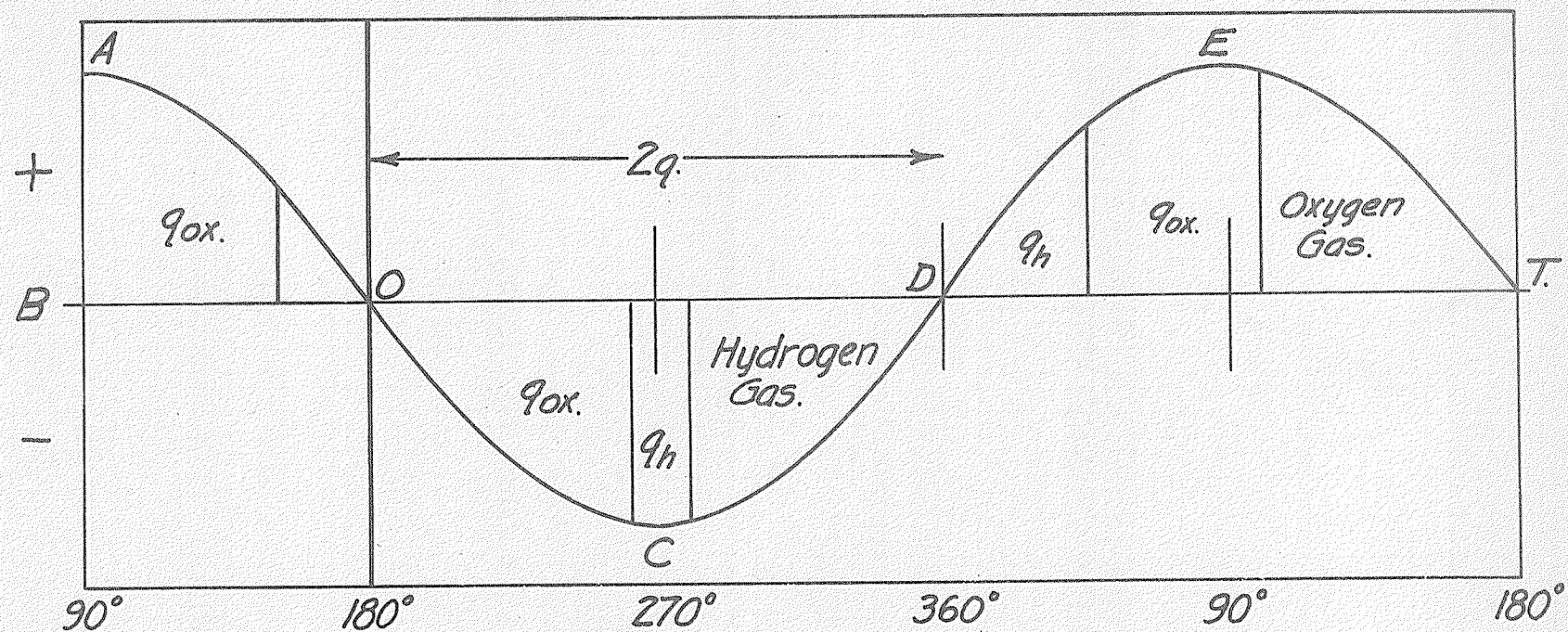
Fig. 10. Diagrammatic Representation of the Relation of the Quantity of Gas produced by an Alternating Current, to the Electrolytic Capacity of the Electrode Surface.

current may be stored by the electrostatic capacity

effect between the charged ions and the electrode,

an effect known to exist at low voltages, but as

the current is induced by a voltage above the decom-

position voltage, and is in this case positive, it

discharges its equivalent in hydroxyl ions. Two

discharged hydroxyl ions unite to form water and

atomic oxygen. Part of this oxygen may combine with

the metal of the electrode to form an oxide of the

metal and part either in the atomic or molecular

condition may be adsorbed on the surface or absorbed

in the surface layer. The remainder, if any, will

form molecular oxygen and pass off from the electrode.

The quantity that is absorbed by combination or other-

wise, depends on the metallic nature of the electrodes,

the nature of the surface, temperature, etc., but

independent, except in certain cases, of current

density or voltage. If the nature of the surface

and the temperature is constant, the quantity which

can be absorbed is constant and can be measured by

the coulombs which produce it. This quantity is des-

ignated q_{ox} . The quantity of electricity that

passes during the quarter wave, that is the area OAB,

is designated by q coulombs. The quantity of oxygen

liberated from the electrodes again measured in the

coulombs that produce it, is equal to $q - q_{ox}$.
At the point O the electrode is stored with oxygen
and is producing a back E.M.F.

The current is reversed and hydrogen is
discharged on the electrode. A quantity of hydrogen
equivalent to q_{ox} will react with the oxygen stored
from the last quarter wave to reproduce water. The
electrode will then be in its original condition,
that is, electrically neutral. A quantity of hydrogen
designated by q_h will combine with the metal, be
adsorbed on the surface, or absorbed in the surface
layer as with the oxygen and the remainder, if any, will
form molecular hydrogen and pass off from the elec-
trode. When the point D is reached the quantity
liberated will be,

$$2 q - (q_{ox} + q_h)$$

Owing to the high voltages sometimes occurring,
the actual mechanism may become complicated by the
discharge of metallic ions, e.g. sodium ions, but
the resultant will be the same as above.

Similarly, in the half wave DET, oxygen
is discharged, a quantity q_h will neutralize the
hydrogen of the previous half wave, and a quantity
q_{ox} will be absorbed by the electrode. The
quantity liberated will be equal to $2 q - (q_h + q_{ox})$.

Representing (q_h + q_{ox}) by 2 Q_0, we have as the electro-chemical equivalent of the total quantity of electrolytic gas produced, in the cycle from O to T, the difference 4 q - 4Q_0.

With current of frequency "f" the quantity produced in one second will be equal to 4 fq - 4 f Q_0, and in one minute, 240 fq - 240 f Q_0. The quantity 240 fq, is the total quantity of electricity that has passed, which will be the average current, multiplied by the time; that is, in one minute. 60 I_1/1.11 coulombs, where I_1 is the current per sq. cm. of electrode surface, from the ammeter reading. From Faraday's Law one coulomb will liberate 0.174 ccs. of electrolytic gas or 0.087 ccs. on one electrode. Therefore the volume, "R"$_1$, of gas liberated at standard conditions, per minute, per sq. cm. will be represented by

$$R_1 = 0.087 \left(\frac{60\ I_1 - 240\ f Q_0}{1.11} \right)$$

or

$$R_1 = 4.71\ (\ I_1 - 4.44f\ Q_0\ ) \text{--------}(2)$$

Thus we have an equation of alternating current electrolysis .

