THE MERCURY WEIGHT COULOMETER

BY

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TABLE OF CONTENTS

INTRODUCTION

The measurement of current quantity is extremely important. Hence many careful studies have been made on coulometers. The most precise is the silver coulometer. However, it is expensive for ordinary laboratory use and many precautions must be taken to obtain the precision specified. The iodine coulometer is also extremely exact for small currents but has not found wide usage in the laboratory for several reasons. Another important volt-ameter is the copper coulometer, which is very simple in manipulation. It is not as reliable as the other two.

The purpose of this research was to develop a mercury weight coulometer, which would be simple in arrangement and operation. It was desired to establish the degree of reliability over certain well defined current density limits.

The Laws of Electrolysis, or Faraday's Laws, from which there are apparently no deviations, are the principles upon which this investigation is based. Since the electro-chemical equivalent of mercury is high, the precision of such a coulometer should be high. The greater the deposit for the current passed the greater should be the accuracy of the coulometer.

These facts led to the conception of the research. The problems arising and the investigations performed are herein described.

THEORETICAL DISCUSSION

A coulometer is a device employed to measure electrochemical decompositions and depositions, which indicate quantities of electricity flowing through a closed circuit. This electrolytic cell is arranged in such a manner that the products can be determined quantitatively, either gravimetrically or volumetrically.

Faraday's researches on electricity and electrochemical action are the basis of the theoretical and quantitative action of a coulometer. In 1834, he propounded the fundamental principles governing the relation of current and electrochemical action (2). They are:

1. The weight of any substance liberated at an electrode during electrolysis is proportional to the quantity of electricity passed through the electrolytic cell.

2. The quantities of substances liberated are exactly proportional to their equivalent weights.

Faraday's laws enable us to calculate the total quantities of substances which will be freed at the electrodes during the passage of a known quantity of current.(1) However, if the electrolyte contains more than one kind of cation or anion, these laws do not indicate the relative

amounts of the constituents being liberated. In the
electrodeposition of metals, we are usually interested
in discharging one particular ion. Therefore, the current
efficiency of electrolysis is considered as that proportion
of current which is actually used to deposit or dissolve
that ion. The cathode or anode efficiency is the ratio of
the weight of metal deposited or dissolved to the weight
theoretically possible from Faraday's laws.

Also in electrodeposition we are concerned not
only with the amperage (current) required to produce a
certain result, but in the potential required.(1) The
potential developed at an electrode in contact with a
solution of its ions is explained and calculated by use
of Nernst's concept of electrolytic solution pressure.
Nernst assumed that each metal possesses a definite
tendency to pass from the atomic to the ionic state. This
tendency is called the electrolytic solution pressure.

Therefore, when a metal is immersed in pure water,
the atoms of the metal give up electrons to it and dissolve
into solution as positively charged ions. However, the
concentration of ions in solution is small, which can be
explained by the "double layer" theory of potential. The
atoms, to become metallic ions, must leave behind on the
metal negative charges, which accumulate. Due to the
presence of the metallic ions in solution, the thin film
of liquid surrounding the electrode becomes positively

charged. The potential difference thus established between the metal and the liquids opposes the formation of more positive ions. The process of solution soon ceases.

This reasoning can be extended more practically to a metal electrode dipping into a solution of its ions. Another effect must now be considered. The electrolytic solution pressure is opposed by the osmotic pressure, which defines the tendency for the ions to plate out of solution as atoms. Three conditions are possible.

I. The osmotic pressure (π) of the ions exceeds the solution pressure of the atoms. The ions plate out on the electrode and pull electrons from it, giving the electrode a positive charge and the solution a negative charge. Then $\pi = P + E$ and $E = \pi - P$.

II. The electrolytic solution pressure is greater than the osmotic pressure. Metallic atoms will ionize and leave the electrode with a negative charge, while the solution will acquire a positive charge. Then $P = \pi + E$ and $E = P - \pi$.

III. The osmotic pressure equals the electrolytic solution pressure. The tendency for the metallic atoms to ionize is balanced by the tendency for the ions to plate out as neutral atoms, and no potential is set up at the electrode surface. Then $P = \pi$ and $E = 0$.

A potential difference, set up in cases I and II, may be computed with the equation

$$E = + \frac{RT}{nF} \ln \frac{\pi}{P}$$

where E is potential difference between the metal and the solution, R the gas constant in joules per degree, T the absolute temperature, n the number of electrons transferred across the junction, F the faraday in coulombs the osmotic pressure, and P the electrolytic solution pressure.

The equation shows that the greater the concentration of ions, the greater will be the osmotic pressure and the more positive the electrode potential. Conversely, the greater the electrolytic solution pressure the more negative the potential.

