THE ELECTROLYTIC PRODUCTION OF PEROXYDISULFURIC ACID

USING PERIODICALLY REVERSED DIRECT CURRENT

AND ALTERNATING CURRENT SUPERIMPOSED

ON DIRECT CURRENT

by

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I. INTRODUCTION

Periodically-reversed direct current and alternating current superimposed on direct current have been applied to some phases of electrodeposition. Very little work has been done on the application of these two types of current to non-metallic chemical reactions. However, it is expected that application of these two types of electrolysis will find increasing applications.

Methods for direct-current, electrolytic production of peroxydisulfuric acid have been developed. This is an example of an anodic oxidation in which the anion is oxidized to a peroxy-anion. The behavior of a platinum anode in sulfuric anolyte with periodically reversed direct current, or with alternating current superimposed on direct current, would serve as an example for the study of this class of reaction.

The factors which influence the production of peroxydisulfuric acid are the temperature, nature of electrode, concentration of sulfuric acid, current density, and the presence of catalysts. However, no

studies have been found in the literature on the effects of periodically-reversed direct current on the yield of peroxydisulfuric acid. Studies of the effect of alternating current superimposed on direct current have been made only at low frequencies[46]. Extension of these studies would be of value in determining the maximum rate of formation of the oxidized anion.

The purpose of this investigation was to study the effect of varying the time ratio of direct to reverse current from one to 20, at an anode current density of 4.5 amperes per square centimeter, and to study the effect of alternating current of 0, 240, and 500 cycles per second, 0.2 to 4.5 amperes per square centimeter, superimposed on direct current, on the electrolytic production of peroxydisulfuric acid.

II. LITERATURE REVIEW

This portion of investigation is concerned with a review of the existing literature pertaining directly to the research problem. This includes the following headings: properties of peroxydisulfuric acid, methods of preparation of peroxydisulfuric acid, electrolysis with periodically reversed direct current, and electrolysis with alternating current superimposed on direct current.

Properties and Uses of Peroxydisulfuric Acid

Peroxydisulfuric acid[34], $H_2S_2O_8$, having a molecular weight of 194.15 is a crystalline solid whose active oxygen content is 8.2 per cent, is very reactive, and not stable. It melts with decomposition at about 65 °C and is not easily obtained in a pure state. It is seldom isolated, but is synthesized and used in solution as an intermediate step in a widely-used process for manufacturing hydrogen peroxide. Peroxydisulfuric acid is extremely reactive toward organic matters, and explosions are said to result upon mixing with many solvents. Even paraffin is charred upon contact.

Solutions of peroxydisulfuric acid, made on a large scale, are reasonably stable when kept cool, but hydrolyze rapidly when boiled in the presence of excess sulfuric acid. Freshly prepared solutions contain little or no hydrogen peroxide, and do not show the typical reactions of this compound. Permanganate is not decolorized, nor is a yellow color obtained upon the addition of a titanium solution as is the case with hydrogen peroxide. Iodide is slowly oxidized to iodine. On the other hand, ferrous ion is oxidized rapidly. Solutions containing peroxydisulfate absorb radiant energy in the near ultraviolet.

Peroxydisulfuric acid solutions, containing a trace of silver ion, oxidize manganous solutions to permanganate. A recent study has shown that such solutions are useful in certain organic oxidations, such as cleavage of 1,3 glycols[25] to yield aldehydes and ketones.

Solution of peroxydisulfuric acid and its salts are analyzed for their active oxygen content by treating with an excess of ferrous sulfate, or ferrous ammonium sulfate, solution, then back titrating with standard permanganate solution.

Peroxydisulfuric acid, in former times, was used to manufacture hydrogen peroxide, and as a bleaching agent in the textile industry. In recent years, peroxydisulfuric acid was found to be a promoter in catalytic-chemical synthesis[60].

Methods of Preparing Peroxydisulfuric Acid

This section contains a description of both chemical and electrolytic methods for manufacturing peroxydisulfuric acid. The chemical method is given briefly since it was abandoned as soon as electrolytic methods were discovered. In describing the electrolytic method, the information on the concentration of sulfuric acid, the nature of the electrodes, temperature, and the current density will be given in detail.

Chemical Methods of Preparing Peroxydisulfuric Acid. J. D'Ams and W. Friederich[11] prepared anhydrous peroxydisulfuric acid by gradually adding one mol of hydrogen peroxide to two mols of chlorosulphonic acid,

$$2 \, ClHSO_3 + H_2O_2 \longrightarrow H_2S_2O_8 + 2HCl$$

The hydrogen chloride was sucked from the crystals and the mother liquor was separated by using the centrifuge.

F. Fisher and K. Humpert[17] observed that presumably peroxydisulfuric acid was formed when fluorine acted on a cold saturated solution of sulfates or hydrosulfates,

$$3K_2SO_4 + F_2 + 2HF = K_2S_2O_8 + 3KF + KFSO_3 + H_2O$$
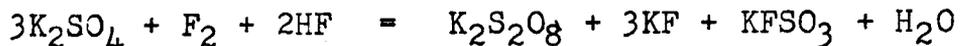
Electrolytic Methods of Preparing Peroxydisulfuric Acid. M. Berthelot[4] passed the electrical discharge through equal volumes of dry sulfur dioxide and oxygen, and a gas that he called sulfur heptoxide, S_2O_7, was formed. The reaction was expressed as,

$$2SO_2 + 2O_2 = S_2O_7 + (O)$$

M. Traube[59] first thought that in electrolysis of sulfuric acid a substance corresponding with the sulfate was produced, and M. Berthelot[4] showed that its anhydride was really heptoxide, S_2O_7.

There were several explanations for the formation of peroxydisulfuric acid at the anode when sulfuric acid was electrolyzed. M. Berthelot[4] considered

that the formation of peroxydisulfuric acid was a
process of oxidation by the hydrogen peroxide
formed at the anode. K. Elbs and O. Schonherr[12],
on the other hand, attributed this formation to two
discharged HSO_4-ions united together to form $H_2S_2O_8$.
Foerster[42,44] stated that the oxidation of sulfate
ions by anodic oxygen was responsible for the per-
oxydisulfuric acid formation.

Ryoichi Matsuda[42,43] in 1936 suggested that the
hydroxyl ion discharged at the anode seemed to play an
important role in the peroxydisulfate formation. In
order to prove this he electrolyzed the solutions of
sulfuric acid and ammonium sulfate of varying concen-
trations at 16 to 20 °C with two platinum electrodes.
He found that the increase of hydroxyl ions was favor-
able to the formation of peroxydisulfate, and the
current efficiency with regard to the total peroxidic
oxygen was increased as the amount of ammonium sulfate
increased.

Factors influencing the production of peroxydisul-
fate are the concentration of sulfuric acid, tempera-
ture, the nature and the treatment of the electrode,
and the current density. W. Sterck[57] found that

the formation of peroxydisulfuric acid was proportional to the concentration of hydrosulfate ion up to a certain value, 40 per cent of sulfuric acid. The poorer yield of peroxydisulfuric acid from this point onward was probably due to its instability in concentrated sulfuric acid, rather than to a decrease in the quantity of hydrosulfate ion.

K. Elbs and O. Schonherr[12] electrolyzed the solutions of sulfuric acid of varying specific gravity from 1.15 to 1.6 with current densities of 5, 50, and 100 amperes per square decimeter. They found that the highest yeild of peroxydisulfuric acid was 78.4 per cent using sulfuric acid of specific gravity, 1.5, at a current density of 100 amperes per square decimeter. They also found that the yield was increased as the current density increases, but, for a certain current density, the yield of peroxydisulfuric acid increased as the specific gravity of sulfuric acid increased from 1.15 to 1.5, and from this point the yield was decreased. This decrease in yield[12] was caused by the acid itself taking part in the conduction of current and being destroyed. It may also be due to the rapid conversion of peroxydisulfuric acid to

permonosulfuric acid by sulfuric acid at this concen-
tration and the subsequent decomposition of the per-
monosulfuric acid.

During the electrolysis of sulfuric acid of 1.4
specific gravity, at 15 °C, to produce peroxydisulfuric
acid, only a trace of hydroxide peroxide was formed at
the anode. The formation of permonosulfuric acid,
during electrolysis, depends on the current density,
temperature, concentration of acid, and treatment of
the electrode. E. Muller and Schellhaass[47] examined
the effect of concentration of sulfuric acid on the
yield of peroxydisulfuric acid. They obtained the
maximum yield with sulfuric acid of specific gravity
of 1.39.

Method of Preparing Peroxydisulfuric Acid with
Direct Current. K. Elbs and O. Schonherr[12,13]
recommended the preparation of peroxydisulfuric acid
by the electrolysis of sulfuric acid of specific
gravity of 1.35 to 1.50. The apparatus employed con-
sisted of a divided cell formed by a porous jar of
100 milliliter capacity, standing in a beaker. A
cylinder of lead of 150 square centimeter surface,
surrounding the jar, formed the cathode. The anode

was of platinum, either wire or plate, dipping into
the jar. The cell was surrounded with ice. Sometimes
the arrangement was reversed, a ring of platinum wire
in the outer cell forming the anode, and a foil lead
pipe in the jar acting both as cathode and as a cooling
worm. The resulting anolyte after being electrolyzed
overnight with a current of two amperes and current
density of 500 amperes per square decimeter and four
volts, contained 510 grams of peroxydisulfuric acid
and 129 grams of sulfuric acid per liter. No hydrogen
peroxide was present. This was treated at 0 °C with
barium carbonate to precipitate the sulfuric acid, and
filtered. Under the above conditions, the yield was
67.5 per cent for the first 50 minutes electrolysis.

Electrolysis With Periodically-Reversed

Direct Current

This section deals with the theory, production, and application of periodically-reversed direct current.

In 1925, one English company[53] was making use of periodic reverse plating. However, it was Jernstedt[29] who aroused a great amount of interest by electroplating with periodically-reversed, direct current in 1947. In the process, the article being plated was made cathodic, the current was reversed making the article anodic for a shorter period of time, and then the current was reversed again making the article cathodic. This cycle was repeated continually during the electrolytic treatment of the article.

Definitions. Before pursuing further the subject, it may be well to define the following terms[28] which are peculiar to periodic reverse plating.

Cathode current efficiency is the percentage of coulombs which is effective in depositing a metal on the article that is being plated while it is cathodic.

Periodic reverse cycle efficiency is equal to the net time of the plating divided by the total

cycle time, provided the switching efficiency is 100 per cent.

Switching efficiency is equal to 100 times the sum of the time of plating and the time of deplating divided by the total time of a cycle. This actually is a measure of the time lost because of failure to accomplish full reversal instantaneously and it depends on a combination of mechanical and electrical factors.

Effective current density is that which by direct current methods would cause the deposition of the same amount of metal in the same time as is obtained with a given periodic reverse process. The following equation may be helpful:

$$ECD = (CCD)(PRSE)$$

where:

ECD = effective current density,
amp per sq cm

CCD = cathode current density, amp
per sq cm

PRSE = periodic reverse switching
efficiency, per cent

Periodic Reverse Plating. The underlying prin-
ciple[53] of periodic reverse plating is that deposi-
tion is carried out for a predetermined short period
of time by conventional direct current after which
the current is reversed and the article is made anodic,
usually for a shorter period of time and at the
same[28] or higher[53] current density than in the
cathodic plating stage. During the direct current
portion of each cycle, a thin deposit is applied in
the usual manner. When the current is reversed, the
high spots and rough projections are partially
deplated[53] in preference to any low or unplated
spots.

Any metal deplated from the base member by the
reverse current is driven[53] into the solution
immediately adjacent to it so that an abnormally
high local concentration of metal ions is present
when plating is resumed during the next interval of
direct cathode current. The plating during the next
direct current interval is greatly improved since it
is applied to a smoother and brighter surface; also,
the efficiency of the plating stage[53] is improved
owing to the high concentration of metal ions near

the surface of the article being plated. Even scratches, recesses, and internal surfaces are alleged to be covered almost as efficiently as any other portion of the base and a much higher speed[21,22,23] is possible owing to the high concentration of metal ions in the vicinity of the metal surface.

It is known[53] that metal plated by continuous direct current is of higher quality during the initial portion of the plating period. The metal plated later tends to become crystalline and to build up at projections and other spots where there is current concentration or presence of more metallic ions in the adjacent electrolyte. Bregman[6] states that the more sacrificial the plating cycle, that is, the more closely does the plating period approach the deplating period, the better the quality of the plate. However, a sacrificial cycle requires a relative long total plating time for a given thickness of deposit. For most applications, reversal of the current deplates[30] from 10 to 50 per cent or more of each increment just plated. The amount to be deplated per cycle is regulated in accordance with the quality of the increment and the desired quality of overall deposit.

As already stated, due to the reverse of the plating current for a short period of time to deplate the unsound and inferior metal[14] deposits, this method results in building up many microscopically thin increments of sound metal more dense and more homogeneous than possible with the continuous current method. In addition, this deposit shows superior qualities of strength, elasticity, density, and freedom from flaws, such as porosity. In general, where periodic reverse plating is successful, one or more of the following advantages is evident as compared to normal, direct current methods:

1. better appearance of plate[29,38]
2. heavier deposits obtainable[6]
3. better mechanical properties obtainable[6,53]
4. faster plating speeds[6,29]
5. higher conductivities[53]
6. higher resistance to corrosion[53]
7. improved anode corrosion[29]
8. reduction of costs[29]
9. reduction in quantity of addition agents required[6].

Use of Complex Wave Forms. In periodic reverse plating the time-current curve may be of any desired form provided the energy of the deplating current is at least 10 per cent of that of the plating current. This was stated in a patent assigned to Westinghouse[58]. Apparently, very little or no work has been done to compare simple periodic reverse plating with plating techniques employing more complicated current forms. Figure 1 gives the time-current curves for some of the basic types of electroplating wave forms.

Periodic Reverse Electrochemical Reaction. To the writer's knowledge, very little work has been reported in the literature regarding the application of periodically reversing direct current during electrolytic reactions. The electrochemical production of lead chromate[49,50] using periodically reversed direct current has been studied. The effect on yield and purity, of varying the direct to reverse time ratio of periodically reversed direct current from one to 20, at an anode current density of 0.0059 ampere per square centimeter, at the temperature of approximately 33 °C was determined. Two baths were

(A) DIRECT CURRENT

(B) RECTIFIED DIRECT CURRENT

(C) PULSED DIRECT CURRENT

(D) PERIODICALLY REVERSED DIRECT CURRENT
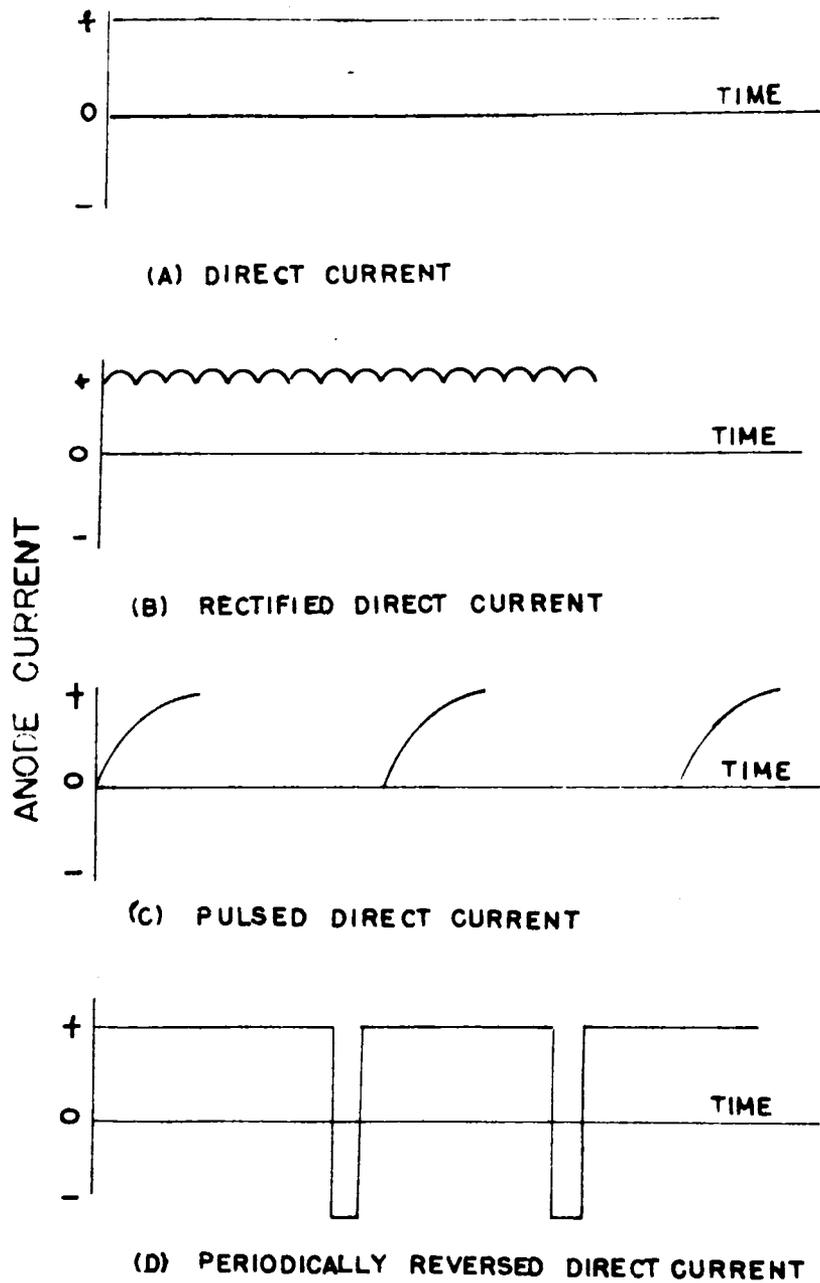
FIGURE I. TIME-CURRENT CURVES FOR VARIOUS

WAVE FORMS

JERNSTEDT, G. W.: PERIODIC REVERSE ELECTRO-

PLATING, METAL FINISHING, **45** NO.2. 69 (1947).

studied: one contained 6.80 grams of potassium chromate, 8.14 grams of sodium nitrate, and 1000 grams of water; the other contained 3.60 grams of potassium chromate, 11.62 grams of sodium nitrate, and 1000 grams of water.

In general, the yield and purity were not improved by using periodic reverse current as compared to using direct current. However, an interesting relation was observed between direct to reverse time and direct to reverse current. The ratio of time of direct to time of reverse current was always greater than the ratio of the direct current to reverse current; the difference decreased as the ratio decreased. The difference is ascribed to the polarization of the electrodes.

Limitations of Periodic Reverse Electrolysis. One of the feature limitations of periodic reverse electrolysis is that most current reversing equipment possesses poor switching efficiencies, which results in higher power costs. The theory of periodic reverse electrolysis is not easily applied since many factors influence the results desired. Such factors are the shape of the time-current curve, duration and

magnitude of direct and reverse currents, anode and
cathode efficiencies, and time-current yield rela-
tionships. Another limitation of the process is
that the overall electrical efficiencies in periodic
reverse plating are rather low because of the
deplating portion of the cycles[6].

Current Reversal Equipment. The success of the
periodic reverse process depends on rapid current
reversal. If the current does not build up to the
maximum amount immediately after reversals in the
cycle, the process becomes less efficient. A few
commercially available periodic reversers are
listed here:

1. Hill Cross pulse selector[14]

2. Plater's Research Corporation electronic
   relay[52]

3. combined reverse current and rectifier
   units[9]

4. cam-operated switches[54].

These reversers, although not operating on the same
principle, accomplish the same result of periodically
reversing direct current.

Electrolysis With Alternating Current

Superimposed on Direct Current

Electrochemical literature shows[23,24] that superimposing an alternating current on a direct current in electrolysis causes a decrease in electrode potential, reduces any irreversibility of the reaction, acts as a depolarizer, reduces hydrogen and chlorine overvoltage, affects the oxygen evolution at the anode, and allows higher current density of the direct current at an electrode.

This section of the literature review deals with the general principles, the effects on the electrode process, and the applications of the superimposed alternating current. Also included is a section relating to electrical circuits for achieving superimposed alternating current on direct current.

Before pursuing the subject, it may be well to define the following terms and to give the types of superimposing alternating current which will be used in this investigation.

Electric Double Layer. According to Stern's[35] theory, the electric double layer is regarded as a

combination of a compact layer of approximately molec-
ular thickness intermediately attached to the electrode
surface and, beyond this, a diffuse layer extending
into the bulk of the solution. The potential differ-
ence between the electrode and the solution is thus
divided into two parts. The potential drop across
the compact layer is a linear function and that across
the diffuse layer is an exponential form, shown as
Figure 2. The whole thing behaves as a plate condenser.

<u>Polarizable Electrode</u>[35]. As is assumed in the
preceding paragraph, the capacity of the double layer
behaves as a condenser and, consequently, a negligible
number of ions cross the electrode-interface during the
charging process. Some electrode systems, in fact,
function in this way but in some other systems there is
little hindrance to passage of the ions from the solu-
tion to the electrode and in the reverse direction. An
electrode functioning under the limiting condition that
no ions cross the double layer is termed a completely
polarizable electrode, and an electrode functioning
under the limiting condition that the ions completely
and freely pass across the double layer is termed a
non-polarizable electrode. In fact, no electrode
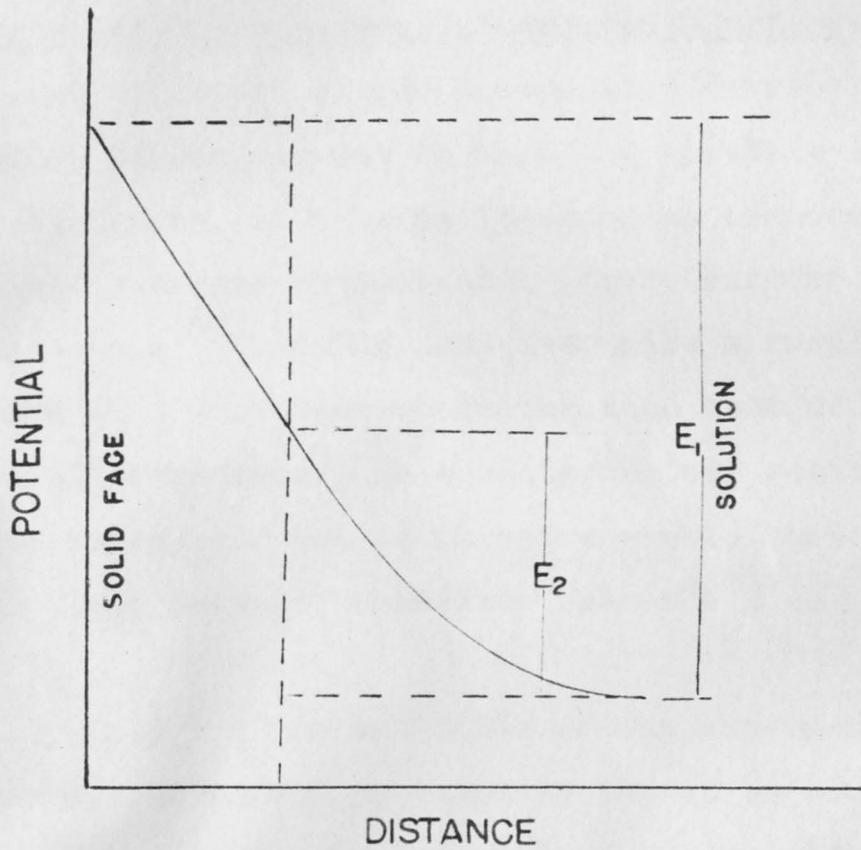
FIGURE 2. REPRESENTATION OF THE POTENTIAL—DISTANCE
RELATION FOR THE ELECTRODE—SOLUTION INTERFACE

system is a perfect example of either limiting case.
There is often some passage of ions across the double
layer during charging so that the double layer behaves
as a leaky condenser.

Types of Superimposing Alternating Current. The
underlying principle of the alternating current super-
imposed on direct current is that, by suitable elec-
trical equipment, an alternating-current component is
introduced into the conventional direct-current circuit.
The components[65], being additive, give a resulting
wave form of a different character than that of its
individual components. In considering the ratio of
the alternating current to direct current, three
general cases present themselves, shown[65] as
Figure 3.

Case I. The amplitude of the alternating-
current component is equal to the direct-current
component, shown as Figure 3a. The current falls
to zero periodically and is equivalent to an
interrupted direct current.