The value of f and Q_0 being constant and independent of the current, the rate plotted against the

current, (current density in this case) gives a
straight line curve with a slope of 4.71, which is
the slope of Faraday's Law.

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Part lX. Critical Current Density and Electrolyte Capacity.

1. Critical Current Density and the Law of
    Alternating Current Electrolysis.

From Equation (2) it is seen that when the
current density is less than 4.44 f Q_0 (which is 1.11
x 4 f Q_0), R_1 becomes negative. Actually R_1 becomes
zero, the value of Q_0 not being fully satisfied. No
resultant decomposition will take place until the
current density exceeds this value of 4.44 f Q_0. This
point is the "critical current density" and is repres-
ented by;

$$I_c = 1.11 \quad x \quad 4 f Q_0 \text{----------(3)}$$

Substituting in equation (2) we get,

$$R_1 = 4.71 \quad (I_1 - I_c)\text{----------(4)}$$

which is the law of alternating current electrolysis
as derived empirically (vide).

2. Electrolytic Capacity.

When the frequency is constant, it is seen
from equation (3) that the critical current density is
dependent on the value of Q_0. This quantity is here
called the "electrolytic capacity," and, as is seen from
its origin, is defined as the average storage capacity
for electrolytic gases, i.e. hydrogen and oxygen, on
one sq. cm. of metallic electrode surface. It is meas-
ured in coulombs. Its value depends on the nature of

the electrode surface, temperature, etc., and is
the quantity in which alternating current electrol-
ysis is particularly concerned.

3. Direct Determination of Electrolytic Capacity.

An apparatus was developed by which an app-
roximate value of Q_0 could be obtained, but by a more
direct method than from the critical current density.
A pair of electric relay switches were accurately
timed to break sharply the connection of the alter-
nating current to the electrodes and connect them to
a milliammeter. The movement of the milliammeter was
dampened by a high inductance and the discharge pro-
longed by resistances. By taking readings of the
current at regular intervals until the discharge was
complete a close approximation of the total amount
of electricity stored on the electrodes at the time
of the break in the current could be obtained.

Operating at a current density of 4.1
amperes, which was the critical current density for
the electrodes used, a large number of discharge
readings were taken. They were either positive or
negative and varied from zero to a definite maximum.
The average maximum value obtained was 14.7 millicou-
lombs per sq. cm. of electrode surface for the electro-
lytic capacity of the metal (iron). Calculating

the value of Q_0 from equation (3) it was found in
this case to be (frequency 60-cycles) 15.0 milli-
coulombs per sq. cm.   Similar agreement was found in
other cases but due to the short time of discharge,
the accuracy of the method was limited.

The relation between the magnitude of
the discharge and the arc at the contact points on
the breaking of the alternating current also gave
confirmation o f the above theory. Maximum dis-
charges were obtained when the current was broken
with a minimum or no arc, and minimum or no dis-
charges were obtained when the arc at the contact
points was a maximum . From Figure 10 it is seen
that at the points O, D and T the current is zero,
and the arc, if the current is broken at this point
is small. (The phase difference at this voltage was
small). At these points the quantity of electrolytic
products on the electrodes is a maximum and a maximum
discharge is obtained. Similarly at the points C and
E the arc is a maximum and the electrodes are in a
nearly neutral condition.

These simple and direct experiments showed
also that the electrolytic products stored on the
electrode exhibit a back electromotive force, and
that , whatever the nature of the absorption which
holds them on the electrode surface, it allows these
products to readily regain the ionic condition.

4. Electrolytic Capacity and Nature of Electrode Surface.

Re-arranging equation (2) we obtain.

$$4.44 \ f \ Q_0 \ = \ I_1 - \frac{R_1}{4.71}$$

But from equation (1) it is seen that $R_1/4.71$ is equal to the current required by Faraday's Law to produce the rate R_1, which current is called I_F. The equation becomes,

$$Q_0 \ = \ \frac{I_1 - I_F}{4.44 \ f} \qquad - \ - \ - \quad (5)$$

The value of the electrolytic capacity Q_0, can therefore be obtained by dividing the difference between the current density at any rate and the corresponding current required by Faraday's Law for that rate, by 4.44 times the frquency. The value of $I_1 - I_F$ at any particular rate is conveniently obtained by measuring the horizontal distance at this rate between the curve of a metal and the curve of Faraday's Law in Figures 8 and 9. The frequency in the above experimental work was 60-cycles.

With silver electrodes the value of Q_0 is constant above a current density of 4.0 amperes and is therefore independent of the current density over this range. Its value is 8.6 millicoulombs. Below 4.0 amperes it decreases in value at first slowly, and

then more rapidly, until at the critical point
its value is 6.0 millicoulombs. A greater diver-
gence is seen with platinum electrodes. The value
of Q_0, constant at 6.7 millicoulombs above 4.0
amperes, decreases to 2.6 mcs. at the critical point
of 0.7 amperes. This variation of the electrolytic
capacity with current density near the critical point
may be accounted for by the lower voltage in this
range, and consequently a lesser "driving force" to
assist in the absorption of the electrolytic products
into the surface layer of the electrode. This effect,
appreciable in the case of platinum, is small with
silver electrodes and is practically non-existent with
the other metals used. The elevation of the current
density above the critical point of platinum, which
means a supersaturation of the electrode surface
over its normal capacity, is accompanied by a vis-
ible change in the surface coating. The surface
coating is probably finely divided platinum possess-
ing a greater surface and a greater storing power than
the normal surface.

Copper, being a readily oxidizable metal, and
copper oxide, a readily reducible substance, it is to
be expected that a copper oxide-coated copper electrode
would give a very high electrolytic capacity and a large

elevation of the critical current density. Such
is actually found to be the case, as shown by the
part "ab" of Curve B in Figure 9. With the bright
copper surface the electrolytic capacity is constant
entirely independent of the current density. Its
value is given in Table II. The curve for copper
was drawn with a straight edge parallel to the
curve for Faraday's Law and touches all points.