It is easily shown that metallic ions do not have the same solution pressure. If several salt solutions possessing the same ionic pressure are placed in contact with a rod of the corresponding metal, the potentials developed in the different cases disagree widely. The deviations are explained by differences in solution pressure. Metals like magnesium and zinc exhibit a high potential, the current would flow from the metal to the solution under the proper conditions (2). Hence, the solution pressure greatly exceeds the osmotic pressure and due to this high solution pressure and their positive nature, they are called strongly electropositive. The E.M.F. developed between

the metal and the solution is called positive. Conversely,
metals like silver and gold in contact with their ions
develop a potential opposite from that of zinc. This
potential causes a current to flow from the solution to
the metal and the osmotic pressure, therefore, exceeds
the solution pressure. These metals are called weakly
electropositive. Since they are negatively responsible for
the E.M.F. developed, this E.M.F. is given a negative sign.

Considerable confusion regarding the sign of the
electrode potential exists in the literature. The convention
most generally accepted is to let the sign of the electrode
potential represent the charge of the electrode against
that of the solution.

Many cells and coulometers are rendered inefficient
if the conditions of the process are not carefully adjusted.
Otherwise polarization occurs. In a broad sense, the term
polarization may include all those effects at the electrodes
which change the electrode potentials from the equilibrium
values (3). That is, where no current is flowing. The
phenomena of polarization have in many cases been obscure,
but the causes may be classified as follows:

(1) Covering of the electrodes - Mechanical and Chemical

(2) Concentration changes

(3) Passivity

(4) Overvoltage

The credit is due to LeBlanc (4) for the
first attempt to disentangle polarization phenomena.
His studies showed that a change in potential due to
polarization depends upon the same principles as the
development of potential differences in cells. Lewis
and Jackson have attributed polarization "to a counter
electromotive force caused either by exhaustion of the
substances used in the electrolytic reaction faster
than they can be replaced, or by the accumulation of
the products of the reaction faster than they can be
removed".

A discussion of the first classification must
include mention of decomposition voltage. If smooth
platinum electrodes are suspended into a solution of
sulfuric acid and a small difference of potential applied,
it will be found that at first a current flows through
the circuit. It, however, rapidly decreases and finally
becomes zero. This same property is observed until a
definite potential (1.7 v) at which a steady continuous
current flows through the circuit is reached. This
potential is called the decomposition potential of the
electrolyte and may be defined as the smallest external
force that must be applied, in order to bring about the
separation of such quantities of cations and anions at
insoluble electrodes that a continuous current flows
through the solutions (4).

In the example above, the gases formed at the electrodes are not set free entirely, but accumulate on the electrode. This accumulation at very low potentials develops a back electromotive force, which is overcome (but still exists) at potentials greater than the decomposition potential.

Another type of polarization is that due to a covering of the electrode caused by chemical changes. If smooth platinum electrodes are dipped into a solution of copper sulfate and a current passed, copper will plate out on the cathode and oxygen will be discharged at the anode. This causes a copper-oxygen cell to be established and the electromotive force developed opposes the direction of the current and increases the resistance of the cell.

There are two methods used to determine decomposition voltages (4). In the first, electrolysis is caused at a voltage such that a continuous current flows. When a sufficient quantity of the products have accumulated, the circuit is broken and the back E.M.F. measured at once with a high resistance voltmeter. The back E.M.F. is the decomposition voltage of the electrolyte. The procedure in the other method is to increase gradually the external E.M.F. and to measure the current in the circuit with a milliameter. By plotting voltage against current, a sharp break in the curve will be observed at a definite voltage. This break represents a sudden increase in current and the

corresponding voltage represents the decomposition voltage.

Decomposition voltages are reduced in most electrodeposition processes by the use of soluble anodes (1). Although a certain definite potential is required to plate out the metal ions at the cathode, an equal and opposite potential is established at the anode by the dissolving of the metal. Since these anode and cathode potentials balance, a small external potential is sufficient to cause continuous electrolysis. Hence, if a soluble anode is used in electrolyzing a solution the applied voltage need not exceed the decomposition of the electrolyte. This holds true for the ideal case only, where a very small current is flowing. When an appreciable current is passed through the solution, the potentials at the anode and cathode are not the same, due to concentration polarization.

A very common type of polarization is that known as concentration polarization (3),(4). It is due to concentration changes around the electrodes when a solution of an electrolyte is electrolyzed between electrodes of the metal of the electrolyte.

Polarization of a cell is divided into anodic and cathodic polarization. Any process that tends to make the anode more positive or the cathode more negative contributes to anodic and cathodic polarization respectively.

During electrolysis the concentration of the metal

ion increases around the anode because the rate of diffusion is not sufficient to carry the dissolved metal from the anode to the cathode as rapidly as it is dissolved by the current. It is more difficult for metals to go into solution from the anode as the concentration there increases and the potential gradient at the electrode is increased as is the ohmic resistance. Likewise, as electrolysis proceeds, ionic concentration is decreased around the cathode because electrolytic deposition is more rapid than ionic diffusion, the potential difference and ohmic resistance are again increased, according to Nernst's equation.

Frequently a potential much higher than the equilibrium potential is required for anodic solution of a metal. If the current density is increased a point is reached at which the anode potential rises suddenly, and there is a corresponding decrease of current (5). At the same time the anode ceases to dissolve and the metal is then said to be passive.