Case II. The amplitude of the alternating-
current component is greater than the direct-
current component, shown as Figure 3b. This
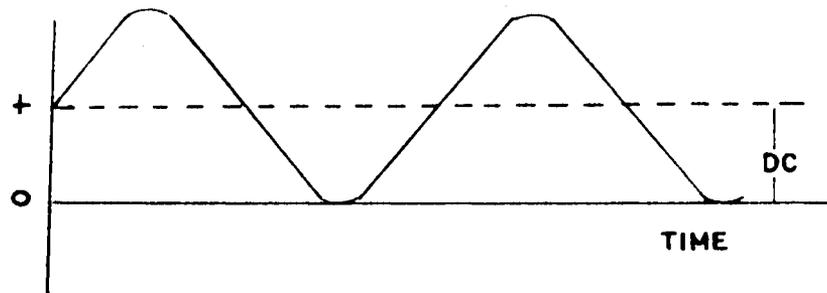
(A) CASE I. AC = DC
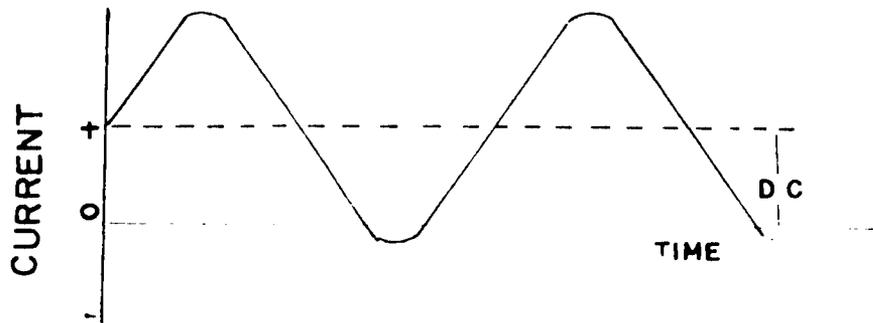
(B) CASE II. AC > DC
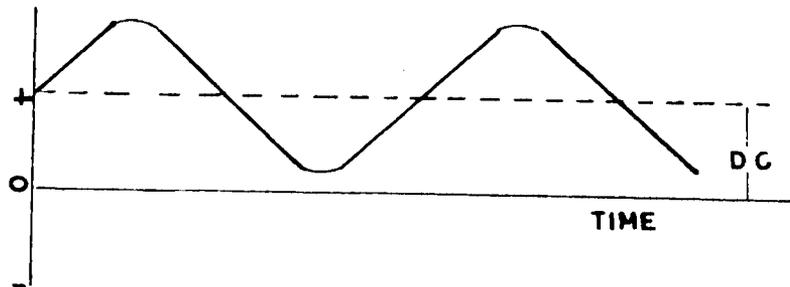
(C) CASE III AC < DC

FIGURE 3, TIME-CURRENT RELATIONS FOR ALTERNATING CURRENT

SUPERIMPOSED ON DIRECT CURRENT

causes the direction of the total current in the circuit to reverse periodically.

Case III. The amplitude of the alternating-current component is less than that of the direct-current component, shown as Figure 3c. In this way, the total current in the circuit is always positive and is equivalent to the pulsating direct current.

The second case is the so-called "periodic reverse current" and is considered of importance to electro-deposition of metals. In this manner of electrolysis, the electrodes of the cell are made alternately anodic and cathodic. The reverse time is shorter than that of the direct time, and this is dependent on the frequency of the alternating current used.

The theoretical, limiting current density for a given cathode reaction is the maximum possible rate of deposition of a given ion. Any attempt to increase further the current may accompany a shift in potential to a higher range where some other ion specie will be deposited. If an aqueous solution contains one cation, an increase in potential (and current density) will result in decomposition of the solvent and evolution of hydrogen.

The current density is a function of the ion concentration of the cathode film, which is the so-called "electric double layer", and of the rate of diffusion of the ions across it. To achieve the maximum rate of discharge of a given cation, conditions should be such that the diffusion rate and the concentration of the ions in the film are increased. In other words, attempts were made to make the ion concentration in the film as high as possible and the thickness of the film as thin as possible. Superimposed alternating current serves to keep film concentration high and film thin.

Depolarization by Alternating Current. Wien[56,63], in 1896, discovered the polarization resistance of an electric cell. Hence, the measured effective resistance of an electrolytic cell may be expressed as,

$$R_s = R_t + R_c \qquad (1)$$

where:

R_s = effective resistance of electrolytic cell, ohm

R_t = electrolytic resistance, ohm

R_c = resistance due to electrode polarization, ohm.

"R_c" is also called the polarization resistance. The dependency of the polarization resistance on the frequency has been studied by Jones[31], Ershler[16], and others[24,56]. They found that the polarization resistance can be expressed by the following equation:

$$R_c = kf^{-n} \qquad (2)$$

where "k" and "n" are both constants and "n" has the value between 0.5 and 1.0. From the equation just given, under an alternating field, the concentration overpotential should be less than that under a direct current field. It is therefore possible to relate the resistance and capacity of an electrode reaction, measured under alternating current to its exchange current. Erschler[16,24] applied the Fick's law to

the metal solution interface (deposition and dis-
solution of a metal) and he obtained the following
equation:

$$R_s = \frac{RT}{zF} \times \frac{1}{i} + R_c \qquad (3)$$

where:

R_s = effective resistance of an electro-
lytic cell, ohm

R_c = polarization resistance

T = temperature, °K

i = current, amp

R = constant

F = 96,500 coulombs per equivalent.

Eschler[16] analyzed the term "R_s" and showed it to
be proportional to "$w^{0.5}$" and "w" is equal to "$2f$",
where "f" is the frequency of the alternating current
used.

It has been already stated that the electric
double layer[35] acts like a leaky condenser. A
number of investigators have reported that the

capacitance of the double layer and frequency have
the following relationship:

$$C_s = k'w^{-0.5} \tag{4}$$

where:

C_s = capacitance of double layer, Farad

w = frequency, radians per second

k' = constant.

Others[56], on the other hand, preferred the follow-
ing expression:

$$C_s = k_2 + k_1/w \tag{5}$$

where "k_1" and "k_2" are constants. "C_s" is the same
as given in equation (5).

Kortum and Bockris[35] studied the dependence
of the total capacitance on concentration and
frequency in an alternating current field. They
stated that, for small concentrations, there will
be no effect of frequency on double layer capacitance.
However, for high concentrations it is dependent on
frequency, and the double layer capacitance will be
decreased as the frequency of the alternating current
increases.

The theory of polarization resistance, "R_c",
which accompanies the polarization capacitance, "C_s",
has been the subject of much speculation. Its dis-
coverer, Wien[63], pointed out that its existence
proves nothing except that there occurs an energy
loss of some kind in addition to that associated
with the true conductivity of the solution itself.
He suggested that it might be due to a poorly con-
ducting surface layer on the electrode, in which case
the lost energy would be degraded.

Heinrich and Klemenc[27] derived general equations
for the case where alternating current is flowing
between two electrodes while they are both either
cathodes or anodes in a direct current circuit between
them and a third electrode. It is shown that the
effect of alternating current is not directly propor-
tional to its intensity, but is expressible by a com-
plex function. For the special case when the direct
current connection is made at such a place on the
transformer winding that the induced potentials and
resistances are equal on both sides, the two outer
electrodes will not change polarity as long as the
alternating current is greater than $\sqrt{3/8}$ of the

direct current. For the special case where only two
electrodes are used, to which both alternating and
direct current are applied, the electrodes will not
change polarity unless the alternating current is
greater than $\sqrt{3/2}$ of the direct current.

The recent work[5,16,18,55,56] on alternating-
current depolarization seems concentrated on the
measurement of the impedance of the interface between
the electrode and the solution, and this[24] has been
considered probably as a very accurately-measurable
property. The work of Erschler[16], Randles[55], and
Gerischer[18], are representative of the modern point
of view. The main concept is as follows: the resist-
ance of a solution is in series with the impedance of
the interface and can be subtracted out of the
measured impedance. What remains is the impedance
of the interface. The impedance[24] of the other
electrode, which is also in series, can be made
negligible by a judicious choice of electrode sizes
and shapes. This impedance is made up of two
parallel impedances, one being the admittance of
the electrical double layer, and the other being
the admittance of the electrode resulting from any

faradaic processes which involves an appreciable
exchange current. There is only a slight and pre-
sumably negligible interaction[24] between the two
kinds of admittance, for which reason they can be
treated independently. The faradaic admittance can
be represented by an "equivalent circuit" made up of
a resistance, "r", and an impedance, "w", in series.
In this circuit, "r" is a pure resistance in the
sense that it does not change magnitude with frequency
and does produce electromotive force in phase with the
faradaic current. The value, "r", is a measure of the
intrinsic speed of the reaction and is simply related
to the exchange current at equilibrium, "i", through
the relation[24],

$$r = dE/di = RT/nFi \qquad (5)$$

where "n" is the number of electrons involved in the
faradaic process. In the above "equivalent circuit",
"w" has been called, by Grahame, the "Warburg imped-
ance"[24]. It is not representable at all frequencies,
even at a single potential, by ordinary resistors, con-
densers, and inductors, but can be represented at any
one frequency and potential by a series or parallel

combination of a resistor and a condenser. Expressed as a series combination, the impedances of the two elements are equal at any one frequency, giving rise to 45 degrees phase shift, and vary inversely as the square root of the frequency.

Gerischer[18,24] has used the alternating-current impedance of an electrode to measure the exchange current as a function of concentrations of the substances which could be participating in the charge-transfer reaction. This procedure gives the coefficients of the charge-transfer reaction.

It is considered that the alternating-current impedance method would be a simple method of measuring the polarizability of an electrode, since concentration polarization is very much less with alternating current than with direct current and also the transfer coefficient, "dE/di", equation (5), is measured directly as a resistance rather than indirectly as a slope of a curve. At the same time it has been possible by alternating-current impedance methods to determine accurate values of the transfer coefficient for a variety of electrode reactions. The value of "n", equation 5, was found to vary and not to be equal to 0.5 as indicated by Tafel[10a].

Experimental Work on Alternating Current Depolarization. Goodwin and Knobel[23], in 1920, studied the effect of superimposing alternating current on hydrogen overvoltage on lead, copper, mercury, and platinum electrodes in normal sulfuric acid at frequencies from 2 to 100 cycles per second. Their work is summarized as follows:

1. An alternating current superimposed on a direct current lowers the cathodic polarization of hydrogen.

2. The magnitude of the polarization is determined primarily by the ratio of alternating to direct current, and appears to be independent of the electrodes and of the current density.

3. The effect varies slightly with frequency, the tendency being to increase as the frequency is diminished. For a variation of frequency from 2 to 100 cycles per second, the polarization increases only 50 millivolts.

4. The effect is practically independent of the power factor, varying less than 30 millivolts for a change in power factor from 0.5 lag to nearly zero lead.

It was claimed[23] that the lowering of the over-
voltage was the result of the formation of oxygen by
the reverse current. This was based on the observa-
tion that no appreciable lowering was observed until
the alternating to direct current was large enough to
produce an actual reversal of the current.

Glasstone[20] investigated the effect of small
alternating currents (with no current reversal) on
cathodic and anodic overpotential for a number of
different metals in normal sulfuric acid and sodium
hydroxide solutions. His results indicated that lower-
ing of the overvoltage takes place only in a limited
number of cases, and he recognized the effect that,
when an alternating current was superimposed on a
direct current, the voltage drop across the elec-
trolytic cell will be an average of a varying volt-
age. Glasstone[20] claimed that previous literature
values of lowering of overpotential by alternating
current were doubtful because the electrical circuits
were so arranged that the ammeter indicated only
average values of the current, not the instantaneous
values.

Ghosh[19] studied the action of a high-frequency,
alternating current on single voltaic cells and on

electrolytic cells for both reversible and irreversible processes. His work is summarized as follows:

1. When an alternating current of high frequency, about 500 cycles per second, passes through a cell consisting of two platinum electrodes in any electrolyte, the electrode potentials change, thus indicating that some chemical action at the electrode surface takes place in that short period of time.

2. When an alternating current passes through a reversible voltaic cell, there is no change in the electrode potential. If, however, one of the electrodes consists of a metal covered with its insoluble salts, the alternating current has a pronounced effect on the electrode.

3. A greater amount of current could be supplied by a cell with one reversible and another irreversible electrode, when an alternating current is in the circuit.

4. In perfectly reversible electrolytic cells the alternating current has no action when impressed on the cell along with direct current.

5. Should the electrolytic cell be irreversible, the alternating current greatly increases the strength through the circuit.

6. The increase in current strength is due to the diminution in the back electromotive force of the polarization.

7. This diminution of the discharge potential is also observed in electrolytic cells consisting of two cathodes and two anodes, the alternating current passing between the anodes or the cathodes, but not passing through the whole circuit.

The work performed by Ghosh[19] did not take into account the ratio of alternating to direct current.

Epelboin[15] studied the electrolytic phenomena at the electrodes caused by superimposed alternating current of small amplitude onto the direct current. For aqueous solutions and fused salts with inert electrodes, the variation of impedance is equivalent to a resistor in series in a fixed capacity. For nickel electrodes in mixed perchloric acid and acetic anhydride the capacity is six times the theoretical value based on complete absorption of perchlorate ion on the electrode.

In 1932, Glasstone and Reynolds[21] studied the effect of high frequency currents on polarized electrodes. They accounted for a decrease in polarization of an electrode resulting from the application of high frequency on the assumption that the high frequency caused an increase in the rate of diffusion of the depolarizer to the electrode. They pointed out that when a circuit containing a large self-inductance is suddenly broken, the potential falls more rapidly than it does when the circuit is under normal conditions. It thus appears that alternating current would act to aid those processes which tend to remove electrochemically active material from the electrode. They stated that the magnitude and mechanism of the high frequency effect appeared to be the same at both anode and cathode.

In a subsequent publication, Glasstone and Reynolds[22] made a study of the effect of high frequency current on the current densities which produce 100 per cent electrode efficiency. They concluded that the effect could not be due to the influence of the alternating current on the electrochemical reaction at the electrode, but that the effect was related to an

increase in the rate of diffusion of the depolarizer. This diffusion was brought about by a mechanical disturbance in the electrolyte. The disturbance was not the result of local heating at the electrode, but would be caused by oscillatory motion of the molecular dipoles of the solvent. The effect was increased by an increase in viscosity and decreased by agitation or heating of the solution.

Atanasiu and Blum[1] gave a critical evaluation of the literature on electrolysis with alternating current. The depolarization action of alternating current, which is weaker as a pulsating current, alters the course of reactions at the cathode and anode because of the following: decrease of polarization voltage and overvoltage, increase of anode activity by decreased passivity, decrease of cathode deposition yield, and change of electrode capacity. The voltage drop upon electrolysis, aside from the economy of electrical energy, permits the isolation of intermediate products in oxidation and reduction reactors. Increase of anodic activity (decrease of passivity), especially for pulsating direct current is of advantage for the extraction and refining of metals and for the dissolution of alloys, but disadvantageous in

oxidation-reduction reactions because of the attack
on the anode. In cathodic deposition, the action of
alternating current or pulsating direct current
decreases the yield and, in some reactions, results
in poorer quality deposition. To improve the metallic
deposition, high frequency, alternating current has
been used.

Electrolysis of Sulfuric Acid With Alternating
Current Superimposed on Direct Current. Matsuda and
Nishimori[46] electrolyzed sulfuric acid of 10 normal
with alternating current superimposed on direct current.
In their previous work[42,43,44,45], they had studied
the mechanism and various experimental conditions
influencing the formation of peroxydisulfate. They
found that the current efficiency of electrolysis of
sulfate solutions without diaphragm did not seem
inferior to those with diaphragm, so it could be
assumed[46] therefrom that cathodic reduction did
not take place to any considerable extent in those
cases. If it is the case, it cannot be expected that
the current efficiency will be improved by such means
as suppressing the cathodic reduction, but it is pos-
sible that the anodic reduction will be influenced,
favorably or unfavorably.

Matsuda and Nichimori[46] used platinum wire,
0.1 centimeter in diameter and 30.5 centimeters long,
as the anode. It was thoroughly ignited immediately
before use and was kept rotating during electrolysis.
The cathode consisted of a platinum plate 5.0 centi-
meters by 2.5 centimeters. It was electrolyzed at a
temperature of 15 °C using the same quantity of elec-
tricity of 3397 coulombs for all cases. Alternating
current of 60 cycles and 100 volts was superimposed
on direct current.

In their first experiment, electrolyzed without
diaphragm, they varied the volume of the electrolyte
from 130 to 490 milliliters and the current density
based on direct current only varied from 10 to 80
amperes per square decimeter, while the alternating
current was 0.1 ampere. In their second experiment,
two different diameter porcelain cylinders, one 33
millimeters and one 55 millimeters, were used as
diaphragms. The volume of the electrolyte was kept
at 130 milliliters, but the anolyte was 45 milli-
liters in the smaller one, and 100 milliliters in
the larger one. The direct current densities and
the amperes of the alternating current were the same
as in the first experiment. The experimental results

obtained with 3397 coulombs of electricity show
that:

1. When the direct current density was 80
    amperes per square decimeter and the volumes
    of the electrolyte were 130, 195, 260, 325,
    and 490 milliliters, the current efficiencies
    based on direct current only were 24.5, 27.9,
    47.4, 28.7, and 19.8 per cent, respectively.

2. The current efficiencies increased as the
    current density increased, and when the
    volume of electrolyte was at 260 milli-
    liters, the current efficiency increased
    rapidly.

3. When diaphragms were used, as in the second
    experiment, and the direct current density
    was 80 amperes per square decimeter, the
    dimensions of the diaphragms did not
    influence the current efficiency appreciably.

4. Comparing the results obtained during the
    first and second experiments, it is interest-
    ing to observe that when the diaphragm was
    used, anodic oxidation took place even with
    smaller current density, while without a

diaphragm, very little current yield was obtained. Also, the current efficiency did not vary appreciably as the current density changed, when a diaphragm was employed.

5. In all cases the formation of Caro's acid was negligible.

6. When 15 normal sulfuric acid was electrolyzed without a diaphragm for five hours at a current density of 30 amperes per square decimeter and with an alternating current of 1.042 amperes per square decimeter, Caro's acid was kept nearly constant during the course of electrolysis. However, when it was electrolyzed with direct current only, Caro's acid decreased with time.

Applications. The applications of alternating current superimposed on direct current are given here briefly, since except for the preparation of lead chromate, they are not closely related to the problem being studied.

The following is a list of applications of super-imposed alternating current on direct current to the electrodeposition of metals:

1. electrodeposition of aluminum[26,37]

2. electrodeposition of gold[64]

3. electrodeposition of cadmium[8,53]

4. electrodeposition of antimony[7]

5. electrodeposition of bright zinc[53]

6. electrodeposition of bright tin[53]

7. electrodeposition of copper-lead alloys[58]

8. electrodeposition of copper[8]

9. electrodeposition of uncommon metals[7].

The only present-day, technical use of super-imposing alternating current[39] in electrolysis is that of the Wohlwill[64] modified gold-refining process.

Electrolytic Production of Lead Chromate Using Alternating Current Superimposed on Direct Current. Murphy and Doumas[48] studied the use of alternating current superimposed on direct current to manufacture lead chromate. The electrolytic solution used contained 3.6 grams of potassium chromate, 11.62 grams of sodium nitrate, and 1000 grams of water, and was

maintained at a pH of 6.0 by periodic additions of a solution of 2.0 per cent chromic acid. It was electrolyzed at a temperature of approximately 30 °C and a constant direct current density of about 0.005 ampere per square centimeter. The ratio of peak alternating current to direct current was varied from 0.25 to 2.91, and the cycles of alternating current were 60 and 500 per second. They found:

1. With 60-cycle alternating current superimposed on direct current, the yield of lead chromate decreased as the ratio of peak alternating current to direct current increased, and appeared to break sharply downward at a current ratio above which there was actual current reversal.

2. With 500-cycle alternating current superimposed on direct current, there was no apparent decrease in yield with increase in current ratio.

3. The purity of lead chromate product obtained using 500-cycle superimposed alternating current was higher than that obtained using direct current only.

4. Anode corrosion efficiency for 500-cycle

   superimposed alternating current was about

   100 per cent, but with 60-cycle current,

   the corrosion efficiency never exceeded

   85 per cent.

Other Applications. The du Pont Company[54] has
presented a method for smoothing rough deposits with
alternating current. Alternating current is employed
not as a part of the plating operation, but as a sub-
sequent or interim operation which may be performed
in the same solution to smooth a copper layer already
electrodeposited. With alternating-current smoothing,
no mechanical polishing is required; nickel and chro-
mium subsequently deposited are of adequate brightness
even though the smoother copper is not itself mirror-
bright. Smoothness is the important consideration.

Oza[51] studied the anodic behavior of A-A type
nickel in sulfuric solution using platinum electrodes.
He believed that alternating current superimposed on
direct current would reduce passivity and speed up
the plating of nickel and other metals that become
passive at low current densities. He found that
anodes which were passive by the application of the

conventional direct current, were made active by the subsequent application of alternating current. The effect of superimposed alternating current on direct current was presumed to depend upon the amount of direct current, the ratio of alternating current to direct current, and the frequency of the alternating current.

Kirby[33], using equipment of his own design, made a study of the passivity of A-A type nickel. He found that the superimposition of an alternating current of 10 milliamperes per square centimeter on nickel electrodes in an agitated normal sulfuric acid bath at 74 to 79 °F increased the limiting current density from 18 to 250 milliamperes per square centimeter. Other results indicated that superimposed alternating current on the anode increases the anode direct current efficiency.

Advantages of Alternating Current Superimposed on Direct Current. The following list summarizes the advantages from electrodeposition carried out with alternating current superimposed on direct current:

1. increased rate of deposition

2. improved brightness of deposit

3. improved smoothness of deposit

4. permits heavier, smoother deposits

5. decreased porosity of deposit

6. improved metal distribution (throwing power)

7. increased hardness of deposit

8. increased density of deposit.

All of the advantages cannot be obtained at the same operation conditions, but by proper control any one desired feature may be emphasized.

Comparison of Superimposed Alternating Current Plating With Periodic Reverse Current Plating. In regard to the effects obtained on plating, periodic reverse current plating is similar to the use of superimposed alternating current on direct current. The major differences in the processes are found in the wave forms obtained. The current may be reversed for periodic reverse plating[30] either by reversing the field excitation of the direct current generator or by means of a current reversing conductor on the low voltage output of the generator. Either method requires a timer to secure the periodic reverse cycles to be used. When rectifiers are employed, heavy-duty, low-voltage contactors may be used. The

use of contactors in the plating circuit results
essentially in a square type of wave form, since
the current builds up almost instantaneously to its
full value in either direction. For a generator,
when the field is reversed, two or three seconds are
required after each reversal before the full current
becomes available.

To achieve current reversal with superimposed
alternating current it is necessary only that the
maximum value of the alternating current must be
greater than that of the direct current compon-
ent[48]. The wave form obtained is usually sinus-
oidal, although special wave types are possible.

As a rule, periodic reverse plating utilizes
equal values of current and voltage during the plating
and deplating portions of the cycle used. Only in
certain specialized cases would the two current
values be different. When alternating current super-
imposed on direct current is concerned, the plating
current is always higher than the deplating current
and the ratio of the two is a function of the direct
current component and the amplitude of the alternating
current. The term, $[(AC_{max.}/DC) - 1]$ is a measure of

the extent to which the reversal of the current takes place. The plating and deplating times are different when superimposing alternating current, or periodic reverse direct current is used. In the periodic reverse plating, the plating and deplating times are controlled by the adjustment of a timer, but those for superimposed alternating current are a function of (1) the magnitude of the direct current component, (2) the amplitude of the alternating current component, and (3) the frequency of the alternating current.

Electrical Circuits for Superimposing Alternating Current. An electrical circuit suitable for studying the effects of alternating current superimposed on direct current should be designed so that each type of current may be varied, and the magnitude read separately. Several circuits have been suggested. In the circuit designed by Weir[61,62], two variable rheostats were connected in parallel with the cell. One of the rheostats was connected through a variable transformer to the alternating current supply, which was 110 volts, 60 cycles per second. In order to prevent the direct current from entering the

alternating part of the circuit, a 28 microfarad con-
denser was placed in the line between the cell and
the alternating current rheostat. An iron core
inductance was placed in the direct current line
between the cell and the direct current rheostat and
meters. The circuit diagram designed by Weir is
shown as Figure 4.