Bright metallic surfaces, as with silver,
platinum and copper, could not be maintained for
experimental determination of the electrolytic
capacity of steel, soft iron and nickel electrodes.
The electrolytic capacity was therefore greater
than with the metallic surfaces. Apparently the
thin oxide coating on these metals was of uniform
thickness as they follow the law of a.c. electrol-
ysis.

At current densities above 6.0 amperes the
values of Q_0 for iron and steel were constant, as
seen from the constant difference between the curves
B and A and the curve of Faraday's Law in Figure 8.
The slight departures near the critical point are
likely due to a combination of the effect of low
voltages and an elevation of the critical current
density.

T A B L E II.

The Critical Current Density and Electrolytic
Capacity of Various Metals in Half-normal Sodium Hydroxide
Solution at $30^{\circ}C$ and with a Frequency of 60-Cycle.

Metal	Current Density or Range.	Critical Current Density, Amps./cm^2	Electrolytic Capacity Millicoulombs per sq. cm.
Silver	4.0-10.0	1.6	8.6
"	1.6	1.6	6.0
Platinum	4.0- 6.4	0.7	6.7
"	0.7	0.7	2.6
Copper	1.9-10.5	1.9	7.1
" (oxide coated)	10.0	10.0	37.6
Steel $0^{\circ}C$	4.5	--	10.9
" $30^{\circ}C$	4.5 -10.0	4.5	16.9
" $80^{\circ}C$	4.5	--	22.6
" (corroded)	8.0	8.0	30.1
" "	14.0	8.0	35.3
Soft Iron.	3.8-10.0	3.8	14.3
Nickel	9.0	4.6	19.6
Aluminum ($0.5N.H_2SO_4$)	0.01	0.01	0.037

The relation of electrolytic capacity to
the nature of the surface is strikingly shown by
the curve for heavily corroded steel in Figure 8.
The critical current density is practically double
that of the normal steel. A further increase in the
electrolytic capacity is observed at high current
densities, due, probably to the increased "driving-
force" of the higher voltage.

The electrolytic capacity of nickel electrodes
becomes constant only at high current densities, changes
in the surface coating probably accounting for the
abnormal curve. Aluminum has a very low electrolytic
capacity, if any, as might be expected from its chem-
ical properties, aluminum oxide being non-reducible
by hydrogen. A similar result was obtained by A.
Gunther-Schulze[1]. Aluminum on the other hand gives
a very high electrostatic capacity [2] and is used for
condensers.

5.   The Effect of Frequency and Temperature.

Experimental work by Maneuvrier and Chappuis[3]
and by Marsh[4], has shown that the rate of electrolysis
decreases with *increase in* frequency. Malagoli[5] considers the
relation a straight line function with a negative slope.
From equation (2), which is

$$R_I = 4.71 (I_1 - 4.44 f Q_0), - - -- - - (2)$$

it is seen that if I_1, and Q_0 are constant the rate
is directly related to the frequency in a negative
direction. If the frequency is zero, that is a direct
current, the rate becomes equal to Faraday's equivalent.
It is doubtful that Q_0 is independent of the time of
charging the electrode. Increasing the periodic time
would allow the electrolytic products to penetrate
the electrode to a greater extent, thereby increasing
the electrolytic capacity. Preliminary experiments
indicate that this is probably the case.

Experimental evidence obtained by the
author, (Part Vl. Section 1.) has shown that the
electrolytic capacity with some metals varies greatly
with temperature, and with others but slightly. The
electrolytic capacity of steel electrodes increases
rapidly as the temperature is raised from 0° to about
80°. An increase of from 10.9 millicoulombs at $0^\circ C$.
to 22.6 millicoulombs at 80° is found on applying
equation (3) to the curve of critical current density
plotted against temperature, (Part VI section 1.)
A decrease in the capacity was observed concurrently with
the production of steam on the electrodes and is pro-
bably due to the washing effect of the bubbles of steam.
A much smaller variation was obtained with platinum.
For example, at a current density of 3.0 amperes the

electrolytic capacity was found to decrease from
6.4 millicoulombs per sq. cm. at 0° to 6.0 at 50°,
increasing again to 7.1 at 85° and decreasing at
the boiling point.

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Part X.   Electromotive Force Considerations.

1. Back Electromotive Force.

      As is generally understood, on the
first passage of current a Helmholtz double-layer is
produced which exerts a back E.M.F: and an equal
and opposite force, which is the theoretical decom-
position voltage, must be applied to overcome this.
A further E.M.F. to overcome overvoltage and the
resistance of the electrolyte, must be applied to
cause the current to flow. Although a large amount
of work has been done relating voltage to current
density and in connection with overvoltage in
general, the relation of voltage to the quantity
of electrolytic products on the electrodes, or to
the coulombs that have passed has not been definitely
established. Kohlrausch[1] assumes that the polariz-
ation voltage is directly proportional to the
quantity of electricity that has passed and gives
experimental proof to show that this is true up to
10 microcoulombs per sq. cm. Despite this limited
range Mengarini[2] considers it applicable over a wide
range, and even in recent times Lattey[3] makes use of
it without question as to its validity. By an orig-
inal and direct method Griffiths and Heys[4] found that
this relation holds up to 3 microcoulombs per sq. cm.
with platinum electrodes, but above this the direct

proportionality no longer exists. Somewhat similar
results were obtained through a different method
by Clark,[5] who found an approximate linear relation
up to about 2.4 millicoulombs per sq. cm., but he
considers it to be more of an exponential than a
linear function . In the course of an investig-
ation into the effect of superimposing an a.c.
on a d.c., Jones[6] obtained the relation between
coulombs and overvoltage (what we refer to as
decomposition voltage) for lead electrodes. He
found that the voltage rose regularly with the
quantity of electricity, to a point where the
curve flattened out.

From the above experimental work it is
apparent that electrodes act as condensers at low
voltages.

2. Determination of Back Electromotive Force.

Experiments were carried out by the
author to determine the relation existing between
voltage and the quantity of electricity passed,
with the purpose of connecting the results to the
theory of alternating current electrolysis. A
potentiometer was used to cause low currents to
pass through two platinum electrodes immersed in

sodium hydroxide solution. The electrodes exposed
a known area of surface and were protected from
stray currents. The current was measured by a
calibrated galvanometer and the potentiometer read-
ings corrected for the fall due to the current pass-
ing and the resistance of the circuit. The poten-
tiometer was varied to maintain a constant current
through the electrodes and voltage readings were
taken at intervals timed by a stop watch. The
electrodes were reversed between each series.