This phenomena is exhibited by chromium, nickel, copper, iron and other metals. Also, many base metals become passive when made the anode of an electrolytic cell. In this state the metals behave like noble metals and do not dissolve in accordance with Faraday's laws, if at all. The anode potential is abnormally high even at low current

densities and the principle reaction is the discharge
of the anion. When the passive condition has been
established and the current broken the anode returns
slowly to the active condition on standing. The active
state is more rapidly regained by using the passive metal
as a cathode in a cell, by touching it with a less noble
metal under the surface, or by scratching the surface.
The attainment of passivity depends on the nature of the
electrolyte. It is opposed by high hydrogen ion and
chlorine ion concentrations but oxidizing anions favor it.
A rise in temperature inhibits passivity and it has also
been found that superposition of an alternating current on
the direct current has the same effect (1).

There is no satisfactory explanation of passivity
but it is certainly associated with, if not entirely due
to, the accumulation on or in the metal of a film of
oxygen or oxide. The first definite views on passivity
were expressed by Faraday who suggested that the surface
of the metal was oxidized or was in such relation to the
oxygen of the electrolyte as to be equivalent to oxidation (5).
This theory held until it was shown that the oxide responsible
for passivity would have to be different from any known oxide
of the metal. It was also contended that a definite oxide
could not be present because the electrode potential of a
passive metal varied over a wide range. The last argument
is refuted by supposing that a solid solution is formed by

the oxide with the metal; the electrode potential would depend on the concentration of this solution.

Objections to the first argument against the oxide film theory have been studied by Evans (5), who has succeeded in obtaining a very thin film of oxide by dissolving away the inner portion of passive iron electrodes. The properties of this oxide are identical with ignited ferric oxide and there is no necessity to postulate the existence of abnormal oxides. Although the existence of an oxide film may be admitted, it may not be the cause but rather the consequence of passivity.

Practically, passivity may be considered as a form of polarization as it requires a certain electromotive force before a current can flow continuously (3). Numerous theories have been advanced to account for the phenomena (6). Two general processes are possible at the anode; these are the solution of the metal as metallic ions or the discharge of anions. The principle theories of passivity are classified depending on which possibility above is considered the major electrode reaction.

First to be considered are the two principle anion discharge theories.

1. When a metal dips into an electrolyte, the following reaction tends to occur:

$$\text{(a) } M^O + 2H^+ \longrightarrow M^{++} + 2H^O \text{ (in the metal)}$$
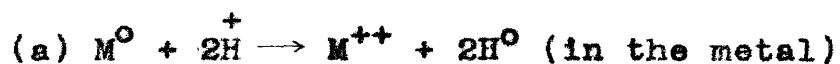
If the metal is very base or the H^+ ion concentration high, the accumulation of H^O in the metal leads to the reaction $2H^O \rightarrow H_2^O$ and may result in the evolution of hydrogen gas and solution of the metal. However, if the metal has a high hydrogen overvoltage or is relatively noble, an equilibrium

$$(b) \quad M^O + 2H^+ \rightarrow M^{++} + 2H^O \quad \text{(in the metal)}$$

may be established before the H^O concentration becomes sufficiently great to cause hydrogen evolution. If the metal is made the anode, the hydrogen may be removed by reaction with some non-metal resulting from anion discharge. Thus, if oxygen is liberated the hydrogen will be removed by the reaction

$$(c) \quad 2H^O + \tfrac{1}{2}O_2^O \rightarrow H_2O$$

Hence, by removing the hydrogen, equilibrium (b) shifts to the right and the metal dissolves continuously. If (c) occurs slowly hydrogen will accumulate at the anode, whose potential will become more positive, anodic polarization occurs and solution of the metal is prevented. Metals which easily become passivated are poor catalyzers for reaction (c).

2. Discharge of oxygen may occur at the anode because of the reaction $2\overline{OH} - 2(-) \rightarrow H_2O + O$. A solid solution of O^O in the surface layers of the metal or a definite oxide may be formed . Either may dissolve chemically in

the electrolyte.

(d) $MO + 2H^+ \longrightarrow M^{++} + H_2O$

If the reaction velocity of (d) is slow, oxygen accumulates to form either of the possible complexes, the potential becomes increasingly positive and solution occurs with difficulty.

These are several theories of passivity polarization which postulate that the primary anode reaction is the solution of the metal. The most important of these are:

1. LeBlanc (6) considers that an ion is electromotively active when it is not hydrated. In any electrolyte the equilibrium exists as follows:

(e) $M^{++} + nH_2O \longrightarrow M^{++} \cdot nH_2O$
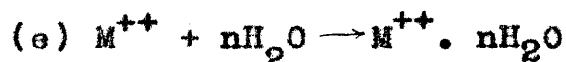
The anodic solution of the metal gives rise to unhydrated molecules which may become hydrated. If the hydration is slow, as believed for passive metals, there will be an accumulation of unhydrated metal ions near the anode. From this LeBlanc concluded that the cause of passivity must be in the solution and not in the anode. However, this explanation seems untrue because the passive condition is not removed by transferring the anode to a new solution. The cause of passivity must then lie in the metal.