Teres[58] used the circuit diagram of Figure 5
to electrodeposit copper-lead alloys with alternating
current superimposed on direct current. The alter-
nating power used for superimposition was derived
from a 60 cycle per second, 110 volt line through a
step-down transformer capable of delivering a maximum
of 10 amperes at 8.0 volts. Between the power line
and the transformer was connected a constant voltage
transformer and autotransformer; the former reduced
line voltage fluctuations and the latter acted as an
adjustment for the alternating current. A bank of
four 140 microfarad condensers were used as a by-pass
for the alternating current, serving the dual purpose
of keeping it out of the direct current ammeter and
reducing the interaction that adjustment of the car-
bon pile rheostat would otherwise have had on the
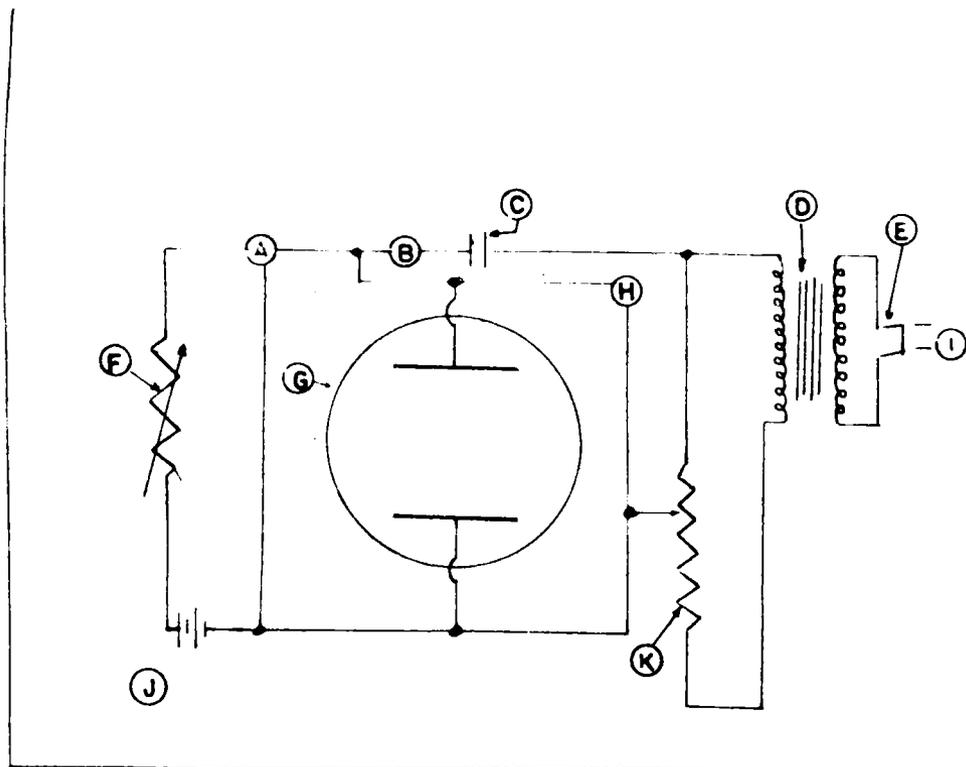
LEGEND

A — DC VOLTAMMETER

B — AC MILLIAMMETER

C — CONDENSER, 20 µF

D — VARIABLE TRANSFORMER

E — SWITCH

F — VARIABLE RESISTOR

G — CELL

H — AC VOLTMETER

I — AC SOURCE, 110 V. 60 CYCLES

J — DC SOURCE, 290 MA

K — RHEOSTAT

AC 110 V, 60 CYCLES

LEGEND

A — DC AMMETER, 0-1.5 AMP
B — DC MILLIAMMETER, 0-500 MA
C — DC MILLIAMMETER, 0-100 MA
D — AC MILLIAMMETER, 0-100 MA
E — VACUUM TUBE VOLTMETER
G — VARIAC, 110 V, AC
H,I,J — RHEOSTATS
K — BATTERY, 24 VOLTS
L,M — SWITCHES
N — PLATINUM CATHODE
O — NICKEL ANODE
P — THERMOMETER
Q — CELL
R — STIRRER
S — CALOMEL ELECTRODE
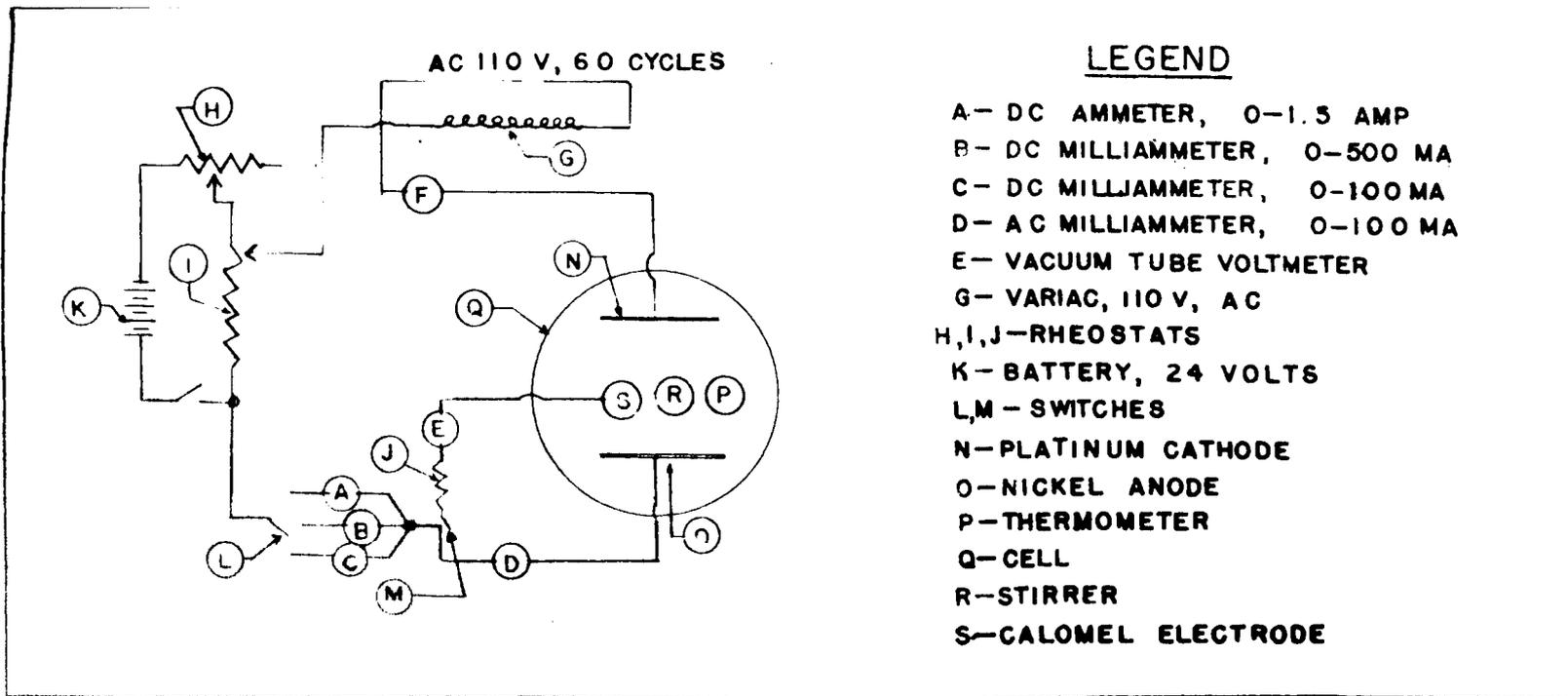
alternating current. The alternating current was measured by means of a 0.1 ohm shunt across which was placed a multirange, alternating current, vacuum tube voltmeter. This alternating current ammeter equivalent was not affected by direct current.

Oza[51] and Kirby[33] give simpler circuit diagrams for achieving the same purpose and they are shown as Figures 6 and 7, respectively. However, some alternating current may flow through the direct current circuit, and vice versa, in these circuits. Readings of each current, through the cell, were taken separately before the other current was turned on.

AC 110 V, 60 CYCYES
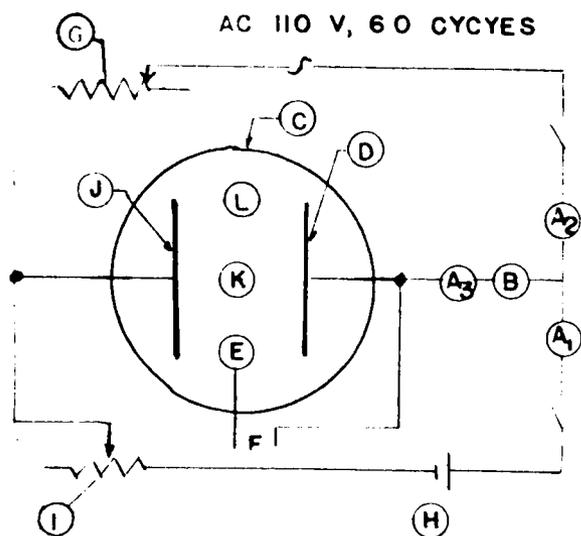
LEGEND

A_1, A_2, A_3 — AC AMMETERS
B — DC AMMETER
C — CELL
D — NICKEL ANODE
E — CALOMEL
F — POTENTIOMETER
G — VARIABLE RESISTANCE
H — BATTERY, 12 VOLTS
I — VARIABLE RHEOSTAT
J — PLATINUM CATHODE
K — STIRRER
L — THERMOMETER

FIGURE 6

EXPERIMENTAL HOOK-UP USED TO STUDY THE EFFECT OF
SUPERIMPOSED ALTERNATING CURRENT ON DIRECT CURRENT ON
THE ANODIC BEHAVIOR OF NICKEL
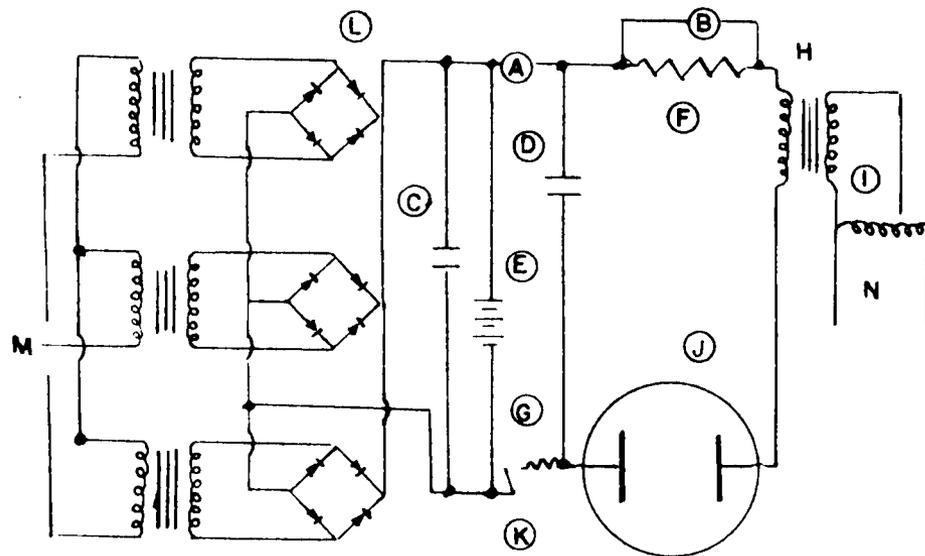
LEGEND

A — DC AMMETER
B — VACUUM TUBE VOLTMER
C — CONDENSER, 2000 μF
D — CONDENSER, 560 μF
E — AIRCRAF BATTERY, 12 V
F — SHUNT RESISTANCE
G — CARBON PILE RHEOSTAT
H — TRANSFORMER, 8 V, OUTPUT
I — VARIAC
J — PLATING CELL
K — SWITCH
L — RECTIFIER
M — AC SOURCE, 220 V, 3 φ, 60 CYCLES
N — AC SOURCE, 110 V, 60 CYCLES

FIGURE 7

EXPERIMENTAL HOOK-UP USED TO STUDY THE EFFET OF SUPERIMPOSED ALTER-
NATING CURRENT ON DIRECT CURRENT ON THE ELECTRODEPOSITION OF
COPPER-LEAD ALLOYS FROM FLUOBORATE SOLUTIONS

TERES, J.: ELECTRODEPOSITION OF COPPER-LEAD ALLOYS FROM FLUOBOATE SOLUTIONS, UNPUBLISHED
M. SC. THESIS, LIBRARY, OHIO UNIVERSITY, COLUMBUS, OHIO. 1950.

III. EXPERIMENTAL

This section of the study includes all information relating to actual laboratory materials, apparatus, data obtained, and results calculated.

Purpose of Investigation

The purpose of this investigation was to study the effect of varying the time ratio of direct to reverse current from one to 20, at an anode current density of 4.5 amperes per square centimeter, and to study the effect of alternating current of 60 to 500 cycles per second, 0.2 to 4.5 amperes per square centimeter, superimposed on direct current, on the electrolytic production of peroxydisulfuric acid.

Plan of Investigation

The following is a general procedure that was used during this study.

Literature Search. The main source of information for this study was Chemical Abstracts. From this publication, various patents and other published

articles pertaining to the chemical and electro-
chemical preparations of peroxydisulfuric acid were
obtained and reviewed. Various books were consulted
for theoretical background, and other periodicals
for more recent work. The more specific physical
and chemical properties of the chemicals involved
were found in handbooks and other existing sources
of information.

General Procedure. The actual procedure to be
performed during the experimental portion of this
study may be divided into two parts: that work which
was to be done using periodically-reversed, direct
current, and that work which was to be done utilizing
an alternating current superimposed on direct current.
In both cases, the bath was to be composed of sul-
furic acid with specific gravity of 1.4; the anode
was platinum and the cathode was lead. When per-
oxydisulfuric acid was prepared with periodically-
reversed, direct current, an electrical circuit was
set up such that the direct and reversed current
could be measured and controlled. The direct cur-
rent density of 4.5 amperes per square centimeter
was used during this portion of the investigation.

When alternating current superimposed on direct cur-
rent was used as the source of electrical energy, a
circuit was assembled such that the alternating and
direct current components could be measured. The
frequency of the alternating-current component
studied was varied from 60 to 500 cycles per second.
The peak, alternating-current density was varied from
0.2 to 4.5 amperes per square centimeter.

Evaluation of Results. In all tests performed,
the various gains in weight of the cathode of the
copper coulometers, and the weight of peroxydisul-
furic acid produced in each electrolysis were deter-
mined and recorded for use in calculations. The weight
of peroxydisulfuric acid was determined using a stand-
ard volumetric analysis. For the periodically-rever-
sed, direct-current tests, various ratios of direct
to reverse time were plotted against the current
efficiency of peroxydisulfuric acid. The same method
of evaluation was used in conjunction with the tests
performed with alternating current superimposed on
direct current.

In measuring the decomposition voltage and the
current-potential relationship, the various values of

the current in amperes and potential in volts were
recorded and plotted.

Materials

The following paragraphs deal with the names
and specifications of the materials used during the
experimental portion of this investigation.

Acid, Sulfuric. CP, 95.5 minimum per cent, code
No 1180, lot No E-111014. Obtained from General
Chemical Division, Allied Chemical and Dye Corp.,
New York, N. Y. Used as electrolyte of the elec-
trolysis baths.

Copper Sulfate. Purity, 100 per cent, ACS,
lot No 9335. Obtained from J. T. Baker Chemical Co.,
Phillipsburg, N. J. Used as a component of copper
coulometer solution.

Copper Sheet. Purity, 99.99 per cent. Obtained
from Christiansburg Lumber Co., Christiansburg, Va.
Used as electrode material in coulometer.

Ethyl Alcohol. Purity, 95 per cent. Obtained
from Industrial Chemical Corp., Baltimore, Md. Used
to make the coulometer solution.

Ferrous Sulfate. Reagent grade, crystal,
catalog No I-146. Obtained from Fisher Scientific
Co., Silver Spring, Md. Used in the quantitative
analysis of peroxydisulfuric acid.

Lead. Sheet, 1/16 in. thick. Obtained from
A. D. Mackay, Inc., 198 Broadway, New York, N. Y.
Used to make lead electrodes for use in cell.

Platinum, Sheet. Thickness, 0.007 in.
Obtained from Fisher Scientific Co., Silver Spring,
Md. Used to make electrodes for use in the cell.

Platinum, Wire. Diameter, 0.040 in. Obtained
from Fisher Scientific Co., Silver Spring, Md. Used
to make electrode for use in the cell.

Potassium Permanganate. Catalog No P-279.
Obtained from Fisher Scientific Co., Silver Spring,
Md. Used in the quantitative analysis of peroxydi-
sulfuric acid.

Apparatus

The following apparatus was used in carrying out the experimental portion of this investigation.

Ammeter. Model 489, dc, multi-stage, range 0-3, 0.30 amp, graduations 0.1 and 1.0, respectively. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure direct current in various electrolysis circuits.

Ammeter. Model 523, ac, multi-stage, 60 cy, range 0-5.0, 0-15.0 amp, graduation 0.1 amp. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure alternating current in various electrolysis circuits.

Ammeter. Radio frequency, thermocouple element, ac, No 10A/8581, 0.7 ohm resistance, range: 0.0 to 0.5 amp. Obtained from Allied Radio Corp., 100 North Western Ave., Chicago, Ill. Used to measure high frequency alternating current.

Balance. Analytical, chain-o-matic, serial No 4A2238, sensitivity = 0.0001 g, capacity = 200 g. Manufactured by Seederer-Kohlbusch, Inc., Jersey City, N. J. Used to weigh various chemicals.

Balance. Triple beam, range = 0 to 10, 0 to 100, and 0 to 500 g, graduation 0.1 g. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to weigh electrodes.

Beaker. Pyrex, 2000 ml. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to hold solutions, and for electrolytic cells.

Buret. Schellbach, straight stopcock, 50 ml, 0.1 graduations, catalog No 3-740. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for titrations in quantitative analysis of peroxydisulfuric acid.

Compressor, Reciprocating. Manufacturer unknown. Used to compress refrigerant.

Cooling Tank for Brine. Obtained from war surplus. Manufactured by Victor Products Corp., Hagerstown, Md. Used for containing cooling brine.

Generator. Serial No 726, 55 v, dc, 90 amp, 1750 rpm. Manufactured by Hertener Electric Co., L. J. Land, Inc., New York, N. Y. Used to generate direct current.

Motor. Serial No 726, 220 v, ac, 20 amp, 3 phase, 60 cy, 1750 rpm. Manufactured by Hertener

Electric Co., L. J. Land, Inc., New York, N. Y. Used to operate direct current generator.

Motor. Serial No 822637, 220 v, ac, 3 amp, 1750 rpm, 3 phase, 60 cy, 1 hp, catalog No 5644. Obtained from Sears, Roebuck and Co., New York, N. Y. Used to drive alternator.

Motor Alternator. No 607 MAWA, 25-29 v, dc, 80-90 amp, 0-11,000 rpm input, 115 v, ac, 13 amp, 1 phase, 0-2500 cycles per second output. Manufactured by Russell Electric Co., Chicago, Ill. Remodeled for use as source of variable frequency alternating current.

Motor, Induction. Serial No 1AH1441, 220-440 v, ac, 8 amp, 1755 rpm, 3 phase, 60 cy. Obtained from Century Electric Co., St. Louis, Mo. Used to drive the compressor.

Periodic Reverser. Model No 10, serial No 130. Manufactured by Platers' Research Corp., New York, N. Y. Used to obtain periodic-reverse current for electrolysis studies.

Porous Cup. Capacity, 250 ml; diameter, 5.7 cm. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as a diaphragm to hold the anolyte.

Pump. Catalog No A260, capacity 3/8 cu ft.
Manufactured by Browning Co., Maysville, Ky. Used
to circulate the cooling medium from refrigerator.

Regulator, Voltage. Serial No 465196, 9 amp,
0-110 v. Manufactured by American Transformer Co.,
Newark, N. J. Used to adjust magnitude of 60-cycle
alternating current.

Rheostat. Slide wire, 2.5 ohm, 13 amp.
Obtained from Phipps and Bird, Inc., Richmond, Va.
Used to control voltage and current to electrolysis
cell in direct and periodic-reverse current studies.

Rheostat. Slide wire, 16 ohm, 5 amp. Obtained
from Phipps and Bird, Inc., Richmond, Va. Used to
control voltage and current to electrolysis cell in
tests using alternating current superimposed on
direct current.

Rheostat. Serial No 8000-B1, maximum voltage,
125, 25 ohm, 10.4 amp. Obtained from General Elec-
tric Co., Schenectady, N. Y. Used to control voltage
and alternating current to electrolysis cell in
superimposed, alternating-current tests.

Standard Electrode. Made with mercury, mer-
curous sulfate, and one normal solution of sodium

sulfate, 0.615 v at 25 °C. Used to measure the decomposition voltage, and current-voltage curve of the electrolyte during the investigation.

Stirrer. Catalog No 18805, 115 v, ac, 60 cy, 0.68 amp. Obtained from General Scientific Co., Chicago, Ill. Used to agitate the anolyte during electrolysis.

Thermometer. General laboratory, engraved stem, mercury filled, 350 mm long, 75 mm immersion, range -5 to 200 °C, subdivisions 1 °C. Supplied by Fisher Scientific Co., Silver Spring, Md. Used to measure the temperature of the electrolysis baths during tests.

Vacuum Tube Voltmeter. Model 209A, serial No 6-13232, 115-120 v, ac, 50-60 cy, single phase. Manufactured by Hickok Electrical Instrument Co., Cleveland, Ohio. Used to measure high frequency voltages in superimposed, alternating-current tests, and to measure the decomposition voltage.

Voltmeter. Model 489, dc, voltage ranges, 0-3, 0-7.5, 0-150. Manufactured by Weston Electrical Instrument Co., Newark, N. J. Used to measure voltages in electrical circuits.

Weights. Serial No 4C2238, 1.0 to 100.0 g.
Manufactured by Seederer-Kohlbusch, Inc., Jersey
City, N. J. Used in conjunction with tne analytical
chain-o-matic balance.

Method of Procedure

The following paragraphs deal with the methods
of procedure employed during the experimental portion
of the investigation.

Operating Procedure for Direct Current Elec-
trolyses. The sulfuric acid of specific gravity 1.4
was used as the electrolyte for all of the direct-
current tests. A diaphragm, which was a porcelain
cylinder having an inside diameter of 5.7 centimeters,
depth of 9.9 centimeters, and wall thickness of 0.4
centimeter, was used. The anolyte was inside of the
porcelain cylinder and was 200 millimeters at the
beginning of the electrolysis. The cathodic solu-
tion was kept at the same level as the anolyte to
decrease transfer between the anode and cathode com-
partment. For the purpose of determining the rela-
tionship between the current density and the

production of peroxydisulfuric acid, the current density employed in performing the direct-current electrolyses was varied from 1.5 to 6.0 amperes per square centimeter.

The anode consisted of a platinum plate with an area of one square centimeter based on one side of the electrode, and was ignited immediately before electrolysis. The cathode was a lead plate; the immersed portion was 8.4 centimeters wide and 26.4 centimeters long. This was made into a cylindrical shape surrounding and outside of the diaphragm. The schematic wiring diagram of the electrical circuit used in performing this part of the investigation is shown as Figure 8. Ammeter, "A", was used as a rough setting of the current flowing through the circuit and coulometer, "C", was employed to obtain a more accurate measure of this quantity.

The temperature of the anode compartment was measured by inserting a thermometer into the anolyte during the electrolysis. Since an attempt was made to keep the temperature of the electrolyte between 5 to 10 °C during the electrolysis, two brine-cooled coils were inserted in the electrolytic cell,
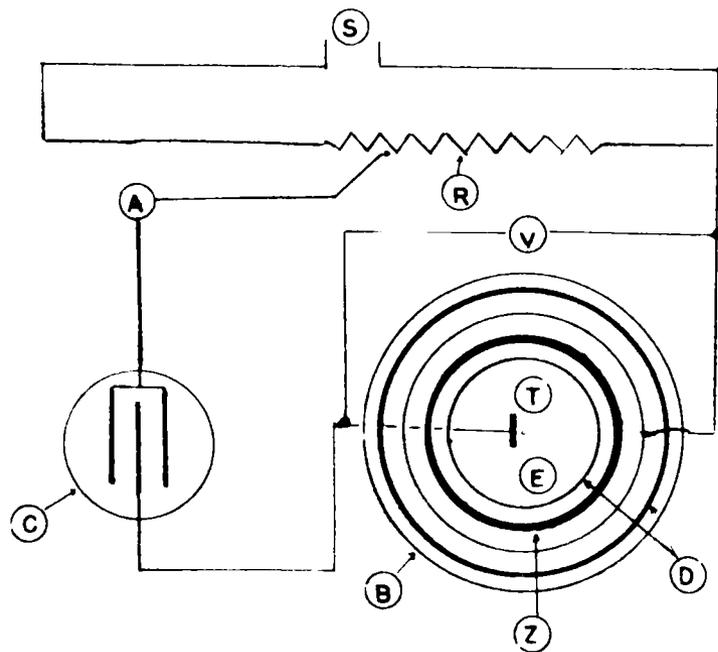
LEGEND

A – DC AMMETER
B – ELECTROLYTIC CELL
C – COPPER COULOMETER
D – COOLING COIL
E – STIRRER
T – THERMOMETER
V – DC VOLTMETER
Z – DIAPHRAGM
S – DC SOURCE

FIGURE 8

WIRING DIAGRAM OF EQUIPMENT USED TO STUDY THE ELECTRO-

LYTIC PRODUCTION OF PEROXYDISULFURIC ACID USING

DIRECT CURRENT

one lead tube surrounding the lead cathode and a glass tube surrounding the platinum anode inside the porcelain cylinder. An electric stirrer in the anolyte was kept rotating as the electrolysis proceeded.