Sufficient evidence has been obtained
to show that, at a direct current density of 100
microamperes per sq. cm. and above, the voltage
rises rapidly until about one millicoulomb per
sq. cm. has passed. Beyond this the voltage inc-
reases but little, no matter how long the current
has been passed. This is shown in Fig. 11.

No visible evolution of gas was obtained
which is accounted for by the solution of the small
quantities of gas in the electrolyte. At current
densities of about one microampere the maximum
voltage was less than half the voltage obtained at
100 microamperes.

3.   Polarization Capacity.

It may therefore be considered that the
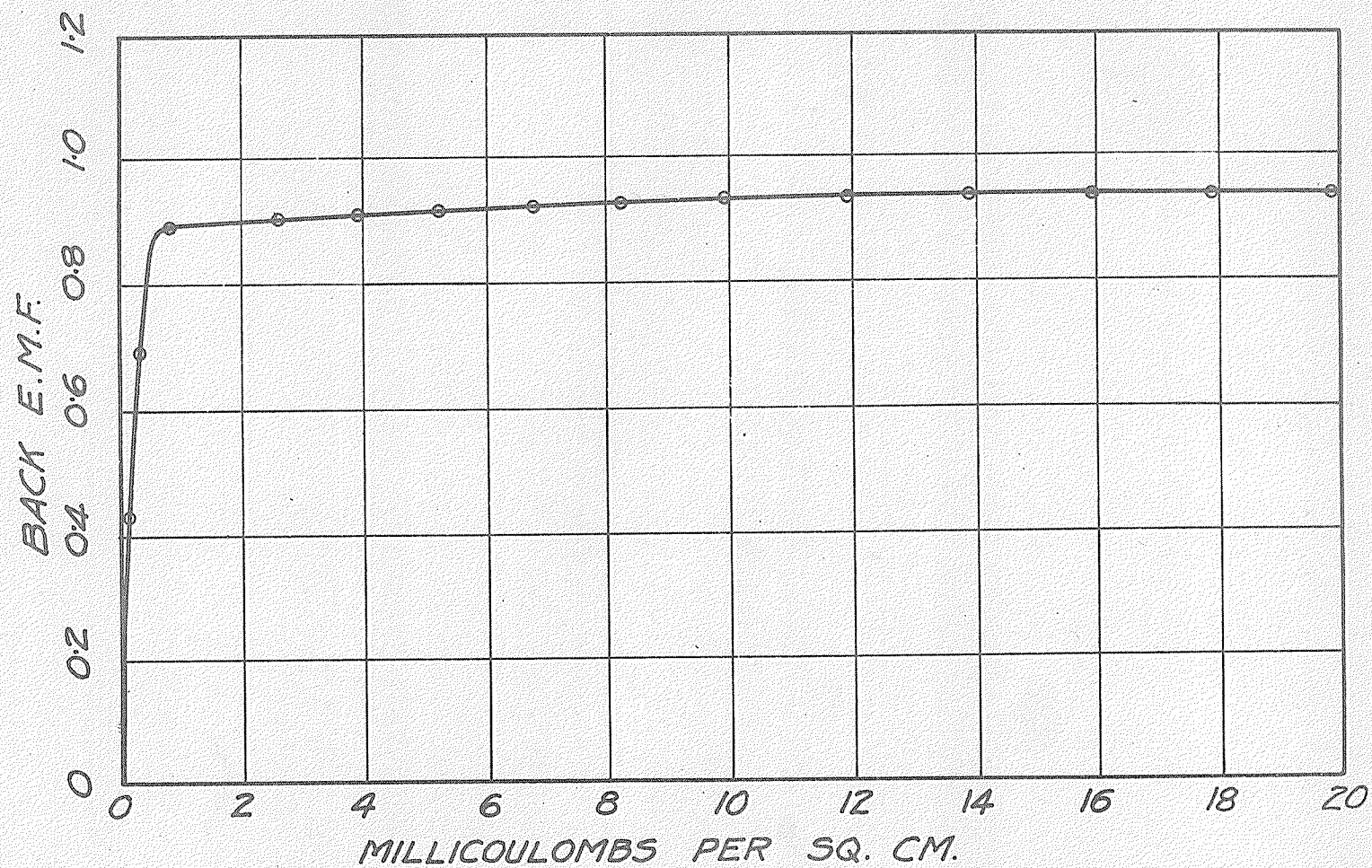electrodes act as "leaky condensers" up to the

Fig. 11. Relation of Back Electromotive Force to the Quantity of Electricity passed through 1 sq. cm. of Electrode Surface.

theoretical decomposition voltage of the electrolyte.
This similarity was first pointed out by Varley[7]
and by Kohlrausch[1]. Above this voltage decomposition
takes place and the electrode becomes polarized, an
increase in voltage or overvoltage,[8] being required
to cause the current to flow. The electrostatic
capacity exhibited by electrodes below the decom-
position voltage has been termed by Kohlrausch the
"polarization capacity", although up to the decom-
position voltage, polarization as we now understand
it, probably does not take place. A large amount
of experimental work[9] was performed to measure this
so-called "polarization capacity" but with conflicting
results. In more recent times Vaillant[10] and Sorrel[11]
measured the polarization capacity in relation to
current density. Clarke[5] and Griffiths and Heys[4]
measured the capacity and related it to the charge
put into the electrodes. The relation of this cap-
acity to frequency has been investigated by Haworth[12],
Merritt,[13] Jolliffe[14], Wolff[15], Banerji[16], Smith
and Moss,[17] and a number of others[18], but as yet no
definite generalizations have been obtained from
their results. The value of this capacity has been
found to be of the order of 10 microfarads per sq. cm. for
platinum electrodes. A value of about 12,000 ohms per sq.
cm. for the resistance of the "leaky condenser" can
be obtained from the leakage curve, given by Griffiths

and Heys,[4] for platinum in sulphuric acid.
Preliminary experiments conducted in this
laboratory indicate that the resistance for
platinum electrodes in sodium hydroxide solution,
is of the order of 25,000 ohms per sq. cm.