2. In other theories of this class it is assumed

that anion discharge occurs to some extent along with
the direct metal ionization process (6). The ionization
of the anode

$$(f) \quad M - 2(-) \rightarrow M^{++}$$

is generally believed to occur rapidly. It has been
suggested that in the case of easily passivated metals,
this reaction is very slow. At one time it was thought
that dissolved H catalyzed this reaction. Its removal
caused passivity of the metal. However, active iron
remains active after all the hydrogen is removed.

Schmit (6) contends that metals showing
considerable passivity are exceptionally hard and therefore
probably possess abnormally high surface tension.
Activation may be aided if the metal surface is broken
down, either by chemical corrosion, gas evolution, or
mechanical roughening.

3. Metal and oxygen discharge may occur simultaneously.
Foerster believes that the oxygen (or oxides) so produced
inhibit reaction (f) and anodic polarization occurs.

4. Finkelstein (1) put forward the theory that metals
which assume the passive state are alloys of metals of
different valences, and that in the active state the metal
of lower valence predominates. If the equilibrium is
displaced in the direction of the ions of the higher
valence, the anode becomes more positive and hence more
passive.

5.   Smits (1) ,(6) developed a theory of passivity
based upon his theory of allotropy, which postulates
that in the metal there is an equilibrium between atoms,
ions and electrons.

$$M \rightarrow M^{++} + 2(-)$$

Hence, if this equilibrium is disturbed "so that the
metal is converted into a less active state, which under
the influence of a negative catalyst may persist for
some time, the term passivity is usually employed".
Oxygen is considered an inhibitor.   The advantage of
this theory over Finkelstein's is that it is unnecessary
to assume different species of ions.

These are the theories of anodic passivation
but the phenomena requires further elucidation.

The decomposition voltage of an electrolyte varies
with the nature of the electrodes used.   Since hydrogen
ions are present in any aqueous solution they may be
discharged along with, or in preference to, metallic ions.
Different voltages are required to discharge hydrogen from
different metal cathodes, a voltage of + 0.78 being necessary
for mercury and + 0.23 for copper (referred to platinized
platinum as standard with an overvoltage of zero) (6).   This
kind of polarization is called overvoltage.

Overvoltage may be defined as the difference between
the equilibrium potential

in a solution and the potential actually required for the discharge of the cation. Because of the high hydrogen overvoltage on some metals, it is possible to discharge those metal ions at a cathode with no evolution of hydrogen, even though the metal is considerably above hydrogen in the electromotive series.

Many factors influence overvoltage (6). Among these, the most important are the condition of the electrode surface and the time for which the current has been flowing. The rougher the electrode surface, the lower the overvoltage. Since overvoltage increases with rising current density, this may probably be explained by a lower current density, due to increased surface area. Also, as electrolysis proceeds at constant current density, the overvoltage gradually rises to a maximum corresponding to this current density and then falls off slightly, probably due to a roughening of the cathode surface. The time required for the attainment of this maximum varies with different metal electrodes. Further, an increase in temperature reduces the hydrogen overvoltage and favors evolution of the gas. Addition of colloidal substances to the electrolyte causes an increase in hydrogen overvoltage. A high metal ion concentration favors metal deposition.

The most generally accepted theory of hydrogen overvoltage is that of reaction velocity. It may be

developed as follows:(6) Hydrogen at atmospheric pressure
dissolves to a detectable amount in most metals to form
some kind of an alloy. It is only when so dissolved that
hydrogen is electromotively active. It is, therefore,
assumed that the dissolved hydrogen exists in some
particularly active form, probably monatomic hydrogen.
Cathodic evolution of hydrogen may be regarded as comprising
two processes:

(a) The primary electrochemical process

$$H^+ + (1-) \rightarrow H^O \text{ (dissolved in the metal)}$$

which tends to accumulate monatomic hydrogen at the cathode
surface and make its potential increasingly negative.

(b) A compensating process which tends to remove
monatomic hydrogen and thereby prevent the potential
becoming more negative. This process may include the
following stages:

1. The reaction $2H \rightarrow H_2^O$ may occur at the electrode
surface or within the surface layers. Two steps may here
be involved; the formation of a metallic hydride by a
reaction as $M + 2H^O \rightarrow MH_2$ and its subsequent decomposition
to give molecular hydrogen. The supposition is supported
by the detection of stibine in hydrogen evolved at an
antimony cathode.

2. The hydrogen so produced in the surface layer must
escape to the surface against the forces which tend to
retain it within the crystal lattice of the metal. Newberry

found that after hydrogen evolution has occurred at a polished electrode minute craters could be seen at the surface, indicating that hydrogen under considerable pressure had accumulated to force a passage through the surface.

3. When hydrogen reaches the metal surface, work must be done against surface forces in order to form gas bubbles sufficiently large to escape.