Analysis of the anolyte was made during the electrolysis. This was done by pipetting five milliliters of the anolyte and then dropping it into an excess of ferrous sulfate solution which was titrated with potassium permanganate solution. Upon completion of the electrolysis, the current flow from the motor-generator set was terminated and the porous cup was removed from the remainder of the apparatus. The volume of the anolyte was measured after electrolysis. The total production of peroxydisulfuric acid was calculated. The copper cathode of the coulometer was washed with cold and hot water and allowed to dry. The gain in weight of the cathode from the copper coulometer was determined. The current passing was calculated from the coulometer data.

The above equipment, described for electrolytic production of peroxydisulfuric acid, is similar to that used in the method of K. Elbs[13].

Operating Procedure for Periodically-Reversed, Direct Current Tests. Before tests were performed using periodically-reversed direct current, the periodic reverser was calibrated. This was previously done by Murphy and Doumas[49,50]. Various settings of the reverse-time and the direct-time dials were made and their respective time cycles were measured by means of an electric timer. Using these data a family of curves was plotted showing the relationship between the direct to reverse time ratio, the direct time setting, and the reverse time setting.

The operating procedure for the periodically-reversed, direct current tests was much the same as that used for the direct current tests; the main difference being that arising from using the periodic reverser. The wiring diagram for the periodic-reverse, direct current tests is given in Figure 9. Two copper coulometers were used in these tests; one for measuring the total current in the circuit, "C_1", and another to measure the net current flowing through the electrolytic cell, "C_2". The gain in weight of the cathodes of the copper coulometers was determined after the electrolysis.
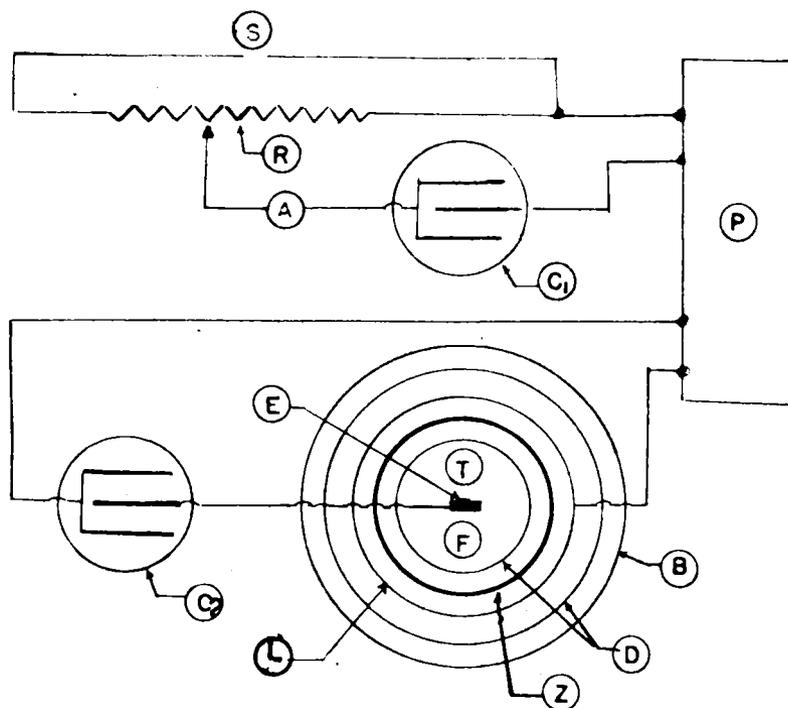
LEGEND

A - DC AMMETER
B - ELECTROLYTIC CELL
C_1 - COPPER COULOMETER, TOTAL
C_2 - COPPER COULOMETER, NET
D - COOLING COILS
E - PLATINUM ANODE
F - STIRRER
L - LEAD CATHODE
P - PERIODIC REVERSER
R - RHEOSTAT
S - DC SOURCE
T - THERMOMETER
Z - POROUS CUP

FIGURE 9

WIRING DIAGRAM OF EQUIPMENT USED TO STUDY THE ELECTRO-
LYTIC PRODUCTION OF PEROXYDISULFURIC ACID USING PERIODICALLY
REVERSED DIRECT CURRENT

Various ratios of direct to reverse time were employed
during the performance of these studies. The remain-
der of the procedure was the same as that used in
conjunction with the direct current electrolyses.

Operating Procedure for Electrolyses Performed
with Alternating Current Superimposed on Direct
Current. The operating procedure for the tests per-
formed with alternating current superimposed on direct
current was similar to that employed for the previous
series of tests performed with direct current and
periodically-reversed direct current. The wiring
diagram of the circuit used for the electrolyses per-
formed with 60 cycles per second, current is given
in Figure 10. The alternating current used was 60
cycles per second for 11 experiments, and a motor-
driven, alternating current generator was employed
in experiments requiring higher frequency. Only one
copper coulometer was used during these tests to
measure the total direct current. Upon completion
of the tests, the product formed and the gain in
weight of the cathode were determined. Various
alternating current densities were employed during
these tests while the direct current density was
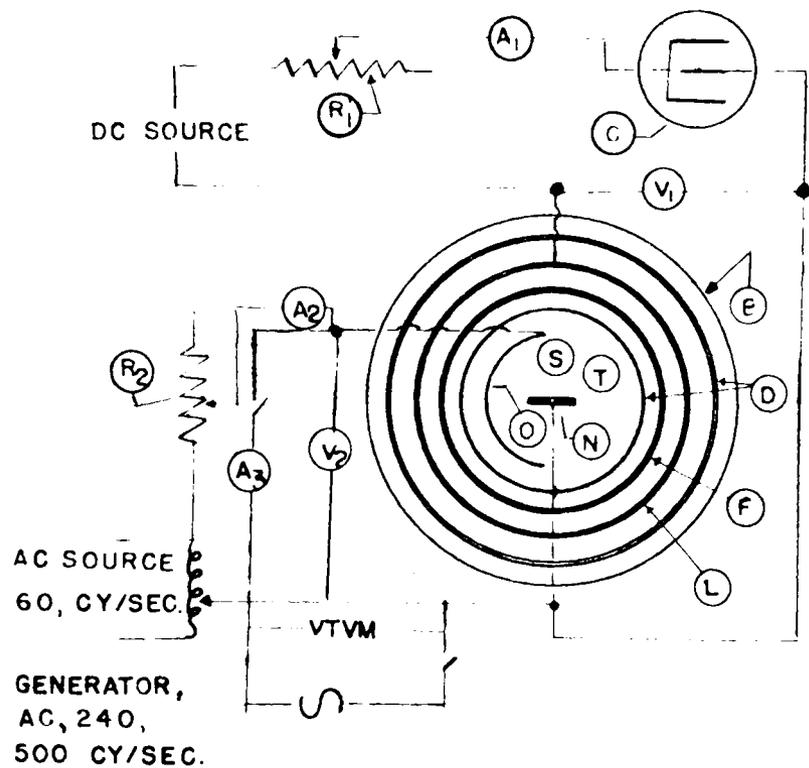
LEGEND

A_1 — DC AMMETER
A_2 — AC AMMETER
A_3 — AC AMMETER, HIGH FREQUENCY
B — CELL
D — COOLING COILS
F — POROUS CUP
L — LEAD CATHODE
N — ANODE, PLATINUM
O — PLATINUM ELECTRODE, AC.
R_1 — RHEOSTAT, 2.5 OHMS, 13 AMP
R_2 — RHEOSTAT,   24 OHMS, 10.4 AMP
S — STIRRER
T — THERMOMETER
V_1 — DC VOLTMETER
V_2 — A C VOLTMETER
VTVM — VACCUM TUBE VOLTMETER
C — COPPER COULOMETER

FIGURE 10

EXPERIMENTAL CIRCUIT USED TO STUDY THE EFFECT
OF SUPERIMPOSED ALTERNATING CURRENT ON THE PRODUCTION
OF PEROXYDISULFURIC ACID

held at 4.5 amperes per square centimeter for 14 experiments at 60 and 500 cycles per second, alternating current, and at 2.2 amperes per square centimeter for eight experiments at 240 and 500 cycles per second. The current density for the higher alternating current was decreased because equipment for control of the high current was not available.

For tests performed with high-frequency, alternating current superimposed on direct current, a rather complex start-up procedure was followed. The circuit was set up according to Figure 10, page 74. The alternating current generator supplying current to the cell was started, as was the direct current generator. Direct current was allowed to flow to the excitor coils of the alternating current generator. The alternating current was increased and adjusted by the rheostat, "R_2", until a reading was obtained from ammeter, "A_2". The ammeter, "A_3", was for the purpose of adjusting the exciting current of the alternating current generator. The switch of the direct current, "E_1", was closed and this current was adjusted by the rheostat, "R_1". The voltage drop across the cell was recorded and the test was started. The remainder of

the operating and shut-down procedure was identical with that used during periodically-reversed, direct current electrolysis.

Relationship Between Root-Mean-Square and Peak Values of High Frequency Alternating Current. The conversion factor, "F", 1.55, is the ratio of peak current to root-mean-square of current[48].

Operating Procedure for Measuring Anode Potential-Current in Sulfuric Acid. The wiring diagram shown in Figure 11, was used for measuring the anode potential and current with superimposed alternating current. When direct current only was used, the switch, "S_2", was open.

Sulfuric acid, specific gravity 1.4, was used as the electrolyte. The temperature of the anode compartment was kept between 5 to 10 °C. The vacuum tube voltmeter was used to measure the anode potential between the platinum anode and the mercury-mercurous sulfate standard electrode.

When the circuit was set up and the rheostat, "R_2", was adjusted to the high resistance position, the direct current generator was started. Before the switch, "S_2", was turned on, the rheostat,

LEGEND

A_1 – DC AMMETER
A_2 – AC AMMETER
B – PLATINUM ELECTRODE, AC.
C – CELL
D – POROUS CUP
E – STANDARD ELECTRODE
H – STIRRER
L – LEAD CATHODE
P – PLATINUM ANODE
R_1 – RHEOSTAT, 431 OHMS, 2 AMP
R_2 – RHEOSTAT, 24 OHMS, 10 AMP.
S_1 – SWITCH
S_2 – SWITCH
T – THERMOMETER
V – DC VOLTMETER
VTVM – VACCUM TUBE VOLTMETER
Z – COOLING COILS

FIGURE II.

EXPERIMENTAL CIRCUIT USED FOR MEASURING
ANODE-POTENTIAL CURRENT
CURVE

mounted on the generator, was adjusted to give a low voltage. The measurement was started at this time by adjusting the rheostat, "R_1", increasing the applied potential to the cell. The readings of the vacuum tube voltmeter, the ammeter, "A_1", and the voltmeter, "V", were recorded.

Operating Procedure for Measuring the Anode Potential-Current in Sulfuric Acid with Superimposed Alternating Current. This part of the measurement is the same as that used with direct current only, except that switch, "S_2", was turned on. During the measurement, the alternating current was kept constant, which was 0.5 ampere throughout the measurements.

Analytical Procedure. Ferrous salts in cold solution are oxidized to ferric by peroxydisulfates. Advantage is taken of this action in the quantitative determination of peroxydisulfuric acid.

$$2FeSO_4 + H_2S_2O_8 = Fe_2(SO_4)_3 + H_2SO_4$$
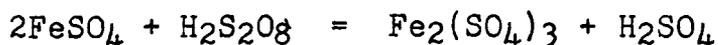
The analysis of the anodic solution was made after varying periods of electrolysis. This was done by using a pipet to withdraw five milliliters of the anolyte, in which the peroxydisulfuric acid

content was estimated. This sample was discharged into a considerable excess of ferrous sulfate solution, standardized against the potassium permanganate solution, and then diluted with an equal volume of hot water, 70 to 80 °C. The excess ferrous sulfate was titrated with 0.1 normal potassium permanganate solution. This titration was subtracted from the permanganate equivalent of the ferrous solution. The difference is equivalent to the peroxydisulfuric acid.

One milliliter of 0.1 normal potassium permanganate solution was equivalent to 0.009807 of peroxydisulfuric acid. Allowance was made for samples removed from the anolyte, for evaporation or for loss by electro-osmosis.

Data and Results

The operating conditions, data and results obtained during the experimental portion of this investigation are presented in tabular form as is described in the following paragraphs.

Calibration Data for the Periodic Reverser. Table I is the calibration data for the Platers' Research Corporation periodic reverser, as obtained by Murphy and Doumas[50].

Periodic Reverser Calibration Curves. Figure 12 is the family of curves which show the relationship between the ratio of direct to reverse time and the dial settings for the Platers' Research Corporation periodic reverser used in this study.

Operating Conditions, Data and Results for the Electrolytic Production of Peroxydisulfuric Acid Using Direct Current. The operating conditions, data and results obtained from the performance of the direct current electrolyses are presented in Table II.

Operating Conditions, Data and Results for the Electrolytic Production of Peroxydisulfuric Acid Using Periodically Reversed, Direct Current. The operating conditions, data and results obtained from the

TABLE I

Calibration Data for Plater's Research

Corporation Periodic Reverser[a]

Reverse Time Setting divisions	Direct Time Setting divisions	Reverse Time sec	Direct Time sec
0	1	-	2.3
0	3	-	6.5
0	5	-	10.7
0	7	-	15.1
0	9	-	19.2
1	0	0.28	-
3	0	1.35	-
5	0	2.68	-
7	0	4.00	-
9	0	5.30	-

(a) Murphy, N. F. and B. C. Doumas: Electrochemical
Preparation of Lead Chromate Using Periodically
Reversed Direct Current, Engineering Experiment
Station Series, No. 104, Virginia Polytechnic
Institute, Blacksburg, Va.
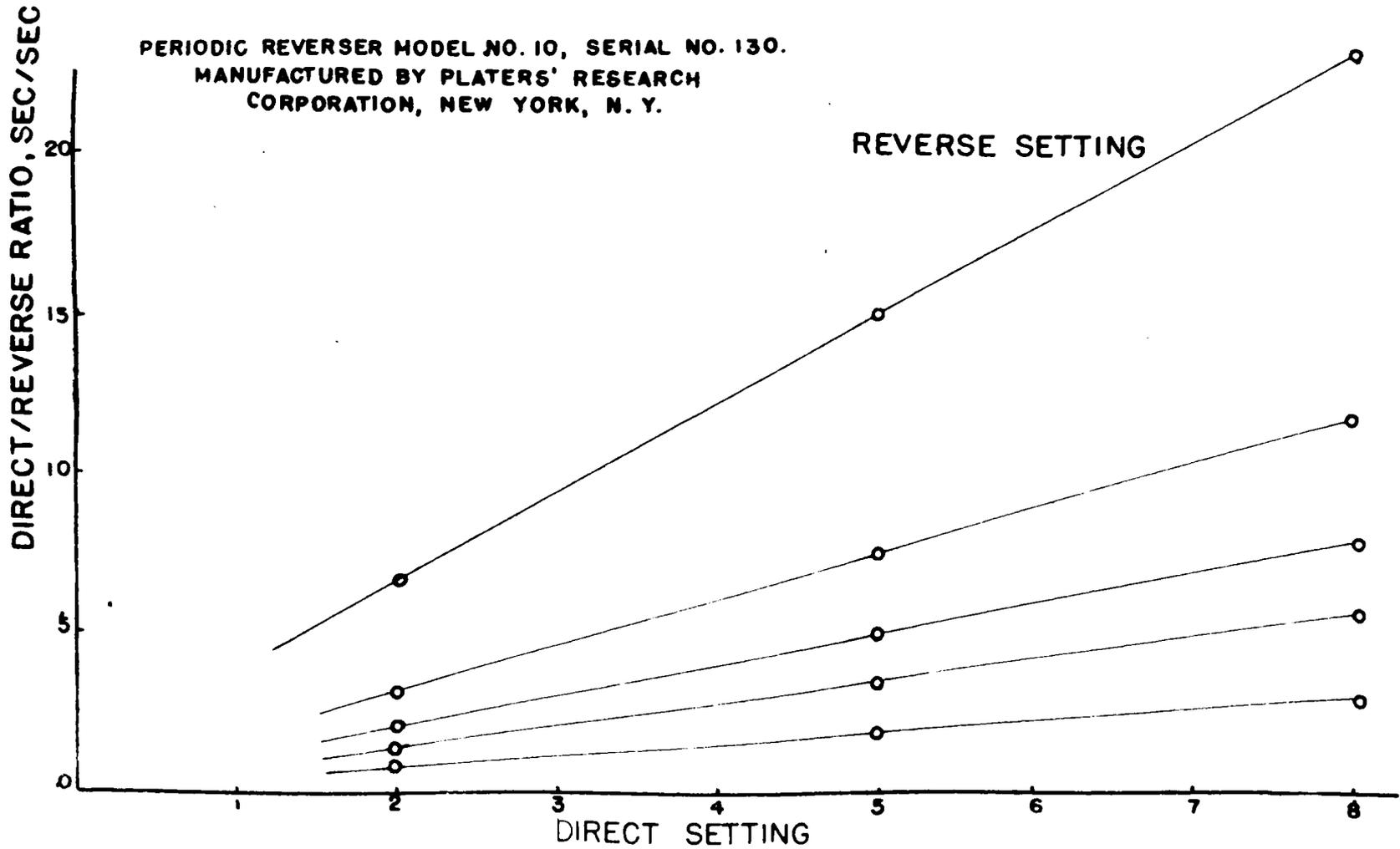
FIGURE 12. GRAPH SHOWING THE RELATIONSHIP BETWEEN THE RATIO OF DIRECT TO REVERSE TIME
AND THE DIAL SETTINGS FOR THE PERIODIC REVERSER

TABLE II

Operating Conditions, Data and Results

Obtained from the Electrolytic Production of

Peroxydisulfuric Acid

(See Pocket on Back Cover)

TABLE II

Operating Conditions, Data and Results Obtained from the
Electrolytic Production of Peroxydisulfuric Acid Using Direct Current[a]

Test No	Volume of Anolyte ml	Current amp	Anode Surface sq cm	Current Density amp/sq cm	Time of Electrolysis min	Voltage Drop Across Cell volts	Temperature °C	Peroxydisulfuric Acid Produced grams	Weight of Coulometer Cathode Before grams	After grams	Actual Current amp-hr	Current Efficiency %
DC-23	200	3	2	1.5	0	5.5	3	0	198.2		0	
	198.75				30		3	4.18			1.29	89.5
	192.5				60		3	7.9			2.57	85
	186.25				90		4	11.3			3.86	82.6
	180				120		4	15		204.3	5.14	80.5
DC-28	200	6	2	3	0	9	4	0	235.9		0	
	196.5				30		3.4	7.17			2.41	82
	188				60		4	14			4.82	77
	179.5				90		5	17.8			7.24	68
	171				120		6	22		247.2	9.65	63
DC-26	200	9	2	4.5	0	9	5	0	224.8		0	
	197				30		7	12			4.52	79.3
	189				60		8	20.2			9.04	61.5
	181				90		10	26.6			13.56	54
	165				150		12	32.7		251.6	22.6	39.8
DC-25	200	12	2	6	0	9	5	0	214.7		0	
	191				30		12	15.65			5.93	86.8
	176				60		15	22.9			11.85	53.4
	161				90		10	25.0		235.8	17.8	40.6
DC-24	200	6	2	3	0	8	5	0	204.3		0	
	196				30		4	8.9			2.85	86.4
	187				60		5	16.1			5.7	78
	177				90		5	18.4		214.5	8.56	59.4

Note: (a) 1. Platinum anode ignited immediately before electrolysis.
2. The anolyte was sulfuric acid of specific gravity 1.4.
3. The immersed area of the lead cathode was 221.8 sq cm.
4. Electrolyzed with stirring.

performance of the periodically reversed, direct

current are reported in Table III.

Operating Conditions, Data and Results for the

Electrolytic Production of Peroxydisulfuric Acid Using

Alternating Current, 60 Cycles per Second, Superimposed

on Direct Current. The operating conditions, data and

results obtained from the performance of the tests

using alternating current, 60 cycles per second, super-

imposed on direct current are given in Table IV.

Operating Conditions, Data and Results for the

Electrolytic Production of Peroxydisulfuric Acid Using

Alternating Current, 240 and 500 Cycles per Second,

Superimposed on Direct Current. The operating condi-

tions, data and results obtained from the performance

of the tests using alternating current, 240 and 500

cycles per second, superimposed on direct current, are

given in Table V.

Data from the Measurements of Current-Anode

Potential Curve in Sulfuric Acid with Stirring.

Table VI gives the data obtained from the measure-

ments of current and anode potential with stirring.