This capacity effect is credited by a
number of authors,[1,12] to the formation of a
gaseous film between the electrode and the
electrolyte, but this conception is hardly
tenable below the decomposition voltage. Further-
more the mechanism by which it is built up,
while still allowing the current to pass, is
difficult to conceive. If the equation,-

$$C = \frac{KA}{4 d} \times \frac{1}{9 \times 10^5} \text{ mfds} - - (6)$$

for the capacity of a parallel plate condenser
(K = dielectric constant, A = area, d =
thickness of dielectric) holds down to atomic
dimensions, the thickness of a gaseous layer, to
produce such a capacity may be obtained. To
give a capacity of 10 mfds, a thickness calcul-
ated from equation (6) of approximately 10^{-8} cms
would be required, which is of atomic dimensions.
The spacial separation of molecules of a gas is of
the order of 10^{-7} cms. and as a layer ten molecules
thick would be hardly sufficient to separate the

walls of the condenser, the minimum thickness
of the gaseous film would have to be of the
order of 10^{-5} or 10^{-6} cms, that is 100 to
1,000 times as great. We must conclude there-
fore that the condenser effect is not due to
a gaseous film as such, or that the equation
for the capacity of a condenser shows very wide
variation at small thicknesses.

If as with Clark[5] and Banerji[16], we
consider the effect as due to the Helmholtz
double layer, a better agreement with the thick-
ness of the dielectric is obtained. If a low
potential is applied to the electrode it will
attract the oppositely charged ions to itself
but will not be sufficient to cause the electron
to cross the intervening space, whatever its
nature may be. The requirements of a condenser
are fulfilled. If the dielectric is compressible
the capacity of the condenser will increase slightly
with the voltage. Such was actually found to be
the case with platinum by Griffiths and Heys[4]
and with a number of other metals by Clark[5].
As one part of the double layer is composed of
ponderable ions, an increase in frequency would

not allow the ions to approach the electrode
as closely and a decrease in the capacity would
be obtained.   Such is found to be the case by
the above experimenters, [12,13,14,15,16,18].

The layers of the condenser are not
rigid but are composed of rapidly vibrating par-
ticles.   It is conceivable therefore that two
oppositely charged particles might come into
sufficient contact to allow an electron to pass
below the decomposition voltage.   This would
account for the leak observed with electrolytic
condensers.

4.   Electrolytic Capacity and Polarization Capacity.

At the theoretical decomposition voltage the
electrostatic condenser breaks down and electrolytic
products are produced on the electrode surface. These
products are not immediately removed from the surface
but are stored in some manner in the surface layer.
Their presence causes an increased resistance or a
polarization of the electrode surface.   Gas will be
liberated when the storage capacity of the electrode
surface is satisfied. The average of the quantities
of electricity per sq. cm. which must pass after the
theoretical decomposition voltage is reached, before

electrolytic gaseous products are liberated
from each of the two electrodes, we have called
the "electrolytic capacity" of the metal, as
determined by this research. The term "polar-
ization capacity", we have limited to the range
below the decomposition voltage and is an electro-
static capacity. Jolliffe[14] used these terms as
if identical, but a distinction has been made in
this research.

The measurement of electrolytic cap-
acity by the rate —   current density curves
or the direct method given above necessarily in-
cludes the effect of the polarization capacity,
and it was for this reason that the above exper-
iments were performed to find the relative effects
of the two capacities. Let us consider a platinum
electrode which exhibits a polarization capacity
of 10 microfarads which is the average value in
an electrolyte with a theoretical decomposition
voltage of 1.0 volts. The quantity of electricity
required to bring the electrode to this voltage
would be 10 microcoulombs. The electrolytic cap-
acity of platinum determined above was about 5
millicoulombs or 500 times as great. The effect

of polarization capacity on the electrolytic
capacity in alternating current electrolysis
of water is therefore negligible under the
conditions of current density, frequency, etc.
given above.

5.   Phase Difference.

The curve of back electromotive force,
(Figure 11) may now be applied to the sine wave
of the alternating current. A current starting
at the point A, (Figure 12), and varying as the
sine of the angle, will follow the path ABC. This
current is passing through two electrodes and an
electrolyte. The voltage required to overcome the
ohmic resistance of the electrolyte, known as the
"IR drop", is shown by the curve DEF. On the
passage of current an electromotive force oppos-
ing the current will be set up immediately, and
will increase at a rate depending on the current
and the polarization capacity of the electrode,
until the theoretical decomposition voltage of the
electrolyte has been reached. This is represented
by the point G and the dotted line. On further
passage of the current the voltage will rise but
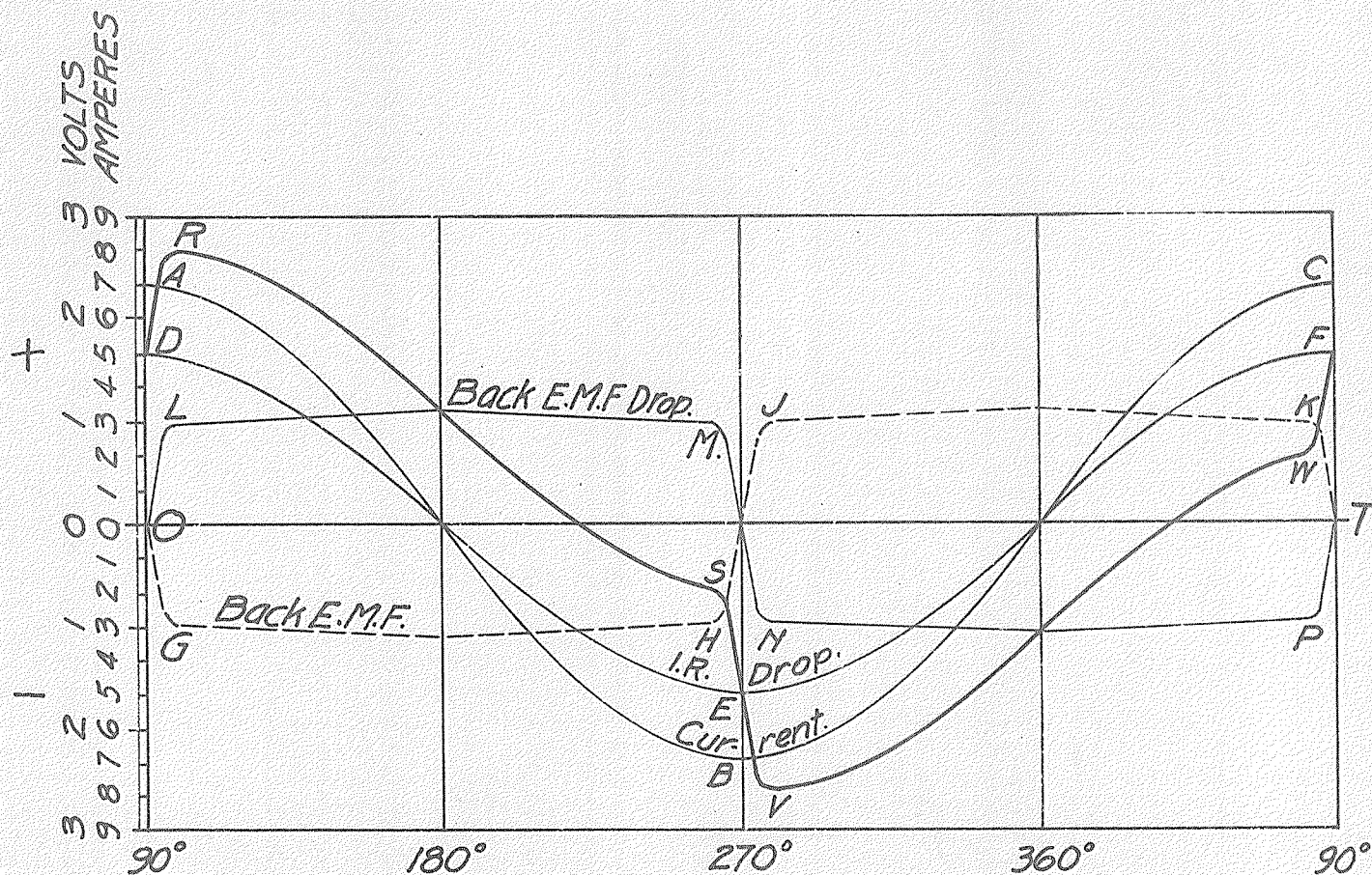slightly, irrespective of evolution of gas.