The velocity of the whole compensating process (b) will be that of the slowest of these stages. In general process (b) will be slower than the discharge of hydrogen (a) and monatomic hydrogen will accumulate until the rates are equal. This steady state corresponds to a definite hydrogen concentration at the cathode surface and therefore to a definite cathode potential and overvoltage.

Most of the theories of overvoltage are included in the above general reaction velocity theory. The differences between them lie in attributing the overvoltage to different stages of the compensating process.

It is usually advantageous in electrodeposition to keep the polarization as low as possible, because of the increased voltage required in solutions of high polarization (1). Also, if the polarization becomes sufficiently high, secondary electrode reactions may occur. One of the simplest methods by which polarization may be reduced is by stirring the electrolyte. Local concentration changes around the

electrodes are thereby avoided. This action is probably due to an increase in both the rate of diffusion and the velocity of any chemical reactions occurring. A rise in temperature opposes polarization, if it is due to local concentration changes.

Frequently it is desirable to increase the polarization of an electrolyte (1). This may be done by increasing the current density, but often this results in an undesirable condition of the deposit. Also, there may be produced secondary reactions such as discharge of ions of another type. Therefore, polarization is usually increased by other methods, including the addition of substances like glue, gelatin, and gum arabic. Their action is probably due to an increase in viscosity of the solution, thereby decreasing the rate of ionic migration. These colloidal agents cause smoother and finer deposits. Polarization may also be increased by use of complex ions. These reduce the metal ion concentration and increase polarization because the velocity of the compensating reaction is not great enough to replace the ions removed. When complex ions are used, finer deposits are obtained, since the low metal ion concentration prevents the formation of large crystals.

REVIEW OF LITERATURE

There is very little information concerning
the electrolytic deposition of mercury in the literature.
Smith (7), Treadwell-Hall (8), and Scott (9) state that
mercury can be deposited from neutral or slightly acid
solutions of mercuric or mercurous salts with a current
of .05 - .1 ampere (although higher currents may be
used). The first two authors recommend also a solution
of the double cyanide of mercury and potassium, containing
caustic alkali. A platinum gauze or a platinum dish is
suggested as the cathode. This research showed the first
to be valueless for quantitative determinations, since
even small deposits would not remain on the electrode
during washing (10).

The deposit is washed with water, then alcohol
and the adhering alcohol removed with filter paper.
However, Smith does not advise the use of alcohol,
because it removes a film of mercury. Further drying
was carried out by placing the samples in a dessicator
containing fused potassium hydroxide or concentrated
sulfuric acid and a small dish of mercury. Investigations
in this research showed these recommendations to be
unreliable (10). There was a continuous loss in weight

of the sample. The explanation is that mercury has an appreciable vapor pressure and seems to be absorbed in the drying agent.

Attempts to use the chloride or nitrate salts of mercury as a coulometer electrolyte were unsuccessful, polarization occurring readily (10).

A mercury volume coulometer has been devised by Wright. It is useful for rapid measurements of current and is arranged so that it can be reset by inverting. By means of a series of shunts this coulometer may be used for all possible current strengths. Its accuracy is $\pm$ 1%, although the amperage may vary from 10 to 150 percent of the rated value.

Since 1930, several methods involving electrolytic deposition of mercury as tests for small quantities have been published (11). The mercury is determined by the increase in weight of a copper or gold cathode. If extremely small quantities are to be determined, the deposit is either distilled into a capillary and the size of the globule measured under a microscope or examined spectroscopically (13).

DISCUSSION OF THE MERCURY WEIGHT COULOMETER

The apparent advantages of a mercury weight coulometer may now be considered.

They may first be discussed from a consideration of Faraday's Laws: (1) for the same electrolyte, the amount of electrolysis is proportional to the quantity of electricity which passes, and (2) the amounts of substances liberated at the electrodes, when the same quantity of electricity passes through solutions of different electrolytes, are proportional to their chemical equivalents.

Hence, a certain definite quantity of electricity will cause to be separated one gram equivalent weight of any element. As a result of many and varied researches, a mean value has been chosen for that current. It is called the faraday and has the value 96,500 coulombs. The unit of electricity is the coulomb and defines the strength of the current flowing and the time of flow.

$$Q = I \times t = \text{coulombs.}$$

The number of grams of an element or group of elements set free by the passage of one coulomb through an electrolytic conductor is called the electrochemical equivalent. From the faradgy and the chemical equivalent

of the element the electrochemical equivalent may be
calculated for that element. Thus, one coulomb will
deposit 0.0003924 grams of divalent copper, 0.001118
grams of silver, and 0.0010395 grams of divalent
mercury.

Therefore, for the same current, deposits of
mercury will be 3.1555 times as heavy as copper and
0.9298 times as heavy as silver. By comparing mercury
to copper, it is seen that errors introduced by weighing
are decreased one-third by use of the former, and per-
centage deviations from theoretical values are equally
reduced because of the heavier deposit. A comparison of
mercury to silver shows these two factors to be increased
by only one-tenth if mercury is used in preference to
silver. Hence, actual deposits, obtained electrolytically
from the respective coulometer solutions, and theoretical
quantities should agree more closely for mercury than for
copper and only slightly less so for mercury than for
silver. Thus, it seems that a mercury weight coulometer
would permit a more precise measurement of current than a
copper coulometer and the former would compare closely in
precision to a silver voltameter.