TABLE III

Operating Conditions, Data and Results

Obtained from the Electrolytic Production of

Peroxydisulfuric Acid Using

Periodically-Reversed, Direct Current

(See Pocket on Back Cover)

TABLE III

Operating Conditions, Data and Results Obtained from the Electrolytic Production of

Peroxydisulfuric Acid Using Periodically Reversed Direct Current[a]

Test No	Volume of Anolyte	Current	Anode Surface	Current Density	Time of Electrolysis	Voltage Drop Across Cell	Temperature	Direct Time	Reverse Time	Direct/Reverse Ratio		Weight of Copper Coulometer Total		Net		Peroxydisulfuric Acid Produced	Actual Current	Current Efficiency [b]
										Time	Current	Before	After	Before	After			
	ml	amp	sq cm	amp/sq cm	min	volt	°C	sec	sec	sec/sec	amp/amp	gram		gram		gram	amp-hr	%
PR-18	200	9	2	4.5	0	9	5	1.35	0.67	2	3.11	143.8		174.7		0		
	196				30		4									6.66	4.54	40.6
	187				60		5									11.5	9.07	35
	178				90		6									15.2	13.6	30.9
	164				120		8									15.65	18.2	23.8
	155				150		8						170.7		188	16	22.7	19.5
PR-19	200	9	2	4.5	0	9	5	3.35	0.67	5	3.41	145.1		189		0		
	197.4				30		5.5									6.93	4.54	42.2
	189.8				60		6									12.2	9.07	37.2
	182.2				90		8									16.35	13.6	33.2
	168.8				130		8									19.2	19.65	27.1
	162				150		9						172		203.7	21.6	22.7	26.3
PR-20	200	9	2	4.5	0	9	5	6.7	0.67	10	8.08	170.7		186.3		0		
	197.6				30		5									8.09	4.66	48.1
	190.2				60		6									13.91	9.31	41.3
	182.8				90		7.5									17.25	14	34
	175.4				120		9									17.7	18.6	26.2
	168				150		11						198.3		207.5	22.5	23.3	26.6
PR-21	200	9	2	4.5	0	9	5	13.5	0.67	20	16.3	166		207.5		0		
	197				30		6									8.78	4.58	53
	189				60		8									14.15	9.16	42.6
	181				90		9									19.9	13.75	39.9
	173				120		10									21.6	18.35	32.5
	165				150		10						192		230.5	26.1	21.9	32.9
PR-22	200	9	2	4.5	0	9	5	1.35	0.67	2	2.07	192		115.8		0		
	197.6				30		5									5.04	4.46	31.2
	190.2				60		6.5									9.2	8.91	28.5
	182.8				90		8									12.25	13.38	27.6
	175.4				120		9									15.7	17.82	24.3
	168				150		10						218.4		125	17.84	22.3	22.1

Note: (a) 1. Platinum anode ignited immediately before electrolysis
            2. The anolyte was sulfuric acid, specific gravity 1.4
            3. The immersed area of the lead cathode was 221.8 sq cm
            4. Electrolyzed with stirring

(b) Based on total current

TABLE IV

Operating Conditions, Data and Results

Obtained from the Electrolytic Production of

Peroxydisulfuric Acid Using Alternating Current

60-Cycle, Superimposed on Direct Current

(See Pocket on Back Cover)

TABLE IV

Operating Conditions, Data and Results Obtained from the Electrolytic Production of Peroxydisulfuric Acid Using Alternting Current, 60-cycle, Superimposed on Direct Current[a]

Test No	Volume of Anolyte (ml)	Time of Electrolysis (min)	Temperature (°C)	Direct Current (amp)	Alternating[b] Current (amp)	Anode Surface (sq cm)	Current Density Alternating (amp/sq cm)	Current Density Direct (amp/sq cm)	Ratio of Peak Alternating to Direct Current (amp/amp)	Peroxydisulfuric Acid Produced (grams)	Cathode Gain of Copper Coulometer (grams)	Actual Current (amp-hr)	Current[c] Efficiency (%)	Observations
SD-31	200	0	5	9	4.5	2	2.25	4.5	0.7	0		0		1. Gas evolved from the surface of electrodes.
	198	30	10							5.03		4.46	31.2	2. Black deposits
	191	60	11							10.85		8.92	33.6	formed on the surface
	184	90	13							16.1		13.4	33.2	of platinum electrodes.
	177	120	14							18.2	21.2	17.85	28.3	3. Anolyte-light yellow.
SD-32	200	0	5	9	2	2	1	4.5	0.316	0		0		
	197.5	30	7							5.45		4.93	30.6	Gas evolved from the
	190	60	10							11.3	11.7	9.86	31.6	surface of the electrodes.
SD-33	200	0	5	9	1	2	0.5		0.157	0		0		
	196	30	12							5.57		5.1	31	Same as experiment SD-32
	187	60	9							11.3	11.1	9.35	30.6	
SD-36	200	0	5	4.5	3.2	1	3.2	4.5	1	0		0		1. Gas evolved from the
	197	60	5							5.26		4.215	35	surface of electrodes.
	189	120	6							9.26	10	8.43	27.6	2. Anolyte changed to brown color and platinum dissolved into the anolyte.
SD-37	200	0	5	4.5	4.5	1	4.5	4.5	1.37	0				
	197.5	60	3											Same as experiment
	190	120	4							1.24	11.4	9.63	3.3	SD-36
SD-38	200	0	5	4.5	3.7	1	3.7	4.5	1.15	0				
	195	60	3							0				
	185	120	3							0.925	10.4	8.77	3.04	Same as experiment SD-36
SD-39	200	0	5	4.5	1	1	1	4.5	0.31	0				
	195	60	4											Same as experiment
	185	120	4							9.55	10	8.43	31.3	SD-32
SD-40	200	0	5	4.5	2.5	1	2.5	4.5	0.786	0				
	195	60	4							5.54				Same as experiment
	185	120	4							9.14	9.5	8.0	31.5	SD-31
SD-41	200	0	5	4.5	0.2	1	0.2	4.5	0.063	0				
	194	60	4							4.77				
	183	120	5							8.1	7.8	6.48	34.6	Same as experiment SD-32
SD-42	200	0	5	4.5	3.4	1	3.4	4.5						
	188	120	6											Same as experiment
									1.07	6.02	10.7	9.02	18.5	SD-36

Note: (a) 1. Platinum anode ignited immediately before electrolysis.
2. The anolyte was sulfuric acid of specific gravity 1.4 .
3. The immersed area of the lead cathode was 221.8 sq cm.
4. Electrolyzed with stirring

(b) Ammeter reading value.

(c) Based on direct current.

TABLE V

Operating Conditions, Data and Results

Obtained from the Electrolytic Production of

Peroxydisulfuric Acid Using High Frequency of

Alternating Current Superimposed on Direct Current

(See Pocket on Back Cover)

TABLE V

Operating Conditions, Data and Results Obtained from the Electrolytic Production of

Peroxydisulfuric Acid Using High Frequency of Alternating Current Superimposed on Direct Current[a]

Test No	Volume of Anolyte ml	Time of Electrolysis min	Temperature °C	Direct Current amp	Anode Surface sq cm	Direct Current Density amp/ sq cm	Alternating Current[b] amp	cycle/sec	Ratio of Peak Alternating to Direct Current amp/amp	Peroxydisulfuric Acid Produced gram	Cathode Gain of Copper Coulometer gram	Actual Current amp-hr.	Current Efficiency[c] %	Observations
SD-43	200 185	0 120	5 6	4.5	1	4.5	0.9	500	0.31	11.5	12.3	10.38	30.3	1. Gas evolved from the surface of electrodes. 2. Anolyte - colorless
SD-44	200 189	0 120	5 9	4.5	1	4.5	1.2	500	0.407	6.27	7.3	6.16	27.6	Same as above
SD-45	200 192	0 120	5 8	4.5	1	4.5	0.2	500	0.069	12.65	10.7	9.02	44.4	Same as above
SD-46	100 97	0 305	5 0	0.6	0.28	2.2	0.46	500	1.19	0	2	1.69	0	1. Gas evolved from the surface of electrodes 2. Anolyte - brown color 3. Platinum anode dissolved
SD-47	100 97	0 270	5 7	0.474	0.215	2.2	0.305	500	1	0	1.5	1.265	0	Same as experiment SD-46
SD-48	100 102	0 330	5 7	1.05	0.478	2.2	0.46	500	0.678	0	9.7	8.17	0	Same as experiment SD-46
SD-49	100 103.5	0 270	5 7	1.05	0.478	2.2	0.3	500	0.46	3.8	6.5	5.48	19.1	Same as experiment SD-43
SD-50	100 104	0 270	5 7	1.05	0.478	2.2	0.36	500	0.507	0.28	6	5.06	1.38	Same as experiment SD-46
SD-52	100 109	0 270	5 6	1.05	0.478	2.2	0.4	240	0.62	4.57	4.9	4.13	30.6	Same as experiment SD-43
SD-53	100 95	0 240	5 3	1.05	0.478	2.2	0.49	240	0.76	0	4.4	3.71	0	Same as experiment SD-46
SD-54	100 95	0 250	4 5	1.05	0.478	2.2	0.45	240	0.695	3.28	4.6	3.87	27.6	Same as experiment SD-43

Note: (a) 1. Platinum anode ignited immediately before electrolysis.
2. The anolyte was sulfuric acid of specific gravity 1.4.
3. The immersed area of the lead cathode was 221.8 sq cm.
4. Electrolyzed with stirring.
(b) Ammeter reading.
(c) Based on direct current.

TABLE VI

Data From the Measurement of Current-Anode

Potential Curve in Sulfuric Acid With Stirring

E_1	I	E_2	E_1	I	E_2
volts	amp.	volts	volts	amp.	volts
0	0	0	2.86	1.5	-
0.35	0	0.55	2.9	1.83	5.7
0.6	0	0.8	3.0	2.15	-
1.4	0	1.7	3.2	2.7	6.5
1.65	0	1.95	3.4	3.4	-
1.88	0.1	2.95	3.6	4	-
2.04	0.15	-	4.0	5.4	-
2.2	0.35	3.5	4.4	7	-
2.43	0.42	-	4.6	7.9	-
2.53	0.55	4.2	4.8	9.0	-
2.62	0.8	-	4.9	9.8	14
2.67	1.0	4.8	5.0	10.8	-
2.7	1.2	-	5.35	11.5	-
2.76	1.3	5.2			

Note: 1. Platinum electrode ignited before using.

2. E_0, electrode potential of mercury-mercurous sulfate electrode, $= 0.615$ at $25^{\circ}C$.

3. E_1 of the cell Hg-HgSO$_4$, N SO$_4^=$; SO$_4^=$, Pt.

4. Potential drop across lead and platinum electrode.

5. Temperature, $7^{\circ}C$.

6. Specific gravity of Sulfuric acid, 1.4.

7. E_2, voltage of cell, Pt / H_2SO_4 / Pb.

Data from the Measurements of Current-Anode
Potential Curve in Sulfuric Acid without Stirring.
Table VII gives the data obtained from the measure-
ments of current and anode potential in sulfuric
acid without stirring.

Data from the Measurements of Current-Anode
Potential Curve in Sulfuric Acid by Using 60 Cycles
per Second, Superimposed Alternating Current. Table
VIII gives the data of current and anode potential
measured with 60 cycles per second, superimposed
alternating current.

TABLE VII

Data From the Measurements of Current-Anode

Potential Curve in Sulfuric Acid Without Stirring

E_1	I	E_2	E_1	I	E_2
volt	amp.	volt	volt	amp.	volt
0	0	2.5	3.45	2.55	7.2
1.5	0	3.2	3.6	3.0	8.0
1.8	0	3.3	4.0	4.0	9.0
2.0	0.25	4.4	4.2	6.0	9.0
2.6	0.75	5.4	4.4	6.5	10.0
3.0	1.5	5.8	4.6	9.3	11.0
3.2	1.8	6.7	4.8	11.5	11.0
3.45	2.55	7.2	4.8		
3.6	3.0	8.0			

Note: 1. Platinum anode ignited before use.

2. E_0, standard potential of mercury-mercurous sulfate electrode, = 0.615 at $25°C$.

3. E_1, potential of the cell.

. $Hg-HgSO_4$, N $SO_4^=$; $SO_4^=$, Pt.

4. Temperature, 5-12 °C.

5. Gas involved from platinum anode.

6. Specific gravity of sulfuric acid 1.4.

7. E_2, voltage of cell, Pt / H_2SO_4/ Pb.

TABLE VIII.

Data From The Measurements of Current and Anode Potential

in Sulfuric Acid Using Superimposed Alternating Current

E_1	I	E_2	E_1	I	E_2
volt	amp.	volt	volt	amp.	volt
0	0	0.42	1.75	1.25	
0.2	0.05		2	1.45	4.0
0.3	0.14	1.5	2.25	1.6	
0.39	0.2		2.5	2.1	
0.5	0.26		2.8	2.45	4.8
0.75	0.5	2.0	3.4	3.8	
1.0	0.70	2.2	3.6	4.5	
1.25	0.85		3.7	5.0	
1.5	1.05				

Note:
1. Platinum anode ignited before use.

2. E_0, standard potential of mercury-mercurous sulfate Electrode, = 0.615 at 25 °C.

3. E_1, potential of the cell,

   Hg - $HgSO_4$, N $SO_4^=$, SO_4, Pt.

4. Temperature, 5 - 12 °C.

5. Gas involved from platinum anode.

6. Specific gravity of sulfuric acid 1.4.

7. E_2, voltage of cell, Pt / H_2SO_4 / Pb.

Sample Calculations

Samples of the calculations performed with the data obtained during the experimental portion of this thesis are given in this section. Included in this section are samples of calculations performed with the data obtained from direct current, periodically-reversed direct current, and alternating current superimposed on direct current tests.

Volume of Anolyte. The volumes of the anolyte at the start and at the end of electrolysis were measured. Then,

$$V_4 = V_1 - V_2 - (n-1) V_3$$

where:

V_1 = volume of the anolyte at the start of electrolysis, ml

V_2 = volume of the anolyte at the end of electrolysis, ml

V_3 = volume per sample taken, ml

V_4 = volume of anolyte lost, ml

n = total number of samples taken, ml.

The volume for each analysis was:

$$V_n = V_1 - V_4/n - V_3 \, n'$$

where:

V_n = volume of anolyte being analyzed, ml

n' = the number of samples taken previous to the sample.

For test DC-23, Table II, page 83, for second analysis:

$$V_4 = 200 - 180 - 3 \times 5$$

$$V_4 = 5 \text{ ml}$$

$$V_n = 200 - 5/4 - 5 \times 1$$

$$V_n = 192.5 \text{ ml.}$$

<u>Anode Current Density</u>. Anode current density
was calculated by means of the following formula:

$$c.\ d.\ =\ \frac{I}{A}$$

where:

      c. d. = current density, amp/sq cm

         I = current flowing through the cell,
                   meter reading, during direct
                   cycle, amp

         A = total surface area of anode, sq cm

From test DC-26, Table II, page 83,

      c. d. = 9/2

      c. d. = 4.5 amp/sq cm.

<u>Peroxydisulfuric Acid Produced</u>. The production of peroxydisulfuric acid was determined from the analytical data and the volume as follows:

$$G = V_n (v_e - v) f/5$$

where:

G = peroxydisulfuric acid produced, gm

v = volume of standardized permanganate used, ml

v_e = volume of standardized permanganate equivalent to the volume of ferrous sulfate solution used, ml

f = peroxydisulfuric acid equivalent to one milliliter of the standardized permanganate solution used, gm.

For test DC-26, Table II, page 83,

$$G = 181 (80.7 - 8.3) \times 0.01012/5 \text{ gm}$$

$$G = 26.6 \text{ gm}.$$

The peroxydisulfuric acid produced per ampere hour was found by the following equation, for test SC-31, Table IV, page 86,

$$G/I = 10.85/8.92 \text{ gm/amp-hr}$$

$$G/I = 1.22 \text{ gm/amp-hr}.$$

Actual Current. The actual current, "I", in ampere-hours, which passed through the cell in time, "t", in minutes, was found from the gain in weight of the coulometer cathode, "W", in grams, thus:

$$I = \frac{W \times 96500}{31.8 \times 3600} \times t \ .$$

For test DC-26, Table II, page 83,

$$I = \frac{(251.6 - 224.8) \times 96500 \times 150}{31.8 \times 3600 \times 60}$$

$$I = 22.6 \text{ amp-hr.}$$

The current passing for intermediate periods was found by taking proportions of the total current on the basis of time, thus:

$$I = 22.6 \times \frac{120}{150}$$

$$I = 18.1 \text{ amp-hr.}$$

In the above equations,

$$96500 = \text{coulombs per faraday}$$

$$3600 = \text{seconds per hour}$$

$$31.8 = \text{equivalent weight of copper}$$

$$150 = \text{total time of electrolysis, minutes}$$

$$120 = \text{time of intermediate period, minutes.}$$

Current Efficiency. The current efficiency for the formation of peroxydisulfuric acid was found from the following formula:

$$C. E. = \frac{G}{I} \times \frac{96500 \times 100}{3600 \times 97.0}$$

$$C. E. = 39.8 \text{ per cent}$$

where:

$$97.0 = \text{equivalent weight of peroxydisulfuric acid.}$$

The current efficiency for the periodic reverse tests was based on the total (direct and reverse) current. For test PR-18, Table III, page 85,

$$C. E. = (16.0/22.7) \times (26.8 \times 100)/97$$

$$C. E. = 19.5 \text{ per cent.}$$

Direct to Reverse Current Ratio from Coulometers.
This calculation was performed by solving the follow-
ing simultaneous equations:

$$w_1 + w_2 = W_1$$

and

$$w_1 - w_2 = W_2$$

where:

w_1 = weight of copper deposited on cathode of net coulometer during direct cycle, gm

w_2 = weight of copper deposited on cathode of net coulometer during reverse cycle, gm

W_1 = weight of copper deposited on cathode of total coulometer, gm

W_2 = weight of copper deposited on cathode of net coulometer, gm.

By using the data of test PR-18, Table III, page 85,

$$w_1 - w_2 = (170.7 - 143.8)$$

$$w_1 - w_2 = (188.0 - 174.7) .$$

Solving simultaneously,

$$w_1 = 20.35 \text{ gm}$$

$$w_2 = 6.55 \text{ gm.}$$

From these weights were calculated the respective
ampere-hours that flowed through the cell during
either the direct or the reverse cycle of the elec-
trolysis.

The direct to reverse current ratios for the
periodic reverse tests were obtained according to the
following formula:

$$R = \frac{w_1}{w_2}$$

where:

R = direct to reverse current ratio,
gm/gm, or amp/amp.

Since the ratio of weights deposited is the same as
the direct to reverse current ratio, from test PR-18,
Table III, page 85,

$$R = \frac{20.35}{6.55}$$

$$R = 3.11 \text{ amp/amp.}$$

Ratio of Peak Alternating Current to Direct

Current. The ratio of peak alternating to direct
current was calculated by the following formula:

$$R' = \frac{f' I_{ac}}{I}$$

where:

R' = ratio of peak alternating to direct
current, amp/amp

I_{ac} = alternating current, ammeter reading,
amp

f' = 1.414 for 60 cycles per second, 1.55
for 240 and 500 cycles per second,
alternating current

For test SC-31, Table IV, page 86,

$$R' = (1.414 \times 2.25)/4.5$$

$$R' = 0.7.$$

IV. DISCUSSION

The first portion of this section deals with a discussion of the more general aspects of the investigation work, particularly the observations made during various tests. The final portion is more specifically concerned with the calculated results obtained from the data recorded during the experimental portion of the study.

General Discussion

The paragraphs presented here discuss previous work pertaining to the investigation, and various observations in regard to the procedures employed during the experimental work.

Previous Work. Duplication of some direct current electrochemical methods[13,42] for preparing peroxydisulfuric acid found in the literature was attempted in an effort to become familiar with known methods. Also, these experiments yielded results which could be compared with results obtained from later tests using periodically-reversed, direct current and alternating current superimposed on direct current.

No work has been found in the literature in con-
junction with the electrochemical production of peroxy-
disulfuric acid using periodically-reversed, direct
current. The work[46] on the electrochemical prepara-
tion of peroxydisulfuric acid using superimposed alter-
nating current found in the literature is limited on
low frequency and small alternating current.

Selection of Anolyte Concentration. The concen-
tration of the anolyte is one of the control factors
for the anodic formation of peroxydisulfuric acid.
Duplicate work[12,43] has been found in the literature.
Matsuda and Nishimori[45] electrolyzed 10, 15, 20, 25,
30, and 36 normal sulfuric acid with direct current at
a temperature of 15 to 18 °C. Their results showed, in
general, that 15 normal sulfuric acid gave the highest
total current efficiency which includes formation of
the hydrogen peroxide, Caro's acid, and peroxydisul-
furic acid. After that, the current efficiency
decreases as the concentration of sulfuric acid
increases. In regard to the formation of Caro's acid,
its current efficiency increases as the concentration
of sulfuric acid increases. This may be explained[44]
as follows: as the more concentrated the sulfuric

acid which is electrolyzed, the more the peroxydisul-
furic acid is decomposed to Caro's acid during the elec-
trolysis. In order to observe the effect of using
periodically-reversed, direct current, or superimposed
alternating current, on the electrochemical production
of peroxydisulfuric acid compared with the direct cur-
rent method, it was considered better to eliminate the
decomposition of the peroxydisulfuric acid and to choose
a concentration of sulfuric acid less than 15 normal.
During this investigation, sulfuric acid of specific
gravity 1.4 was chosen as the anolyte, not only
because the production of hydrogen peroxide and
Caro's acid is negligible as electrolysis proceeds,
but also because this concentration is used in indus-
trial or in laboratory preparation of peroxydisulfuric
acid.

Influence of Temperature on the Formation of
Peroxydisulfuric Acid. Temperature is one of the
most important variables in control of electrolysis,
and it is generally known that a lower temperature is
favorable to anodic oxidation of sulfates. Matsuda
and Nishimori[45] electrolyzed 10 normal sulfuric
acid without diaphragm at a current density of 80

amperes per square decimeter. Their results showed
that the current efficiencies were 66, 30, and 13.2
per cent at the temperature of 5, 15, and 25 °C,
respectively. The lower the temperature the greater
the current efficiency obtained. It is known[45] that
the conductivity of a solution decreases but its degree
of electrolytic dissociation increases with decrease in
temperature. Also, the decomposition of peroxydisul-
furic acid is endothermic.

Treatment of Platinum Anode. The nature of the
platinum anode surface affects the current efficiency
of the formation of peroxydisulfuric acid. The litera-
ture has shown[44] that igniting the platinum anode is
decidedly favorable to the current efficiency of the
formation of peroxydisulfuric acid. Under the same
experimental conditions and concentration of the
anolyte, the current efficiency was 67 per cent when
the anode was ignited and 46 per cent when unignited.
If the platinum anode was heated to the same tempera-
ture when flames of acetylene, hydrogen, and coal gas
were used, the acetylene flame gave the highest total
current efficiency and the hydrogen flame gave the
lowest. Using electricity to ignite the anode,

alternating current was superior to direct current and gave the highest current efficiency of all.

During this investigation, a bottled butane gas-oxygen flame was used to heat the platinum anode immediately before electrolysis.

Influence of Current Density. Duplicate work[12,42,43] has been done on the influence of current density on the formation of peroxydisulfate. The results of electrolysis of 10 normal sulfuric acid and of mixed solutions of sulfuric acid and ammonium sulfate at different current densities showed that in all cases no hydrogen peroxide was detected. The highest current efficiency, with regard to the peroxidic product, was obtained in the case of electrolysis of saturated ammonium sulfate solution. Production of Caro's acid was small in all cases.

Increase in the current density was favorable, in general, to the anodic oxidation, and the effect of the increase on the current efficiency with respect to the total peroxidic oxygen was the greatest in the case of 10 normal sulfuric acid. The more concentrated the solution with regard to the ammonium sulfate, the less

marked was the effect of current density on the efficiency.

It was concluded that the hydroxyl ion discharge at the anode seemed to play an important role in the peroxydisulfate formation and that the nascent oxygen is the oxidizing agent.

<u>Formation and Decomposition of Peroxydisulfuric Acid</u>. The electrolytic production of peroxydisulfuric acid is complicated by many factors which have been described in the previous paragraphs. In the electrolysis solution, two peracids[40] of sulfur exist; one is the proposed product, and one is the permonosulfuric acid or Caro's acid having the formula, H_2SO_5.

When an aqueous solution of fairly concentrated sulfuric acid is electrolyzed at smooth platinum anode using a high current density, peroxydisulfuric acid is first formed according to the following equation:

$$2SO_4^= = S_2O_8^= + 2e$$
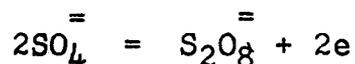
In the presence of sulfuric acid, however, this acid is not very stable and changes more or less

quickly, depending upon the concentration of the sulfuric acid, into Caro's acid, as shown by the equation:

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4$$
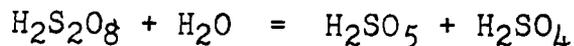
The Caro's acid is subsequently decomposed into sulfuric acid and oxygen.