Fig. 12. Diagramatic Representation of the Phase Difference and Distortion of Wave Form produced by the Back E.M.F. of an Electrolytic Cell.

This overvoltage will increase with current density.

On reversing the current the back
electromotive force will fall but slightly, until
the hydrogen produced has neutralized the oxygen
absorbed on one electrode and vice-versa on the
other. If we assume that the individual electro-
lytic capacities of the metal for hydrogen and
oxygen are equal, and operate at the critical curr-
ent density, the back E.M.F. will drop suddenly
at the point H to zero and immediately set itself
up in the opposite direction, until the same decom-
position voltage has been reached. It will then
proceed along the path JK until the hydrogen on one
electrode and the oxygen on the other have been
completely neutralized, and fall to zero at the
point T. If the individual electrolytic capacities
of the metal for hydrogen and oxygen are not equal
the reversal of the single electrode potential at
each electrode will take place at different moments.
The drop from H to J in the Figure will take place
in two parts at the instants of these reversals,
the first drop taking place before the point H is
reached. Operating above the critical current den-
sity the curve of the back electromotive force will
not change its shape, but will be displaced to the

left, depending on the distance of the current
density from the critical point. Operating
below the critical point the value of the
electrolytic capacity will not be fully satis-
fied, but the curve will be the same as in the
Figure. The first two of these variations from
the above conditions will thus casue the point
of maximum back E.M.F. to be displaced to the
left.

An equal and opposite E.M.F. of the same
shape as the back E.M.F. will then have to be
impressed to maintain the current flowing. This
E.M.F. is shown in the Figure by the curve OLMNPT.
Combining this curve with the curve of the "IR drop",
DEF, the resultant voltage curve, DRSVWF, shown by
the heavy line, is obtained.

As is seen in the Figure, there is a diff-
erence between the phase of the current and of the
voltage, the current leads the voltage as in a
condenser circuit. This phase difference has been
discussed by Cooper.[19] The theoretical consider-
ations of Mengarini[2] led to a phase difference in
which the voltage led the current but this is not
in accordance with observation. Confirmation of
the above theory is found in the alternating current

and voltage curves obtained by Hopkinson,
Wilson, and Lydall,[20] which show a phase diff-
erence as high as 72^0 with the current leading
the voltage. Their curves for the voltage do
not follow the sine law and show considerable
irregularity. In some cases indications of
the distortion shown in Figure [12], are seen.

The extent of this phase difference and
the distortion of the wave form will decrease
as the current and the resistance are increased.
For the same current and resistance this diff-
erence will vary for different metals, and vary
with their critical current density and the
individual electrolytic capacities of the elec-
trode for hydrogen and oxygen.

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Part XI. Practical Consideration.

The first principle to be observed in preventing alternating current electrolysis is the obtaining of uniform current densities. Pipe or rod electrodes with exposed, rounded ends, as at present used, will produce high current densities on these ends. The current density used commercially in steam-producing electric boilers is about 0.75 amperes per square inch, as calculated on the assumption of uniform current density. Above this density decomposition of the electrolyte becomes serious. From the above experimental work, it is seen that electrodes producing steam can be operated at a current density of 13 amperes per square inch without decomposition of the electrolyte, which density is some distance from the critical point of 19 amperes per square inch. Such a high current density as 13 is impracticable due to difficulties in handling the steam, but the present-day boiler can be made safe and its heating capacity increased to a considerable extent if the electrode chamber is designed to obtain as far as practicable the conditions of uniform current density.

Two suggested designs of such electrode chambers are shown in figures 13 and 14. In one the three electrodes are placed symmetrically and vertically

in a metallic cylindrical tank, as shown in figure 13.
No special arrangement at the top is necessary as
long as the water level remains below the steam
outlet. The essential feature is the large porcelain
insulator at the bottom. This is a circular plate
which fits the bottom of the chamber with three
shallow pockets for the ends of the electrodes,
(figure 13b). No great thickness of the porcelain
is necessary, as there is no strain upon it. A hole
is provided through the centre of the porcelain and
the electrode chamber for the water supply. The
above arrangement with electrodes of two inches
diameter, separated from one another and the walls
of the chamber by ten inches, gives a high uniformity
of current density.