A consideration of polarization effects should
reveal an advantage of mercuric ion deposition over that
of silver or cupric ions. The mercuric ion is heavier
than either and it is believed that natural stirring due

to continued removal and replacement of the ion would be
more appreciable. The concentration of the electrolyte
should, therefore, be kept more uniform and diminish
possibilities of polarization caused by concentration
differences around the electrodes.

The value of the hydrogen overvoltage of mercury
is greater than that for either copper or silver and this
property is a distinct advantage in coulometer practice.
The hydrogen overvoltage for silver is + 0.15, for copper
+ 0.23, and for mercury + 0.78 (5). Therefore, the
possibility of the liberation of hydrogen at the cathode
and its subsequent accumulation to cause polarization is
considerably less for mercury than for the others. Further-
more, a current efficiency of a hundred/is more easily
realized.

The electrolyte suggested for use in the coulometer
studied in this problem has a small hydrogen ion concentra-
tion. Hence, anodic solution of mercury should not be
hindered because anodic polarization or passivity should be
practically negligible. This conclusion is reached from a
consideration of the anion discharge theories of passivity.
Also, since the hydroxyl ion concentration is low, passivity
of the anode due to liberation of oxygen and the consequent
formation of a metal oxygen complex is small.

With a realization of these factors, it is obvious
that the potential and resistance of the coulometer itself

would be small, and the external potential required for a passage of current would also be small.

The coulometer proposed in this paper may be pictured:

$$\text{Hg} \ \bigg| \ \begin{matrix} \text{KHgI}_3 \\ \text{KI} \\ \text{H}_2\text{O} \end{matrix} \ \bigg| \ \text{Hg}$$

The various ions in the electrolyte are: K^+, Hg^{++}, H^+, $\bar{I}$, $\bar{OH}$, $Hg\bar{I}_3$. The following reactions may occur:

A. At the cathode

    1. $K^+ + 1(-) \longrightarrow K^0$

    2. $H^+ + 1(-) \longrightarrow H^0$

    3. $Hg^{++} + 2(-) \longrightarrow Hg^0$

B. At the anode

    1. $\bar{I} - 1(-) \longrightarrow \frac{1}{2}I^0$

    2. $\bar{OH} - 1(-) \longrightarrow \frac{1}{2}O_2^0 + \frac{1}{2}H_2^0$

    3. $Hg^0 - 2(-) \longrightarrow Hg^{++}$

The electrical conductance of the solution is due to the ions of the electrolyte together with the ions of water, but at the electrode that process occurs which involves the expenditure of the minimum amount of energy (14). Thus is explained the evolution of H_2 by the electrolysis of a solution of potassium sulfate by a current of moderate strength. The K^+ may take on an electron and then react with water as indicated by the equation

$$K^0 + H^+ + \bar{OH} \longrightarrow K^+ + \bar{OH} + H^0$$
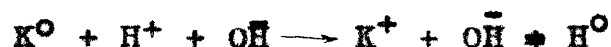
This is the so-called "secondary action" explanation and involves the transfer of an electron from K^o to H^+. This can happen only if the H^+ has a greater attraction for electrons than does K^+. Hence, if this is true, H^+ will be discharged primarily at the cathode. Hence, reaction A3 only occurs at low current density.

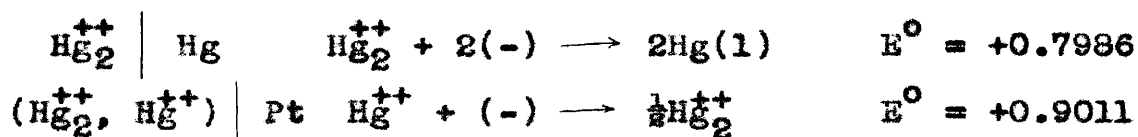Freudenberg (14) was the first to recognize the possibility of effecting the quantitative separation of different metals by means of graded electromotive forces. He showed that it was only necessary to select a salt of each metal, whose decomposition potentials differ as widely as possible, and electrolyze at an electromotive force intermediate between these potentials. The salt having the lower decomposition potential will decompose first. When deposition is complete, the current will practically cease flowing. However, if the external potential is raised above the decomposition of the second salt, the second metal will be deposited.

These principles apply to the electrolyte above. The separation potential of K^+ is -2.92 volts, the reduction potential of Hg^{++} to Hg_2^{++} is + 0.9011 volts and of Hg_2^{++} to $Hg(l)$ is + 0.7986 volts (14). The separation potential of $\bar{I}$ is + 0.52 and of $O\bar{H}$ (in base) + 0.88. Hence, mercuric mercury will be reduced to the atomic state before K^+ will be discharged. The high hydrogen overvoltage prevents the

liberation of hydrogen and therefore reaction A3 is the only one occurring at the cathode. The potential necessary for the oxidation of the anode mercury is less than that required for discharge of either Br^- or OH^- ions. Therefore, reaction B3 occurs at the anode. The ion HgI_3^- may be attracted to the anode but it apparently is not discharged.