Decomposition Potential of Sulfuric Acid of Specific Gravity 1.4. The current-anode potential of sulfuric acid was measured against standard mercury-mercurous sulfate electrodes with different kinds of current and different experimental conditions. The data obtained during those measurements are given in Tables VI, VII, and VIII, pages 88, 90, and 91. Three plots have been made. By comparing Figures 13 and 14, it is seen that, using direct current only, there is not much difference in the first decomposition potential, measured with or without stirring, and its numerical value is approximately 1.7 volts. A decomposition potential at 2.4 volts appears in all of the solutions. A third decomposition potential appears at 3.65 volts for the unstirred solution. However, the decomposition potential obtained by using alternating current of 0.5 ampere superimposed on direct current

NOTE:
1. PLATINUM ANODE IGNITED BEFORE USE.
2. TEMPERATURE, 7 °C.
3. H_2SO_4, SP. GR. 1.4.
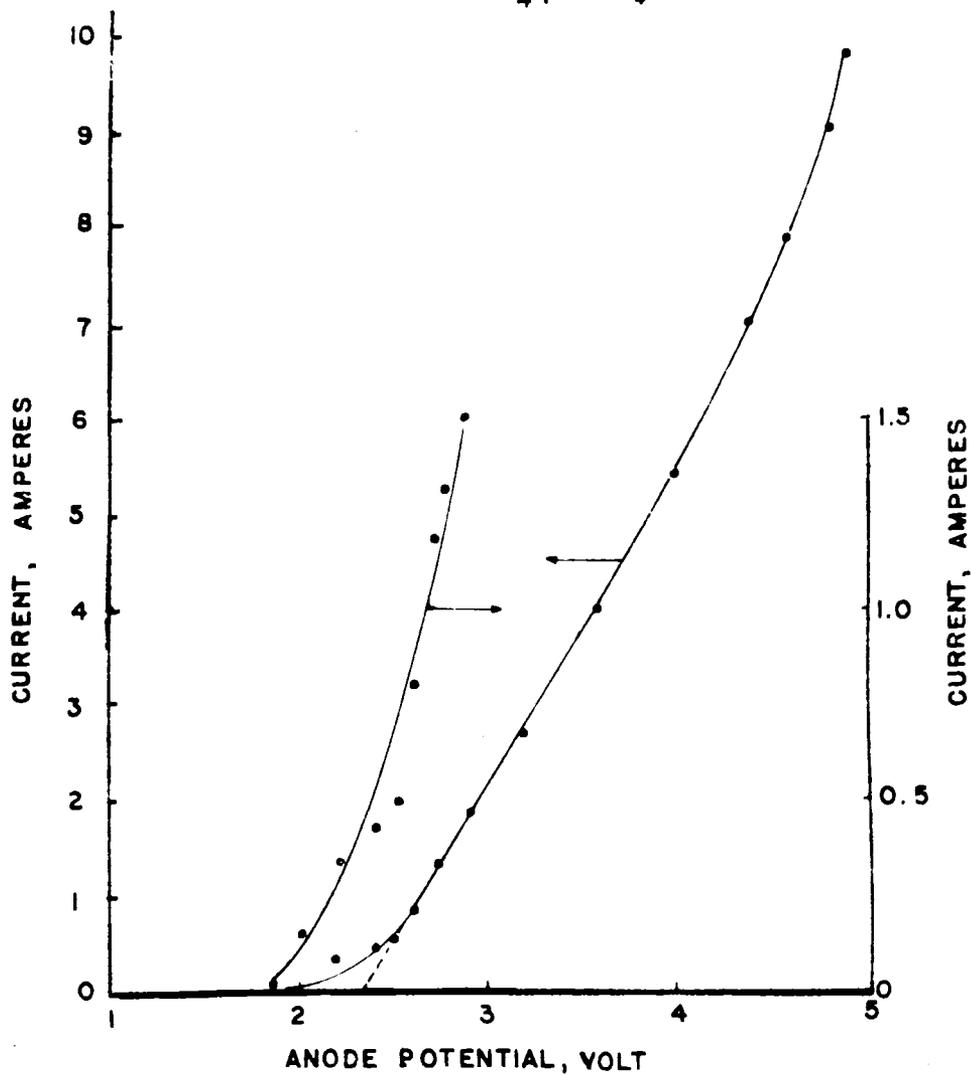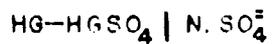4. REFERENCE ELECTRODE:

$$HG-HGSO_4 \mid N. SO_4^=$$

FIGURE 13. RELATIONSHIP BETWEEN CURRENT AND ANODE POTENTIAL IN SULFURIC ACID WITH STIRRING
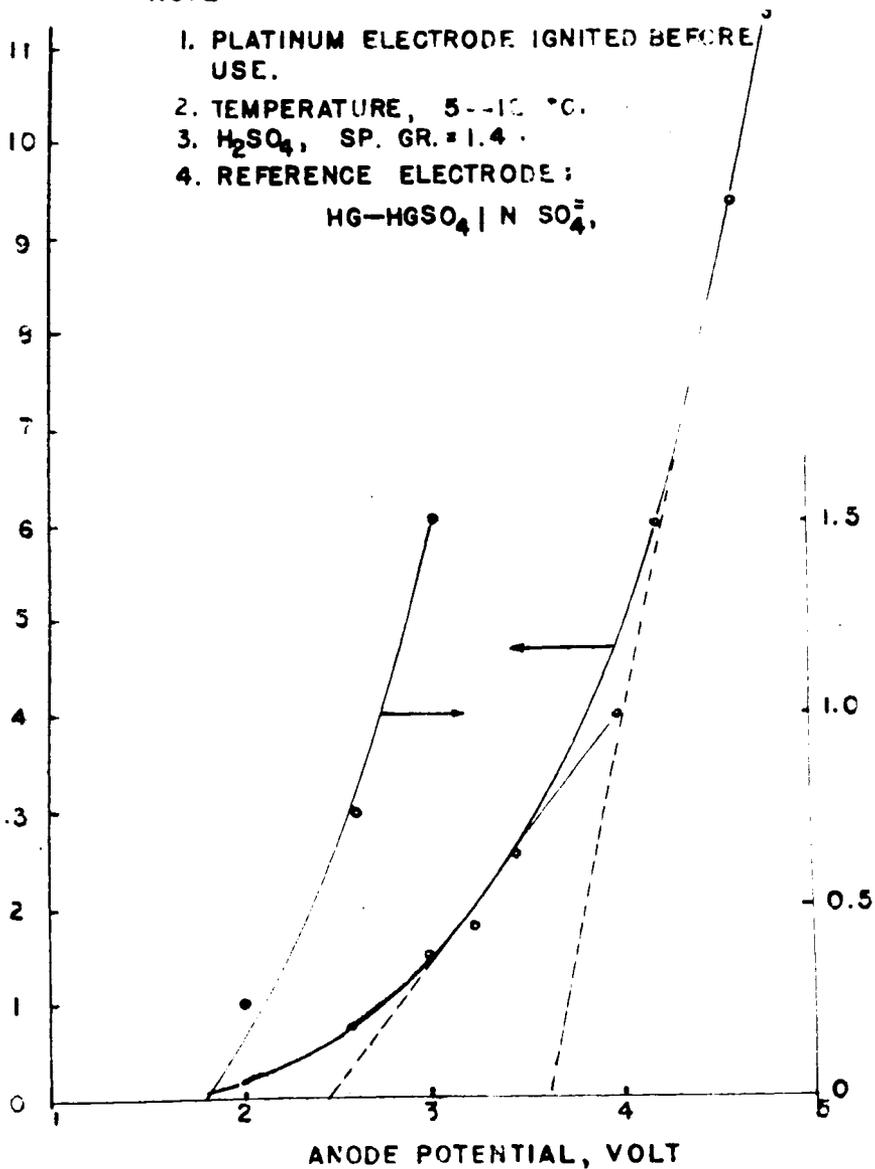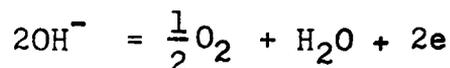
FIGURE 14. RELATIONSHIP BETWEEN CURRENT AND ANODE POTENTIAL IN SULFURIC ACID WITHOUT STIRRING

was less than 0.1 volt, as shown in Figure 15, which compared with that using direct current only is an indication of a reversible anodic reaction. The direct current decomposition potential of 2.4 volts is reached only at a high current density when super-imposed alternating current is present.

In the previous paragraphs, the factors affecting this type of anodic oxidation have been discussed. It was shown that a high current density is necessary or favorable to the formation of peroxydisulfuric acid. In other words, the higher the oxygen overpotential of the platinum anode, the better the yield of peroxydisulfuric acid obtained. A lower yield or current efficiency would result from using either periodically-reversed, direct current or superimposing alternating current as the source of electrical energy to produce peroxydisulfuric acid, since both types of current lower the anode overpotential.

A study of the decomposition potentials leads to the following interpretation. The first decomposition potential corresponds to the reaction:

$$2OH^- = \frac{1}{2}O_2 + H_2O + 2e$$

NOTE:

1. H_2SO_4, SP. GR. = 14
2. TEMPERATURE, 0-6 °C.
3. ALTERNATING CURRENT, 0.5 AMPERES (RMS), 6C CYCLE/SEC.
4. REFERENCE ELECTRODE,
   $HG-HGSO_4$ | N. SO_4,
5. AREA OF ELECTRODE, I SQ CM

CURRENT, AMPERES

ANODE POTENTIAL, VOLT
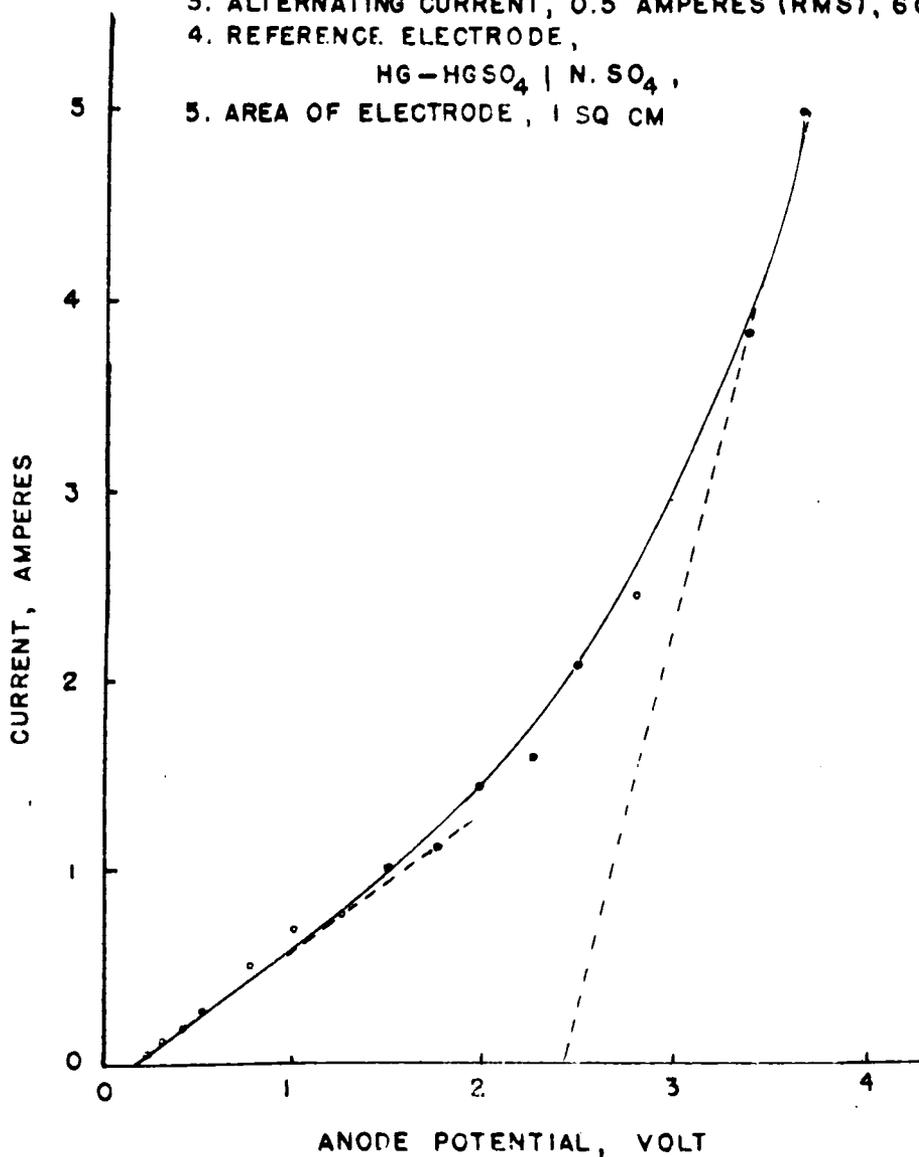
FIGURE 15. RELATIONSHIP BETWEEN ANODE-
POTENTIAL AND CURRENT WITH SUPERIMPOSED
ALTERNATING CURRENT

This is the reaction affected by the oxygen overvoltage of the anode. The second decomposition potential is that responsible for the formation of peroxydisulfuric acid, as follows:

$$2SO_4^= = S_2O_8^= + 2e$$
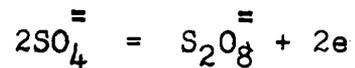
The third decomposition potential may correspond to destruction of peroxydisulfuric acid, according to the equation:

$$S_2O_8^= + 2H_2O = 2H_2SO_4 + O_2 + 2e$$
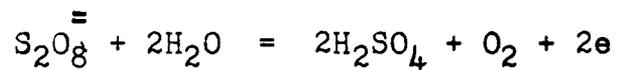
This reaction would correspond to that observed on electrolysis of a solution of sodium peroxide.

Discussion of Results from Direct
Current Electrolyses

The preparation of peroxydisulfuric acid using direct current was performed primarily for comparative purposes. Some discussion pertaining to results should be given here.

Hydrogen and Oxygen Bubbles. Gas bubbles were observed as the electrolysis proceeded. This resulted from the decomposition of water yielding hydrogen at the cathode and oxygen at the anode. The rate of gas evolution, although not measured, increased as the current density increased. This should use part of the electrical energy supplied to the cell and decrease the current efficiency of the formation of peroxydisulfuric acid.

Effect of Current Density. Tests DC-23 to DC-28 were performed with different current densities. The data and experimental conditions are shown in Table II, page 83. A plot showing the relationship between current density and peroxydisulfuric acid formed is given in Figure 16. Increasing the anode current density caused an increase in weight of

DATA FROM EXPERIMENTS
DC-23, 24, 25, 26, 28

NOTE:
1. PLATINUM ANODE BEFORE ELECTROLYSIS.
2. SP. GR. OF H_2SO_4 = 1.4.
3. TEMPERATURE, 5 – 10 °C.
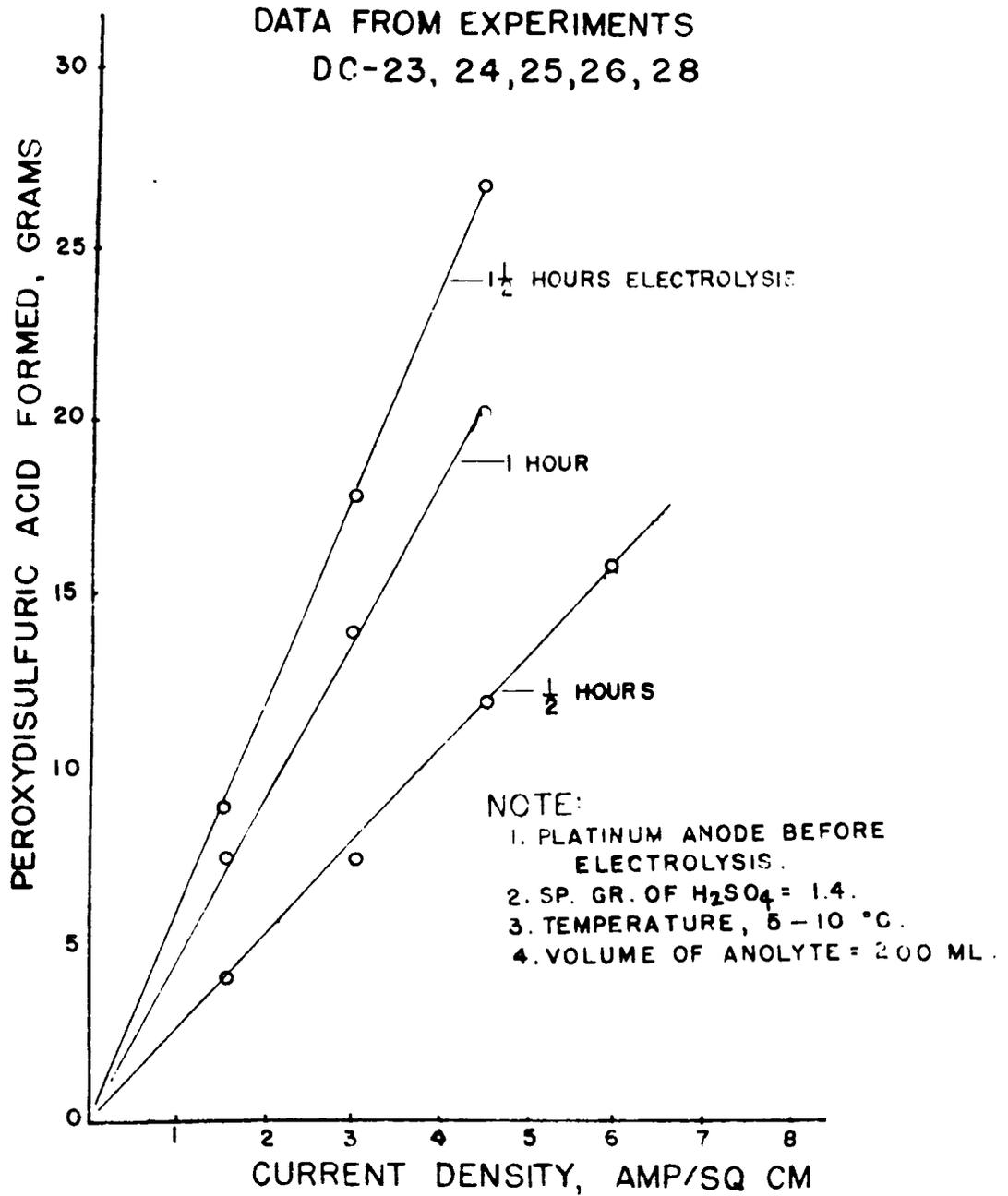4. VOLUME OF ANOLYTE = 200 ML.

FIGURE 16. RELATIONSHIP BETWEEN THE CURRENT DENSITY AND ELECTROLYTIC PRODUCTION OF PEROXYDISULFURIC ACID USING DIRECT CURRENT

peroxydisulfuric acid formed, and at a temperature between 5 to 10 °C during the electrolysis and for a period of less than one and one-half hours, the yield was a straight line function of the current density.

If the temperature was higher, as in test DC-25, Table II, page 83, the straight line relationship was broken and the current efficiency went down. This was caused by an increase in the rate of decomposition of peroxydisulfuric acid as the temperature increased.

A group of curves showing the relationship between current density and current efficiency is given in Figure 17. These, too, are almost straight lines as the current density increases from 1.5 to 6.0 amperes per square centimeter at periods of electrolysis of 1.0, 1.5, and 2.0 hours. It is seen that the current efficiency decreases with current density.

In the previous section, it was stated that an increase in the current density was favorable to this type of anodic oxidation, or increase of the product. However, this is not the case for efficiency for formation of peroxydisulfuric acid. The current efficiency may increase with current density, while the latter is small, then it decreases at increasing

DATA FROM EXPERIMENTS
DC— 23,24,25, 26,28

1. PLATINUM ANODE IGNITED BEFORE ELECTROLYSIS.
2. SP. GR. OF H_2SO_4= 1.4.
3. TEMPERATURE, 5 – 10 °C.
4. VOLUME OF ANOLYTE = 200 ML.

FIGURE 17. RELATIONSHIP BETWEEN CURRENT
DENSITY AND CURRENT EFFICIENCY OF
ELECTROLYTIC PRODUCTION OF PEROXY-
DISULFURIC ACID USING DIRECT
CURRENT

current densities. In other words, there may be a
maximum in the current efficiency curves. This was
studied and explained by Matsuda and Nishimori[43,44].
They proposed the following reactions as the elec-
trolysis proceeds:

$$2SO_4^= = S_2O_8^= + 2e \qquad (1)$$

$$2OH^- = (O) + H_2O + 2e \qquad (2)$$

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4 \qquad (3)$$

$$H_2SO_5 + (O) = H_2SO_4 + O_2 \qquad (4)$$

The first two reactions occurred at the electrode sur-
face and the last two in the electrolyte solution. The
higher the current density used, the greater the extent
of reaction (2) producing nascent oxygen which would
accelerate reaction (4) to reduce Caro's acid forming
molecular oxygen and sulfuric acid. In consequence,
more peroxydisulfuric acid would be decomposed to
form Caro's acid maintaining the balanced condition.

The interpretation of the decomposition potential
curves leads to another explanation for the decrease
in efficiency at higher values of current density.

There may be an electrochemical decomposition of the peroxydisulfuric acid, as shown previously.

Relationship Between the Time of Electrolysis and Current Efficiency. A group of curves showing the relationship between the time of electrolysis and the current efficiency obtained during tests DC-23, DC-25, DC-26, and DC-28 are given in Figure 18. From these curves, it is seen that the current efficiency was lowered as the electrolysis proceeded at a certain current density. The rate of decrease in current efficiency is greater at a higher current density than that of a lower current density. This would be attributed to the faster decomposition of peroxydisulfuric acid, as explained in the preceding paragraphs, in a more concentrated solution.

Another group of curves showing the relationship between the time of electrolysis and peroxydisulfuric acid produced per ampere hour is given in Figure 19. The production was decreased during the electrolysis in all four cases. The explanation is similar to that given above.

NOTE: DATA FROM TESTS DC-23, 25, 26, 28.

1. PLATINUM ANODE IGNITED BEFORE ELECTROLYSIS.
2. SP. GR. OF H_2SO_4 = 1·4.
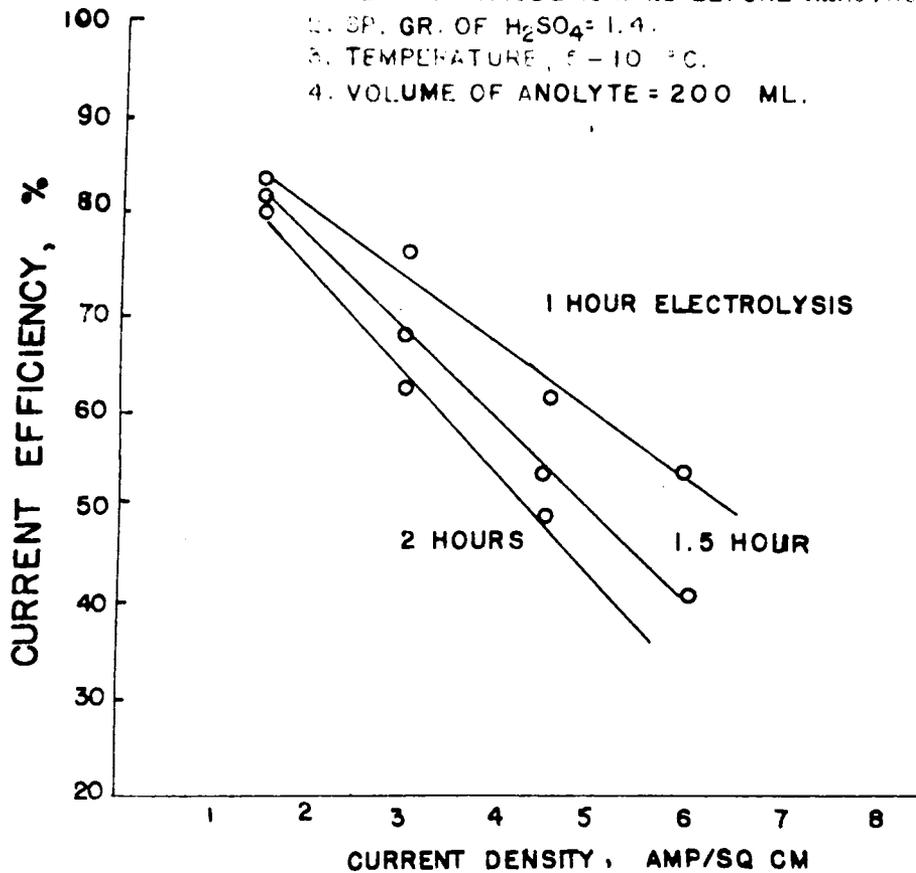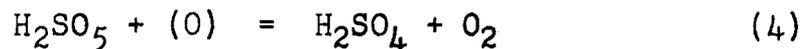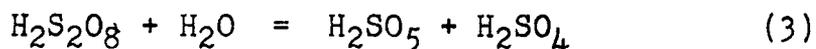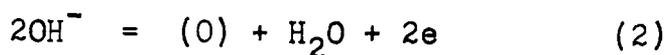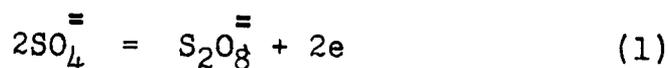3. TEMPERATURE, 5 — 10 °C.
4. VOLUME OF ANOLYTE = 200 ML.
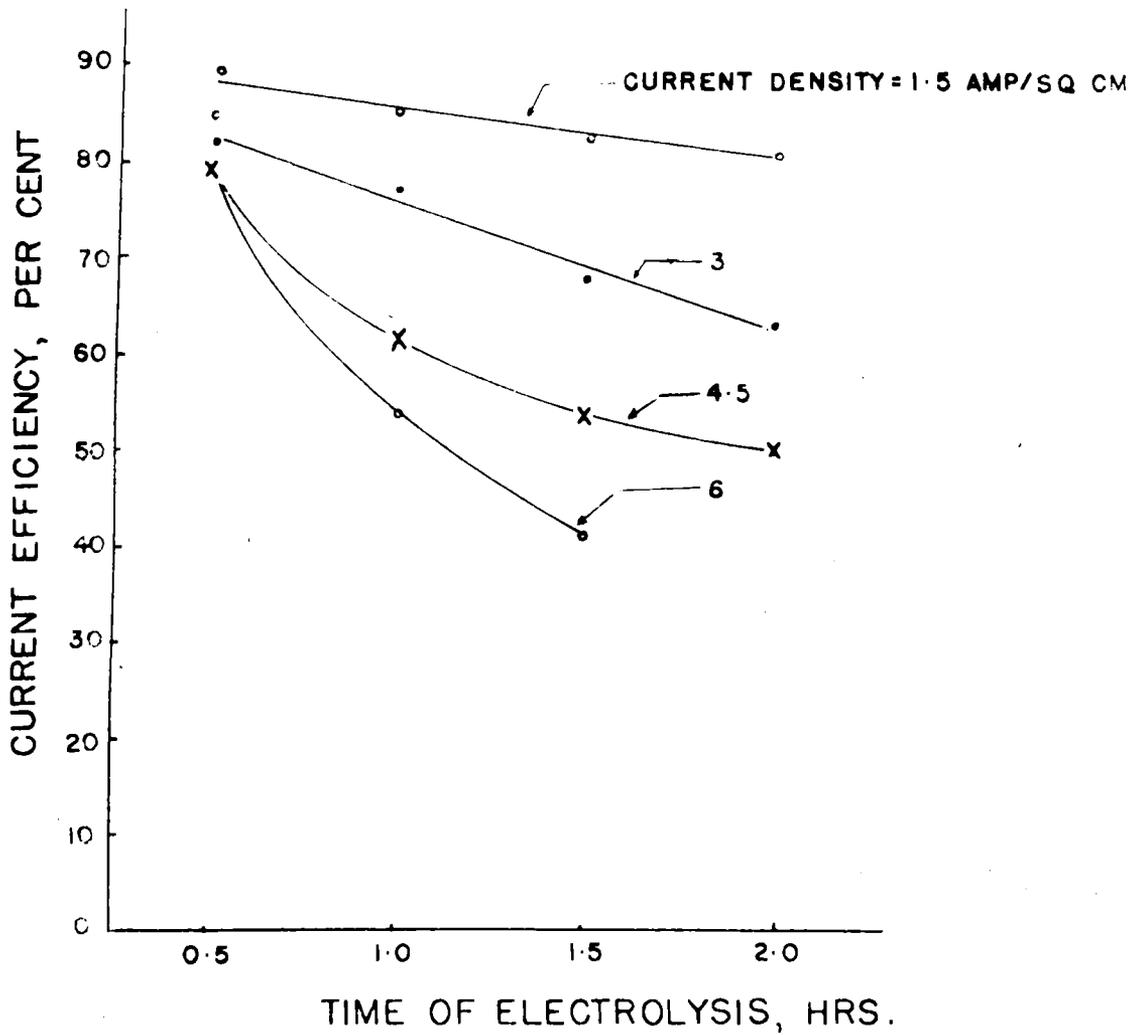
FIGURE 18. RELATIONSHIP BETWEEN CURRENT
EFFICIENCY AND TIME OF ELECTROLYSIS IN
PRODUCTION OF PEROXYDISULFURIC ACID
USING DIRECT CURRENT

NOTE: DATA FROM TESTS DC-23,25,26,28.