Concentric cylinders might also be employed
as shown by figure 14. In this design the electrode
chamber built from two cylindrical walls and acts as
one electrode. The other cylindrical electrode is
inside. The porcelain insulator is a flat ring with
a circular groove, as shown in figure 14b. Numerous
small holes give access to the water supply. This
design is advantageous because of its compactness, but
is limited in this form to single-phase current. A
shamrock group of three such chambers, or an arrange-
ment of three cylindrical and concentric cylinders in
the same way as above is adaptable to three-phase current.

In the second case the diameters of the cylinders would
be such as to equalize the load. The limitation of
the compactness of such a design would not be in the
current density but in the handling og the steam. This
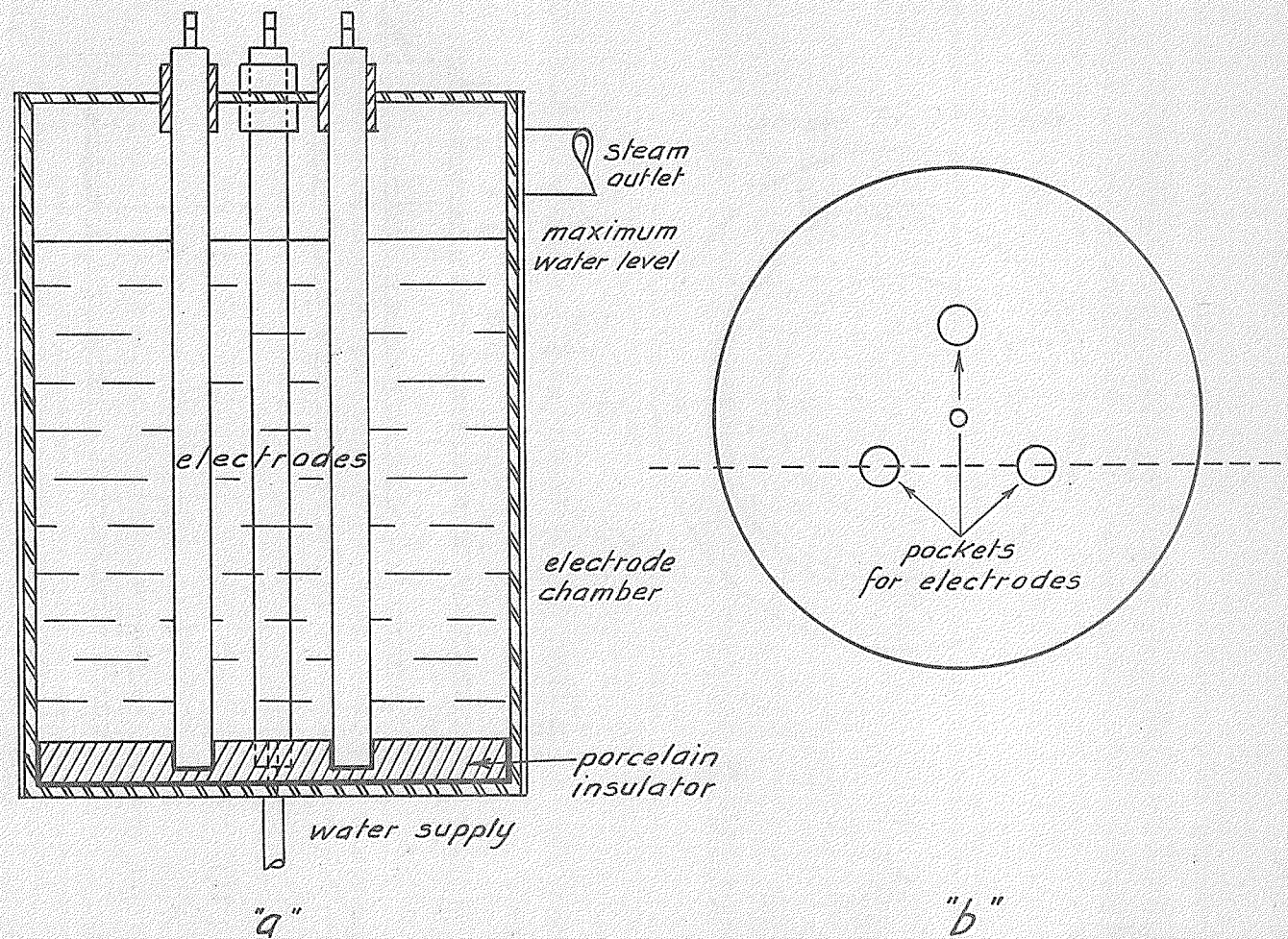is a problem for the electrical heating engineer.

steam outlet

maximum water level

electrodes

electrode chamber

porcelain insulator

water supply

"a"

pockets for electrodes

"b"

Fig. 13. Proposed Design (1) of Electrode Chamber in Electric Boilers for the Prevention of Generation of Explosive Gases.