Mercuric ion in the presence of atomic mercury is reduced to the mercurous state. The equilibrium ratio was calculated from the potential of the half cells:

$$Hg_2^{++} \mid Hg \qquad Hg_2^{++} + 2(-) \longrightarrow 2Hg(l) \qquad E^O = +0.7986$$

$$(Hg_2^{++}, Hg^{++}) \mid Pt \qquad Hg^{++} + (-) \longrightarrow \tfrac{1}{2}Hg_2^{++} \qquad E^O = +0.9011$$

The E.M.F. of the cell $Hg \mid Hg_2^{++} \parallel (Hg_2^{++}, Hg^{++}) \mid Pt$ is $E^O = E_1^O + E_r^O$.

$$E^O = -0.7986 + 0.9011 = +0.1025 \text{ volts.}$$

The reaction occurring is $Hg^{++} + Hg^O \longrightarrow Hg_2^{++}$ and the equilibrium ratio is

$$\frac{a_{Hg_2^{++}}}{a_{Hg^{++}}} = K.$$

However, $E^O = \dfrac{RT}{nF} \ln K$ and substituting

$$0.1025 = .05915 \log K \text{ and } K = 54.08 \text{ at } 25^O C.$$

This value of K indicates that the concentration of the mercurous ion must be 54 times that of the mercuric ion for equilibrium to be established between those ions. In the electrolyte, the following equilibria exists.

$$HgI_3^- \rightleftharpoons Hg^{++} + 3I^- \qquad (1)$$

$$2Hg^{++} + 2(-) \rightleftharpoons Hg_2^{++} \qquad (2)$$

$$Hg_2^{++} + 2(-) \rightleftharpoons 2Hg^0(l) \qquad (3)$$

$$Hg^{++} + Hg^0 \rightleftharpoons Hg_2^{++} \qquad (4)$$
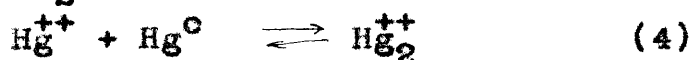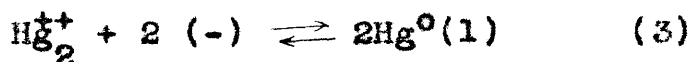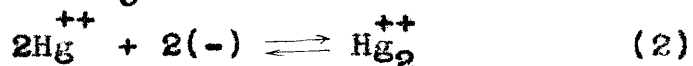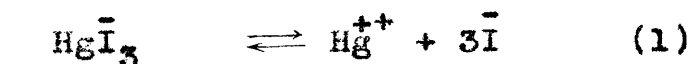
When equilibrium is established and maintained between these four the passage of a faraday will discharge one equivalent of mercuric ion. It is sometimes found that electrodepositions do not occur in accordance with Faraday's Laws. These deviations are not due to a failure of the laws but to the following causes:

1. The separation of more than one substance at either electrode and not taken into account.

2. The mechanical loss of the products of electrolysis.

3. The occurrence of secondary reactions of the electrodes.

4. Current leaks and short circuits.

Applying the third factor to this research, it is seen that if the equilibria between 2,3, and 4 is not reached, deposition of mercury will be low because part of the current will be utilized to increase the mercurous ion concentration. If the equilibrium is disturbed in favor of the mercuric ion, the deposition of mercury will be greater than theoretical until equilibrium conditions are restored.

DESCRIPTION OF THE COULOMETER

The mercury weight coulometer is an extremely simple piece of apparatus. As the anode, a platinum wire electrode, sealed in glass, is suspended in a glass "saddle" to the bottom of a beaker and completely covered with mercury. The size of the beaker, as discussed under the experimental work, is dependent upon the weight of mercury to be deposited. This is, of course, dependent on the current density employed and the duration of the run. For small current densities and for short runs a 150 cc. beaker is suitable. The cathode is a weighed amount of mercury contained in a shallow weighing bottle (Parr type), in which is suspended a platinum electrode. The beaker is then filled with the electrolyte.

DESCRIPTION OF MATERIALS

The electrodes:

The electrodes must necessarily be unattackable.
Strips of clean platinum wire, sealed in soft glass
tubing, and covered by mercury serve as both the anode
and cathode.

The Mercury:

As stated above, the electrodes of platinum wire
are submerged in pure mercury. The metal used was care-
fully purified by a method described by Hulett and
Minchein.

The mercury is finely divided and is permitted
to fall through a column containing .1N mercurous nitrate
and .1N nitric acid to remove the principle impurities
of contaminating base metals. It is then distilled under
vacuum in a current of air. A high degree of purity is
obtained.