1. SP. GR. OF H_2SO_4 = 1.4
2. TEMPERATURE, 5-15 °C
3. PLATINUM ANODE IGNITED BEFORE ELECTROLYSIS.

CURRENT DENSITY = 1.5 AMP/SQ CM

PEROXYDISULFURIC ACID FORMED, G./AMP-HR.

TIME OF ELECTROLYSIS, HRS.
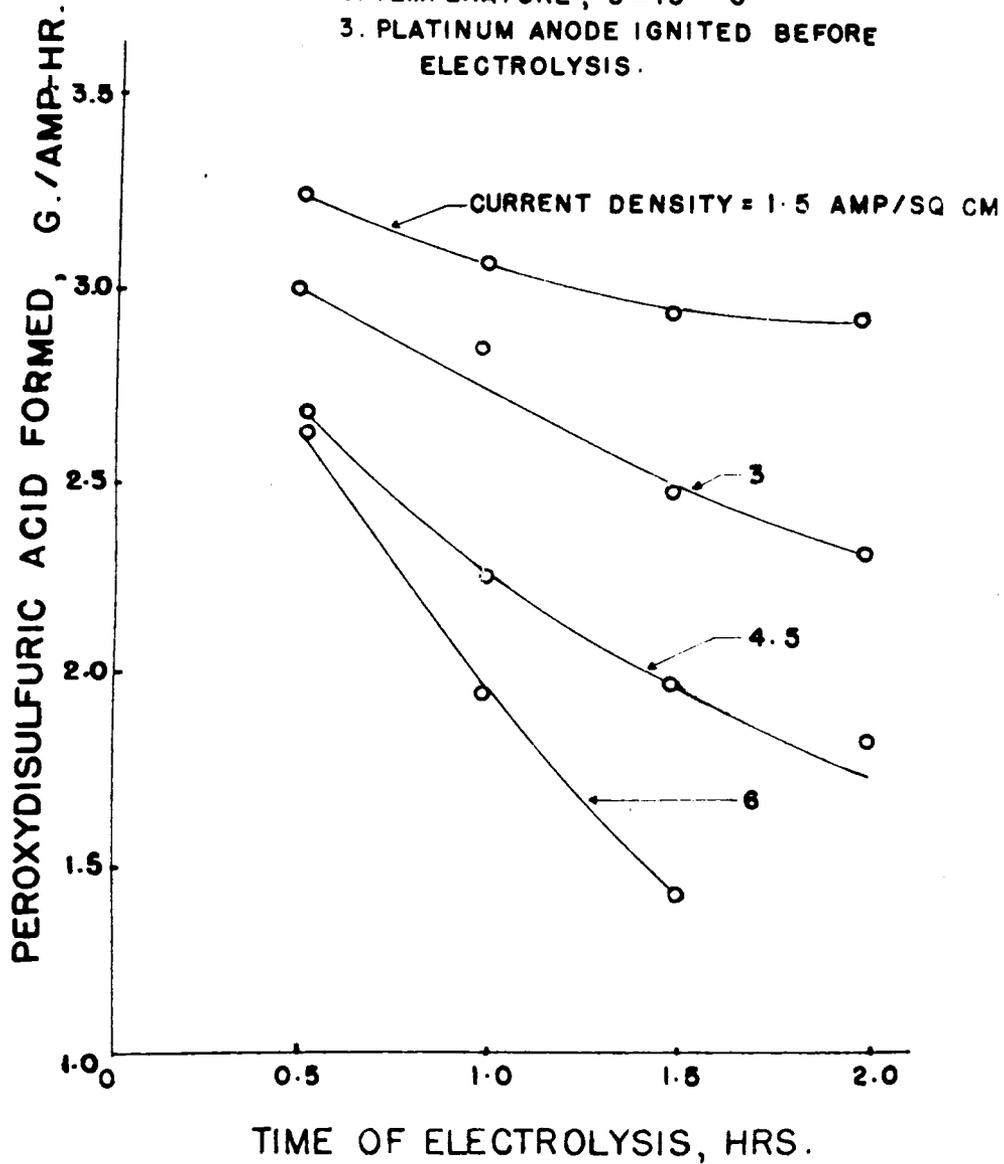
FIGURE 19. RELATIONSHIP BETWEEN TIME OF ELECTROLYSIS AND PRODUCTION OF PEROXYDISULFURIC ACID USING DIRECT CURRENT

Discussion of Results for Periodically-
Reversed, Direct Current Electrolysis

A series of electrolysis tests, PR-18 to PR-22,
were performed to determine the effect of using period-
ically-reversed, direct current on the production of
peroxydisulfuric acid. The operating conditions were
kept as close as possible to that used in the direct
current electrolyses. The platinum anode was ignited
immediately before electrolysis, until almost white
hot, in all cases. It should be noted that the poten-
tial drop across the cell, reported in Table III, page
85, was measured only when the current was flowing
directly. This was not very accurate, especially for
the low time ratio.

Production of Peroxydisulfuric Acid Using Period-
ically-Reversed, Direct Current. A plot showing the rela-
tionship between the production of peroxydisulfuric acid
and direct to reverse current ratio is given in Figure 20.
It is seen that the weight yield, based on total time,
was lowered as the current ratio decreased, which means
that the period of direct current decreased since the
reversed period was kept constant at 0.67 second in
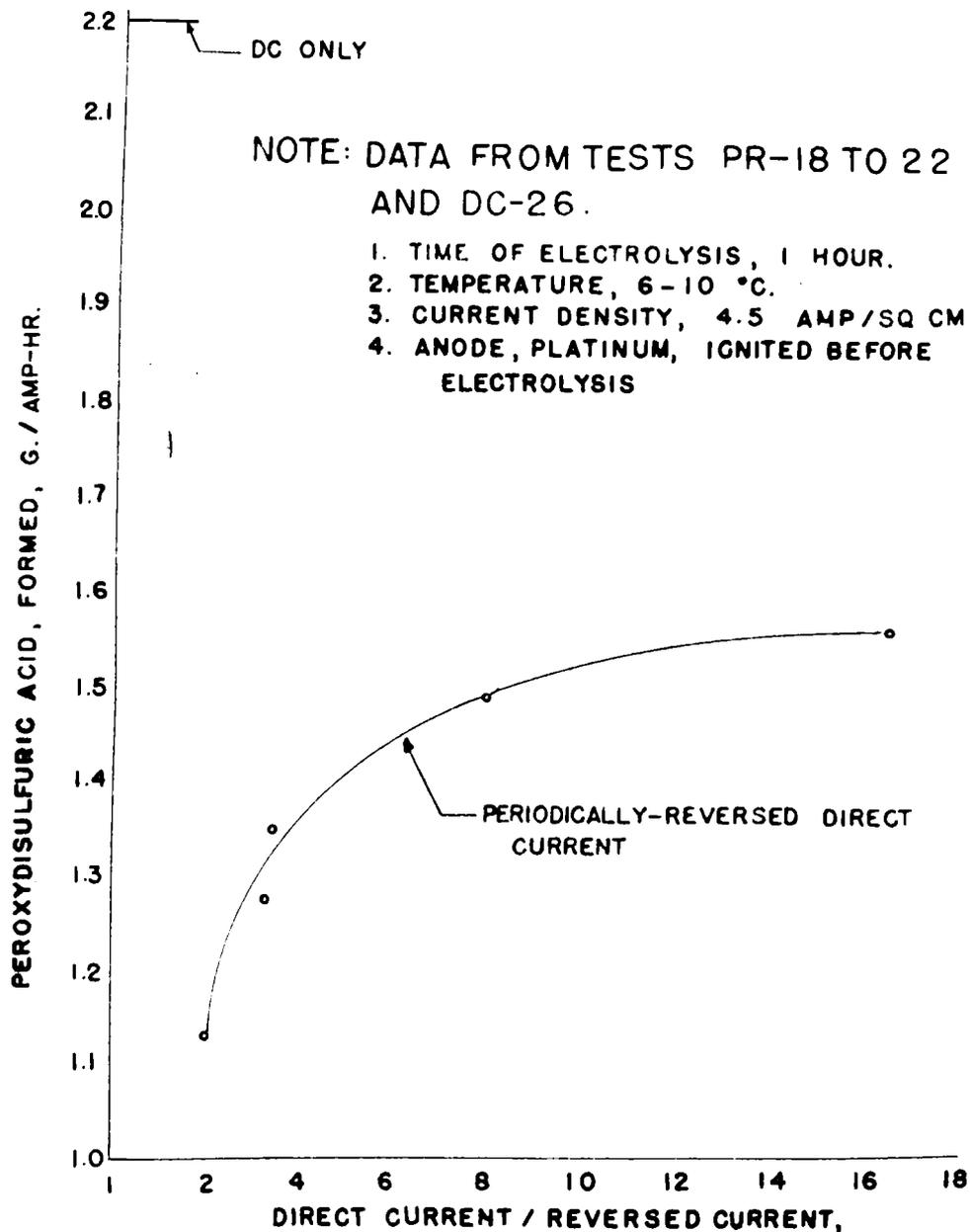
FIGURE 20.   RELATIONSHIP BETWEEN CURRENT
RATIO AND PRODUCTION OF PEROXYDI-
SULFURIC ACID

all cases. The weight yield was low in all of the
five experiments in comparison with those using direct
current only. This could be explained by three
reasons. The low yield could be caused by (a) the
depolarizing action of the periodically-reversed,
direct current, as will be explained later, (b) the
failure to form the peroxydisulfuric acid during the
reverse current portion of the cycle, and (c) the
reduction of the peroxydisulfuric acid during the
reverse current cycle. The anodic gas evolved more
rapidly, especially for the low current ratio, than
for direct current only.

It was also observed that the lead cathode was
attacked during this part of the investigation. It
should be understood that the cathode was changed to
anode during the reverse cycle, and thus the lead cath-
ode dissolved into the solution forming lead sulfate.

Depolarization Action of Periodically-Reversed,
Direct Current. A plot of the current efficiency
against the reverse to direct current ratio is shown
in Figure 21. The current efficiency was lowered as
the ratio of reverse to direct current increased,
breaking sharply between the ratios of zero and 0.061.

NOTE: DATA FROM TESTS PR-18 TO 22
AND DC-26.

1. PLATINUM ANODE IGNITED BEFORE
   ELECTROLYSIS.
2. TEMPERATURE, 5-10 °C.
3. TIME OF ELECTROLYSIS, I HOUR.
4. ANODE CURRENT DENSITY, 4·5 AMP/SQ CM
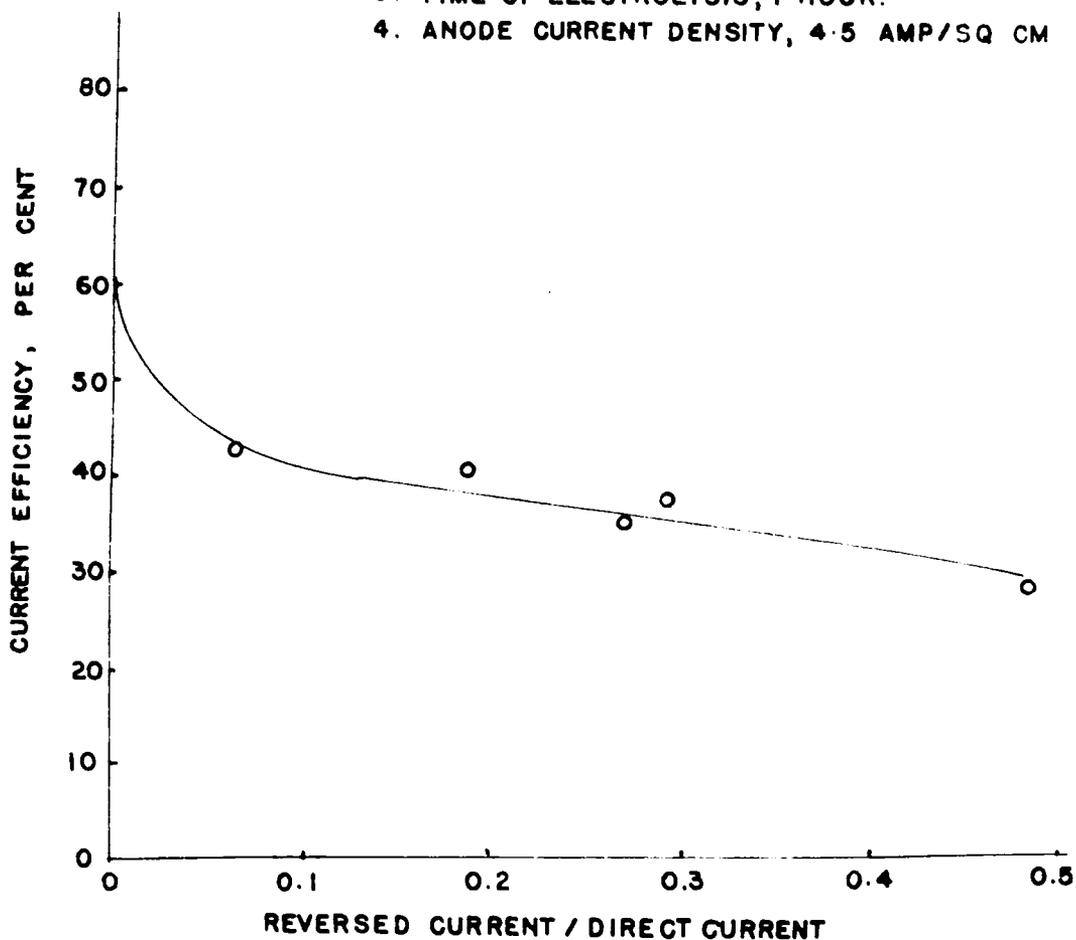
FIGURE 21. RELATIONSHIP BETWEEN CURRENT RATIO
AND CURRENT EFFICIENCY OF PRODUCTION
OF PEROXYDISULFURIC ACID USING
PERIODICALLY-REVERSED
DIRECT CURRENT

This will be compared with the behavior of superimposed alternating current later.

To explain the decrease in current efficiency at low values of reverse to direct current ratio, a depolarizing action of a small reverse current must be assumed. The decomposition potential of sulfuric acid of specific gravity 1.4 was not measured with periodically-reversed, direct current, but it is believed that periodically-reversed, direct current has the same depolarizing action as the alternating current superimposed on direct current, although not exactly equal in magnitude.

As Kortum[36] has stated, it is possible to deposit certain anions simultaneously with, or preferentially to, the hydroxyl ion by using high current densities and electrodes at which the oxygen overpotential is high. Since the oxygen overpotential was lowered by using periodically-reversed, direct current, more oxygen gas was evolved at the anode and thus less of peroxydisulfuric acid was produced. A lower current efficiency resulted.

Ammeter Fluctuations During Current Reversal. A rather interesting behavior of ammeter, "A", Figure 9,

page 72, was observed during current reversal. Test PR-19 illustrates the action which was observed in all cases. At the beginning of the test, the rheostat, "R", was adjusted so that a reading of nine amperes was obtained on the ammeter, "A". Since the middle platinum plate electrode was anode and the outer electrode, lead, was cathode, oxygen gas evolved at the anode. Upon current reversal the reading of the ammeter, "A", was greater than nine amperes, then decreased rapidly. Since the reversed time was only 0.67 second and precipitation at the cathode obscured the surface of the lead electrode, no difference in behavior was observed when the current was reversed.

However, since the electrode changed alternately from cathode to anode, the following reaction should occur.

When the electrode is cathode:

$$e + H^+ = (H) \qquad (1)$$

$$(H) + (H) = H_2 \qquad (2)$$
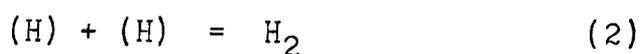
When the electrode is anode:

$$(OH)^- = (OH) + e \qquad (3)$$

$$2(OH) = H_2O + \frac{1}{2}O_2 \qquad (4)$$
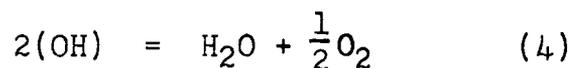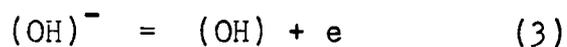
For a short time after reversal:

$$(OH) + (H) = H_2O \qquad (5)$$
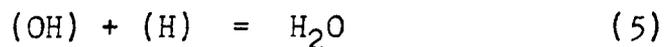
The first two equations illustrate the reaction taking place at the lead cathode during the current cycle in which the center platinum is anodic. Equations (3) and (4) show the reactions taking place at the lead electrode during the current cycle in which the center platinum is cathodic. During the reverse cycle, on the former electrode, the reaction of Equation (2) is terminated since no more nascent hydrogen is supplied. Instead, hydroxide ions are neutralized and react

with the residual hydrogen on the electrode according to Equation (5).

The fluctuation of the ammeter, "A", on current reversal is an indication that an overvoltage exists in the cell circuit. When current is first reversed, nascent hydroxyl ions react with nascent hydrogen absorbed on the surface of the electrode. The absorbed nascent hydrogen, which may be the cause of the so-called hydrogen overvoltage, is used up. Then, the current drops back as the oxygen over-voltage builds up. The opposite reactions take place at the electrode which changed from anode to cathode.

Time and Current Ratio. Inspection of the direct to reverse time and current ratio in Table III, page 85, shows that they do not agree. In most of the tests the ratio of direct to reverse time was found to be almost 1.2 times the corresponding current ratio. This dis-crepancy may be attributed to the fact that the reverse current flowing through the cell was usually 1.2 times that current flowing during the direct cycle. This being true, more copper would be plated onto the coulometer cathode during the reverse cycle than would be deposited during the direct cycle for the same time

interval. The true cause of the discrepancy is that the polarization on the reverse cycle, as was discussed in the previous section, caused the increased reverse current which, in turn, caused the ratio of direct to reverse current to be smaller than the ratio of direct to reverse time. A plot of the ratios of direct to reverse time and current is given in Figure 22, to illustrate the disagreement between the two values. The data plotted were obtained from tests PR-18 to PR-22, inclusive, and lie along a straight line, the deviation at the lower end probably being experimental error.

Comparison of Current Efficiencies. The current efficiencies obtained during this part of the investigation are given in Table III, page 85. Inspection of these values, at a time of electrolysis of one hour, shows that the highest one is 43 per cent and the lowest one is 29 per cent when the direct to reverse time ratios are 20 and 2, respectively. For two hours of electrolysis, the current efficiencies decreased to 33 and 24 per cent. On comparison of those current efficiencies with that of test DC-26 using direct current only, it is seen that those values are lower

NOTE: DATA FROM TESTS PR-18 TO 22.
1. ANODE IGNITED BEFORE ELECTROLYSIS.
2. TEMPERATURE, 5-10 °C.
3. CURRENT DENSITY, 4·5 AMP/SQ CM.
4. H_2SO_4, SP. GR.= 1·4 .
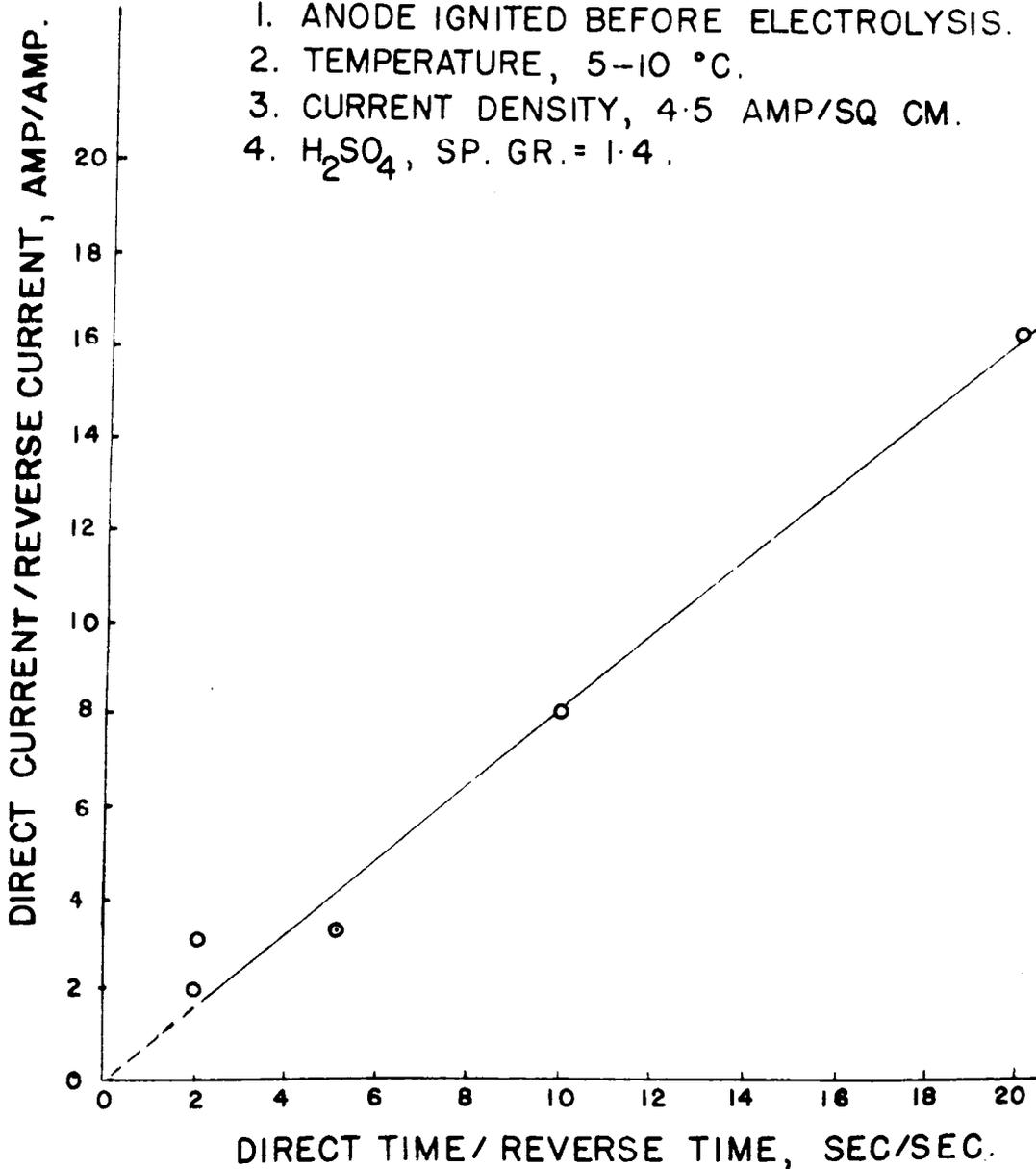
FIGURE 22. RELATIONSHIP BETWEEN TIME RATIO
AND CURRENT RATIO IN ELECTROLYSIS OF
SULFURIC ACID USING PERIODICALLY
REVERSED DIRECT CURRENT

than the direct current efficiencies as the time ratio decreased. A group of curves showing the relative values of efficiencies with different time ratios are given in Figure 23.