steam outlet

maximum water level

electrode chamber

cylindrical electrode

porcelain insulator

water supply
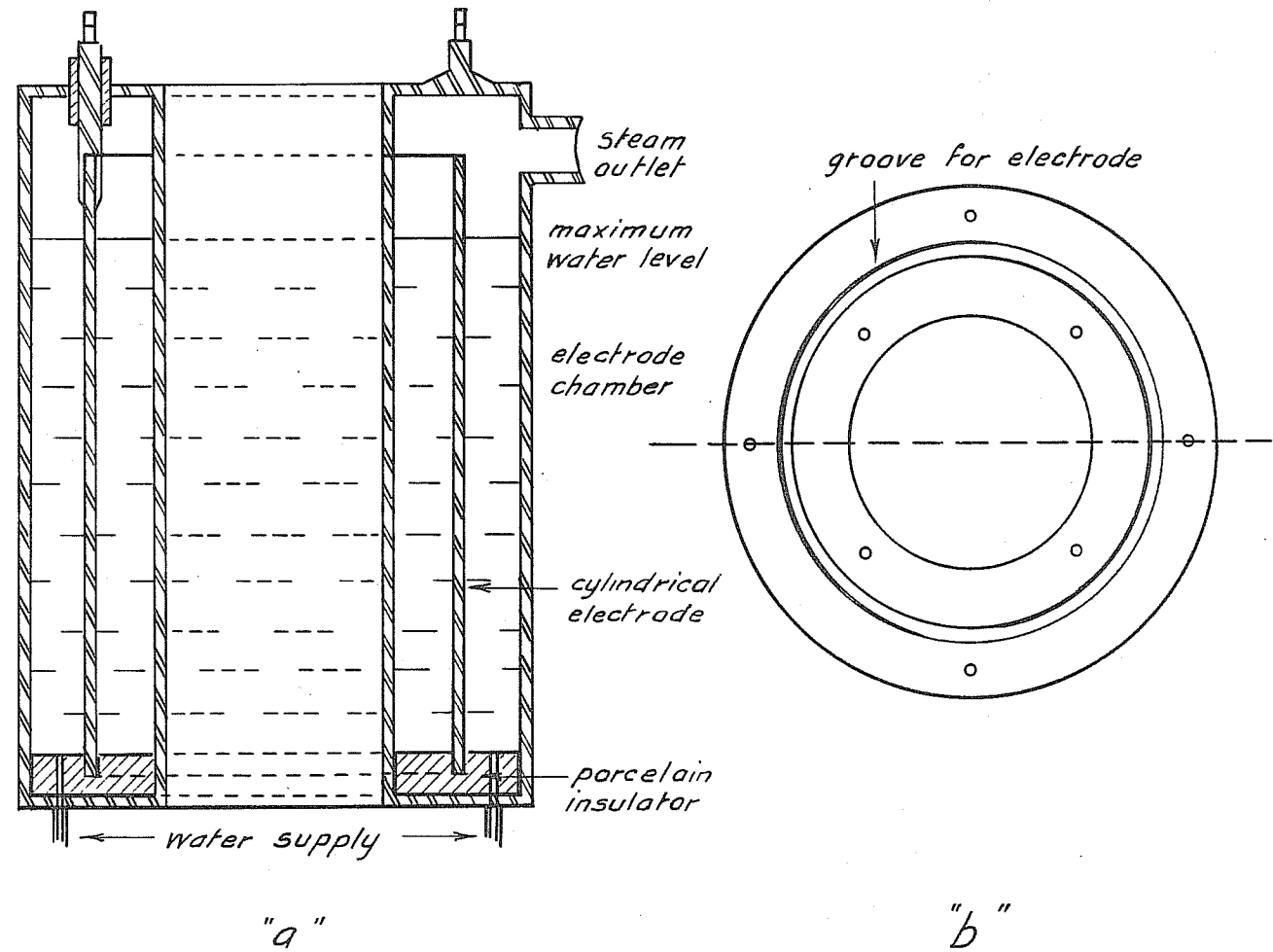
groove for electrode

"a"

"b"

Fig. 14.   Proposed Design (2) of Electrode Chamber in Electric
Boilers   for   the   Prevention of Generation   of Explosive Gases.

Part XII.   SUMMARY.

(1) The primary factor in alternating current electrolysis is current density.

(2) In alternating current electrolysis a critical current density below which no electrolytic gases were evolved was determined for seven metallic electrodes when the conditions of frequency, temperature, pressure, voltage and electrolyte were maintained constant.

(3) Above the critical current density alternating current electrolysis was shown to follow the law of direct current electrolysis, and may be made coincident with it by subtracting the critical current density from the current density employed. In other words, when the critical current density is reached, all the current above that point generates electrolytic gases, which are given off from the electrode.

(4) The critical current density with iron electrodes varies with temperature, rising from $0^{\circ}C$ to about $80^{\circ}C$ and falling to the boiling point.

(5) The rate of gas evolution with iron electrodes
likewise varies with temperature, falling
from $0^{\circ}C$ to about $80^{\circ}C$ and rising to to the
boiling point.

(6) Arcing in itself makes no appreciable difference
in voltages below 110.

(7) The existence of a critical current density is
credited to an electrolytic capacity of the
electrodes to store up the products of elec-
trolysis. Direct determinations of this cap-
acity have been made.

(8) The electrolytic capacity was shown to be dep-
endent upon the nature and condition of the
electrode surface.

(9) The relation of the back E.M.F. to the quantity
of electricity passed was determined and related
to the wave of the alternating current, producing
a phase difference.

(10) The generation of explosive gases in the water-
resistor type of electric heater can be prevented
by a design of electrode chamber that would secure
and retain under operating conditions uniform
current density.

(11) The current density in such a heater can be considerably increased over present usage without danger of the generation of explosive gases.
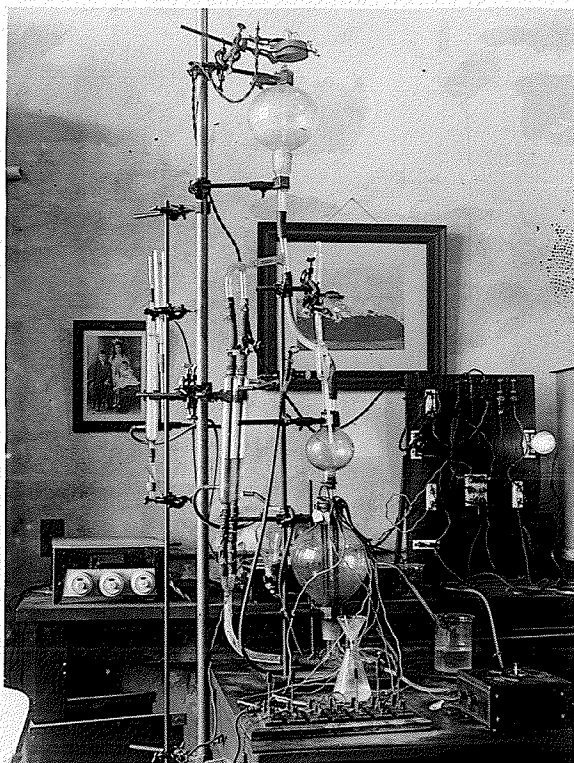
Acknowledgement.

PLATES.

Plate I. Miniature electric water boiler
used in determining the cause of the pro-
duction of explosive gases. (see page 26.)

Plate II. Apparatus for determining the
rate of alternating current electrolysis
at various current densities and frequen-
cies. (see page 30.)

I

II