Discussion of Results from Alternating Current Superimposed on Direct Current Electrolyses

A series of electrolyses were performed to study the effects of varying current density and frequency of an alternating current superimposed on direct current on the production of peroxydisulfuric acid. An attempt was made to keep the operating conditions during these experiments the same as that used with direct current and with periodically-reversed, direct current. The specific gravity of sulfuric acid was 1.4 in all tests. The temperature during the electrolyses was kept below 10 °C. The platinum anode was ignited immediately before each electrolysis. The frequencies used in this part of the study were 60, 240, and 500 cycles per second.

Formation of Peroxydisulfuric Acid with 60-Cycle, Alternating Current Superimposed on Direct Current. In the series of tests with 60 cycles per second,

NOTE: DATA FROM TESTS PR-18 TO 22 AND
DC-26.

1. H_2SO_4, SP.GR. = 1·4·
2. PLATINUM ANODE IGNITED BEFORE ELECTROLYSIS.
3. TIME OF ELECTROLYSIS VARIED.
4. IN TESTS, PR-18 TO 22, THE REVERSE TIME WAS
   KEPT AT 0.67 SEC.
5. TEMPERATURE, 5-10 °C.
6. CURRENT DENSITY, 4·5 AMP/SQ CM
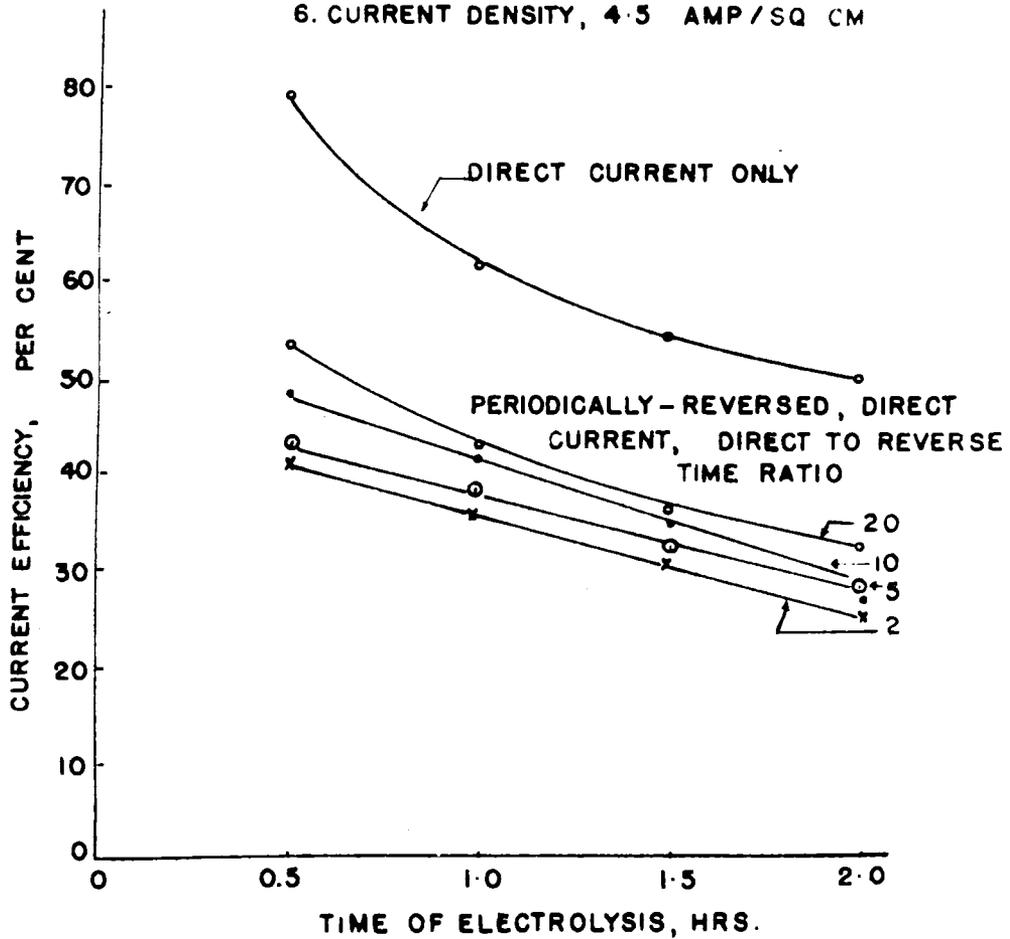
FIGURE 23· RELATIONSHIP BETWEEN TIME OF ELEC-
TROLYSIS AND CURRENT EFFICIENCY OF
PRODUCTION OF PEROXYDISULFURIC
ACID

alternating current superimposed on direct current,
10 experiments were performed. During these experiments, the direct current density was kept constant at
4.5 amperes per square centimeter, and the alternating
current was varied. It was observed that the production of peroxydisulfuric acid decreased sharply as the
ratio of peak alternating to direct current increased
from zero to 0.2, as shown in Table IV, page 86. After
that point, the production was nearly constant until
the ratio was almost equal to one. Then, a second
break appeared and practically no peroxydisulfuric
acid was obtained.

The decrease in the production of peroxydisulfuric acid is attributed to the depolarization
characteristic of superimposed alternating current.
Since the anodic formation of peroxydisulfuric acid
simultaneously with neutralization of the hydroxyl
ion requires a high current density and electrodes at
which the oxygen overpotential is high, the depolarization action of the superimposed alternating current
will result in increased oxygen evolution and decreased
formation of peroxydisulfuric acid.

When the ratio of peak value of alternating to direct current is between 0.2 to 1.0, the total current is equal to a pulsed direct current. The depolarization action of superimposed alternating current has been considered as a function of frequency only, no matter what is the ratio. If this is so, the same amount of direct current would produce the same amount of peroxydisulfuric acid at any ratio for a fixed frequency. This is the case only for a range of peak alternating to direct current ratio within certain limits.

When the ratio of peak value of alternating to direct current was greater than one, the polarity of the electrodes changed alternately, although the time during which the platinum electrode was anode was longer than the time it was cathode. Very little peroxydisulfuric acid was produced. Under this condition, two possible reactions occur: one, peroxydisulfuric acid formed while the electrode was anodic could be destroyed while it was cathodic; the other, under the influence of alternating current, platinum could be activated and dissolved into the anolyte. The latter case uses part of the electrical energy

which might have formed peroxydisulfuric acid. The more rapid gas evolution at both the alternating current and direct current electrodes would support the idea of reduction of peroxydisulfuric acid.

Formation of Peroxydisulfuric Acid with 500-Cycle, Superimposed Alternating Current. A series of eight experiments were performed with 500 cycles per second, alternating current superimposed on direct current. Production, similar to that with 60 cycles per second, superimposed alternating current was obtained; however, in this case, the break point was between the ratios of 0.44 and 0.50 instead of at one. When the ratio of peak alternating to direct current was greater than 0.67, no peroxydisulfuric acid was formed at a current density of 2.2 amperes per square centimeter and 4.5 hours electrolysis. An interesting phenomenon is that the direct current density seems to have no effect on the yield in the presence of 500 cycles per second, superimposed alternating current, as seen from the production per ampere-hour obtained with different current densities (Table V, page 87).

Here again, the depolarizing action of superimposed alternating current should be emphasized. The

decomposition potential of sulfuric acid obtained from the measurements made using superimposed alternating current was less than 0.1 volt. It is much lower than that obtained using direct current only, which was approximately 2.3 volts. In this case, any increase of current density does not increase the decomposition potential. This being so, increasing or decreasing the current density does not affect the efficiency as it does for direct current electrolysis. It would be interesting to determine just what minimum ratio of peak alternating current to direct current would result in lowering the decomposition potential.

Formation of Peroxydisulfuric Acid with 240-Cycle, Alternating Current Superimposed on Direct Current. Three experiments were performed with 240 cycles per second, alternating current superimposed on direct current. In this case, the break point was between those obtained with 60 and 500 cycles per second.

Summary of Effect of Frequency. A summary of the electrolyses of sulfuric acid of specific gravity 1.40 to produce peroxydisulfuric acid, at a temperature of zero to 10 °C, with different frequencies of

alternating current superimposed on direct current, is as follows:

1. With 60 cycles per second of alternating current, the current efficiency decreased from 61.5 to approximately 31.0 per cent as the ratio of peak value of alternating to direct current increased from zero to 0.2. This was due to the depolarizing action of superimposed alternating current. The current efficiency was constant, 31 per cent, in the range of the ratio of peak alternating to direct current of 0.2 to one. As discussed previously, in this case the total current was equal to a pulsed direct current and it is assumed that the depolarizing action of this type of current was constant over a range of ratios. When the ratio is greater than one, the platinum was dissolved in the sulfuric acid, and almost no peroxydisulfuric acid was formed.

2. With 500 cycles per second of alternating current, the ratio of peak alternating to direct current at which the current efficiency suddenly decreased to almost zero was at 0.44.

3. With 240 cycles per second of alternating current, the break point was between those obtained with 60 and 500 cycles per second of alternating current.

From the above observations, the ratio of peak alternating to direct current at which the current efficiency suddenly dropped to zero varied inversely as the frequency of the alternating current superimposed on the direct current.

Behavior of Platinum Electrode. In the tests with 60 cycles per second, alternating current superimposed on direct current, black spots formed on the surface of the platinum anode and the color of the anolyte was changed to light yellow at a ratio of peak alternating to direct current of approximately 0.7. The anolyte was changed to a brown color when the ratio was greater than one. The surface of the platinum electrodes was roughened by the electrolysis.

When 500 cycles per second, alternating current was used, the anolyte was changed to a brown color at a ratio of 0.5. During test SD-46 with the ratio of 1.19, the diameter of the platinum anode, of 0.8 centimeter in length, was decreased from 0.102 to 0.070 centimeters at a current density of 2.2 amperes per square centimeter in 5.5 hours. That wire was almost completely dissolved in the anolyte in the next experiment, test SD-47. The phenomenon shows

that platinum in sulfuric acid was activated and dissolved by alternating current superimposed on direct current.

Current Efficiency. Current efficiencies obtained during these tests with 60, 240, and 500 cycles per second, alternating current superimposed on direct current are plotted against the ratio of peak alternating to direct current in Figure 24. The value of the current efficiencies are approximately the same, except when near the break point.

Comparison of Current Efficiencies. The current efficiencies obtained with 60 cycles per second, alternating current superimposed on direct current fall in the range of 26 to 37 per cent so long as the ratio of peak alternating to direct current is less than one. The efficiencies obtained with 500 cycles up to a ratio of 0.4 were almost the same as those obtained with 60 cycles per second, superimposed alternating current. In comparing the the current efficiencies with those obtained by using periodically-reversed, direct current, no appreciable difference appears (comparing Figure 24 with Figure 21, page 124),
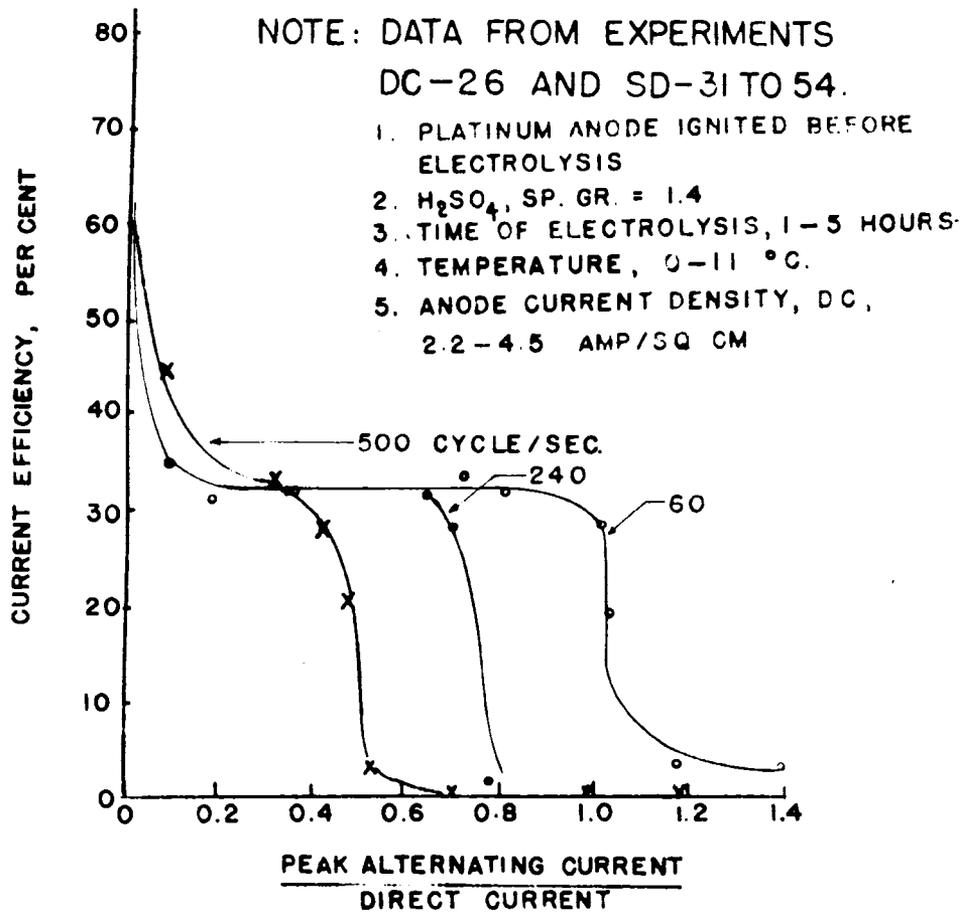
FIGURE 24.— RELATIONSHIP BETWEEN THE RATIO OF PEAK
ALTERNATING TO DIRECT CURRENT AND THE CURRENT
EFFICIENCY ON THE PRODUCTION OF PEROXY-
DISULFURIC ACID.

when the ratio of reversed to direct current is less than 0.5.

The current efficiency obtained with direct current only, as in test DC-26, was 61 per cent at a current density of 4.5 amperes per square centimeter and for a time of electrolysis of one hour. This is almost twice those obtained with superimposed alternating current.

One should measure the hydrogen and oxygen evolved during electrolysis with ratio of peak alternating to direct current of more than 0.1 and less than 0.5, and then determine if the reduction in efficiency (compared with direct current efficiency) was caused by the evolution of gas, or arose from a change in the electro-chemical equivalents required for the product produced.

Recommendations

The following recommendations are made as a result of this investigation.

Time-Current Relationship. It is recommended that a recording ammeter be placed in the circuit. The procedure would make it possible to obtain a time-current curve for the particular direct to reverse time ratios studied and would better indicate the operation of the periodic reverser.

Catalytic Reduction of Peroxydisulfuric Acid. Since the production of peroxydisulfuric acid decreased when superimposed alternating current was applied to the cell, a study concerning the reduction of peroxydisulfuric acid at a platinum electrode, using superimposed alternating current as a source of electric energy should be interesting.

Solution of Platinum. Since platinum was activated and dissolved in sulfuric acid during the electrolysis with superimposed alternating current, a detailed study of the behavior of platinum in sulfuric acid or other acids, using different frequencies, is recommended.

Study of Other Chemical Reactions. It is rec-ommended that a study of the following electrochemical reactions with either superimposed alternating current or periodically-reversed, direct current be made. The first group are electrochemical oxidations:

1. Electrolysis of acetylene in alkaline solu-tion to produce formic acid.

2. Electrolysis of aniline to produce quinone or hydroquinone.

3. Electrolysis of glucose to produce glyconic acid.

4. Electrolysis of alkaline solution of alcohol in the presence of chlorine to produce chloroform.

5. Electrolysis of potassium salt of ethyl malonic acid to produce diethylsuccinate.

6. Electrolysis of carbonate to produce percarbonate.

7. Electrolysis of borate to produce perborate.

8. Electrolysis of chlorate to produce perchlorate.

9. Electrolysis of manganese sulfate to produce permanganic acid.

10. Anodic dissolution of nickel.

11. Anodic deposition of chlorine or bromine.

12. Anodic deposition of sulfur from sulfide.

The following groups are electrochemical reductions:

1. Electrolysis of nitrobenzene to produce aniline.

2. Electrolytic reduction of sugar to alcohols.

3. Electrolytic conversion of oleic. acid to stearic acid.

4. Electrolytic deposition of lead from lead nitrate (high concentration overpotential).

5. Electroplating of silver or other metals.

Limitations

This investigation was limited to the study of the effect of periodically-reversed, direct current and alternating current superimposed on direct current as the source of electrical energy. Other direct current experiments were performed for comparison purposes only.

Electrodes. Platinum anode and lead cathode were used in all of the experiments.

Temperature. The temperature of electrolysis for the large majority of the tests was between 5 to 10 °C. The highest temperature was 16 °C (test DC-25). The lowest temperature was 0 °C (tests SD-46 and SD-52).

Time of Electrolysis. The time of electrolysis was between 60 to 270 minutes, and depended upon the direct current density.

Volume of Anolyte. The volume of anolyte was 200 milliliters for a large majority of the tests, and 100 milliliters for part of the tests using superimposed alternating current.

Diaphragm. A porous cup, capacity 250 milli-
liters, was used as the diaphragm to separate the
anode and cathode compartments.

Electrolytic Solution. The anolyte was surfuric
acid of specific gravity 1.4 in all of the tests. The
solution in the cathode compartment was the same as the
anolyte.

Tests performed using periodically-reversed, direct
current, had the following specific limitations:

Direct to Reverse Time Ratios. The direct to
reverse time ratios of periodically-reversed, direct
current studied were 2.0, 5.0, 10.0, and 20.0. The
reversed time was 0.67 second in all of the tests.

Anode Current Density. The anode current density
during the direct portion of the time cycle was main-
tained at 4.5 amperes per square centimeter and the
anode surface area was two square centimeters.

The limitations placed on the tests performed
using an alternating current superimposed on direct
current are given in the following paragraphs:

Frequency of Alternating Current. Superimposed
alternating current frequencies of 60, 240, and 500

cycles per second were investigated during this phase of the study.

Direct Current Density. The direct current density on the platinum anode inside the diaphragm was maintained at 2.2 and 4.5 amperes per square centimeter. The former was used for these tests using high ratio of peak alternating to direct current, and the latter for the lower ratios.

Alternating Current Density. The alternating current density was varied from 0.2 to 4.8 peak amperes per square centimeter.

Electrical Circuit. In this phase of the study the direct and alternating current circuits were connected in parallel with the electrolytic cell.

Meter Measurements. Direct current flow was measured by means of a copper coulometer, and the alternating current flow was read from ammeters, which were accurate to only 0.05 ampere for 60 cycles per second and 0.01 ampere for 500 cycles per second.

V. CONCLUSIONS

For electrolyses of sulfuric acid of specific gravity 1.4 to produce peroxydisulfuric acid with a porous, ceramic diaphragm at the temperature of 5 to 10 °C performed with direct current, periodically-reversed, direct current, and alternating current superimposed on direct current, with platinum anode and lead cathode; and:

A.   Under the above experimental conditions with direct current only, the following conclusions may be drawn:

1.   The production of peroxydisulfuric acid was increased from 4.18 to 15.65 grams per 1.5 hours as the anode current density increased from 1.5 to 6.0 amperes per square centimeter.

2.   At the current density of 4.5 amperes per square centimeter, the current efficiencies were lowered from 79.3 to 39.8 per cent, as the time of electrolysis was prolonged from 30 to 150 minutes.

3.   In general, the current efficiencies were lowered as the time of electrolysis

increased using current densities of 1.5 to 6.0 amperes per square centimeter.

B. Under the above experimental conditions, at an anode direct current density of 4.5 amperes per square centimeter, with periodically-reversed, direct current, the following conclusions may be drawn:

1. The current efficiencies were lowered to 35.0, 37.2, 41.3, and 42.6 per cent at direct to reverse time ratio of 2, 5, 10, and 20, respectively, in comparison with 61.5 per cent obtained with direct current only, for one hour of electrolysis.

2. The ratio of time of direct to reverse electrolysis was always greater than the ratio of the direct current to reverse current, the difference decreasing as the ratio decreased.

C. Under the above experimental conditions, using alternating currents of 60, 240, and 500 cycles per second, superimposed on direct current, it is concluded that:

1. Compared to direct current electrolysis, using the same amount of electricity, the current

efficiencies were lowered from 61.5 per cent to approximately 31.0 per cent, regardless of the frequency of alternating current.

2. The ratio of peak alternating current to direct current at which the current efficiency suddenly dropped to zero decreased from 1.0 to 0.75, to 0.5, as the frequency of alternating current increased from 60 to 240, to 500 cycles per second, respectively.

3. Increasing the frequency of superimposed alternating current had no appreciable effect on the current efficiency for the ratio of peak alternating to direct current of less than 0.5 for 500 cycles per second and 0.75 for 240 cycles per second, as compared to the electrolysis with 60 cycles per second, alternating current.

4. During the electrolysis with the frequencies of 240 and 500 cycles per second, the current efficiencies obtained with direct current densities of 2.2 and 4.5 amperes per square centimeter were approximately the same, or 31 per cent.

VI. SUMMARY

It was the purpose of this investigation to study the effect of varying the direct to reverse time ratio of periodically-reversed, direct current from 1.0 to 20.0 at an anode current density of 4.5 amperes per square centimeter, and to study the effect of alternating current of 60, 240, and 500 cycles per second, 0.2 to 4.5 amperes per square centimeter, superimposed on direct current on the electrolytic production of peroxydisulfuric acid.

Electrolyses of 200 milliliters of sulfuric acid of specific gravity 1.4, at a temperature of 5 to 10 °C were performed with direct current. The anode current density was varied. The surface area of platinum anode and lead cathode was 2.0 and 221.8 square centimeters, respectively. For one hour of electrolysis, the yields were 7.9, 14.0, 20.2, and 22.9 grams of peroxydisulfuric acid at the anode current density of 1.5, 3.0, 4.5, and 6.0 amperes per square centimeter, respectively. The current efficiencies corresponding to these anode current densities were 85.0, 77.0, 61.5, and 53.4 per cent. The

results showed that the yield was increased and the current efficiency was decreased with increase in the anode current density.

Electrolysis of the same concentration and volume of sulfuric acid using periodically-reversed, direct current yielded 14.2 grams at an anode current density of 4.5 amperes per square centimeter and at a temperature of 5 to 8 °C. The time of electrolysis was one hour and the time ratio of direct to reverse electrolysis was 20. The current efficiency obtained under these conditions was 42.6 per cent. Decreasing the direct to reverse time ratio gave lower yields and current efficiencies. Apparently, there is no advantage in using periodically-reversed, direct current over the use of direct current for this reaction under the above experimental conditions.

Electrolyses of 200 milliliters of sulfuric acid of the same concentration were performed with 60 cycles per second, alternating current superimposed on direct current. The direct current density was 4.5 amperes per square centimeter for the ten tests, but the surface area of the platinum anode was changed from two to one square centimeter and the direct current was

decreased from 9.0 to 4.5 amperes. The current efficiency decreased sharply from 61.5 to approximately 31.0 per cent as the ratio of peak alternating to direct current increased from zero to 0.2 and then it remained constant until the ratio reached one. The current efficiency decreased suddenly to almost zero when the ratio was greater than one.

The same sulfuric acid was electrolyzed under the same experimental conditions with 240 and 500 cycles per second, alternating current superimposed on direct current. Both direct and alternating anode current densities were varied. The direct current density was 2.2 and 4.5 amperes per square centimeter. The current efficiencies obtained during these tests were almost the same as that obtained with 60 cycles per second, alternating current within a specific limit of the ratio of peak alternating to direct current. The ratio of peak alternating current to direct current at which the current efficiencies suddenly dropped to zero was 0.75 for 240 cycles per second, and 0.5 for 500 cycles per second, instead of one for 60 cycles per second, superimposed alternating current.

The platinum anode was activated and dissolved
into the sulfuric acid when the ratio of peak alterna-
ting to direct current was greater than 1.0, 0.75, and
0.5 for 60, 240, and 500 cycles per second, alternating
current superimposed on direct current.

Apparently, there is no advantage in using alterna-
ting current superimposed on direct current over the
use of direct current for electrolytic production of
peroxydisulfuric acid.

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VIII. <u>ACKNOWLEDGMENTS</u>

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