The electrolyte:

Under certain conditions, described under experimental
work, the electrolyte employed by Wright in his mercury
volume coulometer is used. It is an aqueous solution of
225 grams HgI_2 and 750 grams KI per liter. In order to
prolong the life of the weight coulometer, it was found
necessary to saturate the electrolyte with KI, which seems
to act as a depolarizer.

The exact formula of the salt in solution is uncertain (12),(15). Many compounds have been suggested, including a solution of potassium tetraiodomercuriate, one of potassium iodide in potassium tri iodomercuriate, and a solution of a double salt of mercuric and potassium iodides, having the formula $HgI_2.2KI.2H_2O$. Many investigators show that the second one is the most likely, especially between $20^{\circ}C$ and $30^{\circ}C$, between which temperatures phase rule studies show the first unable to exist. Also liquid solid equilibria show that only one compound $HgI_2.KI.H_2O$ crystallizes from aqueous solution between $0^{\circ}C$ and $80^{\circ}C$. Other workers claim that if the component salts are present in aqueous solution in the ratio $HgI_2.2KI$, that crystals of the double salt $HgI_2.2KI.2H_2O$ are formed.

The facts are not very definite as to the formation of $2KI.HgI_2$ but the evidence for the existence of a solution or mixture of KI and $KHgI_3$ is very clear. According to the calculations, Page 29 , the concentration of the mercurous ion must be 54 times that of the mercuric ion for equilibrium to be established between those ions and at ionic mercury. It is likely, however that the high concentration of potassium iodide binds the Hg^{++} in the radical HgI_3^{-} so firmly that only a few Hg_2^{++} ions are necessary to establish equilibrium.

The electrolyte used in this research was prepared from C.P. chemicals, the mercuric iodide being made as directed by Biltz, Hall, and Blanchard (16).

OPERATION OF THE MERCURY WEIGHT COULOMETER

The set-up and procedure in using this coulometer
is recommended as follows:

A puddle of mercury sufficiently deep to cover
completely a platinum wire electrode is placed in a
250 c.c. beaker. For half-hour runs at a cathode
current density of .05 or .075 amps./sq.cm. or for
longer determinations at a C.D. of .005 amps./sq/cm.
a 150 c.c. beaker is suitable. In a Parr weighing
bottle a smaller puddle, deep enough to cover a platinum
wire electrode is weighed to the fourth place. The
weighing bottle is then suspended in the electrolyte.
The latter is the cathode, the former the anode.

After the run, the weighing bottle is removed
from the electrolyte, washed with KI solution, and
finally washed with distilled water by decantation. A
great portion of the water remaining after this process
may be removed with a 1 c.c. pipette. All but a
negligible quantity of water may be removed by touching
narrow strips of filter paper to the mercury and bottle.

The sample is then ready to be reweighed. The
increase in weight indicates the current that has passed

through the coulometer, since one coulomb causes a deposition of 0.0010395 grams of mercuric mercury.

An electrolyte, containing 225 grams of HgI_2 and 750 grams KI per liter, is suitable for half-hour runs at a current density of .075 - .05 amps./sq.cm. For longer runs, the coulometer solution must be saturated with KI. At a current density of .005 amps./ sq.cm. and slightly higher, the first solution may be used for determinations of much longer duration. The electrolyte may be used for runs totaling about five ampere hours, after which it yields low deposits of mercury.

APPARATUS

It is advisable to outline the method used in checking the coulometer. The source of current was a 6 volt storage battery. In the circuit was placed a standard tenth ohm resistance, capable of carrying 15 amperes, made by Leeds and Northrup, and guaranteed to $\frac{1}{25}$ %. The voltage drop across this resistance was measured by a Type K Potentiometer, manufactured by the same company. It was calibrated and voltages read could be reproduced to $\pm$ .01 millivolt. An Eppley Standard Cell, with an electromotive force of 1.01877 volts was used as a standard. The deflection of a Leeds and Northrup Type R Galvanometer was determined by means of a lamp and scale reading device manufactured by them.

The voltage drop was measured at frequent intervals. In tests of a half hour's duration, readings were taken every half minute and in those of a longer period, readings were taken every minute. The voltage would gradually fall and in order to determint I t quantities (or coulombs) the decreasing values of the amperage were plotted against seconds. The area under the curve was integrated with a Keuffel and Esser Planimeter and the corresponding coulombs thus obtained. These were added to the number of coulombs

obtained by multiplying the final reading of amperage by seconds. The total coulombs passed was therefore secured.

The duration of the passage of current for one, two, or three hour determinations was estimated by means of a watch calibrated against Arlington time signals. A stop-watch, calibrated against this watch was used for periods of one-half hour.

The weights used to determine the actual deposition mercury were calibrated by Richards' method.

DISCUSSION OF ERRORS

Calculations were made to determine if buoyancy corrections need be made on the weight of mercury deposited. It was found that for a deposit of two or three grams a correction of one-tenth milligram could be made. However, it was not applied because the correction was within the limits of experimental error. Experimentation showed that weighings of a given object could be reproduced to $\pm$ one-tenth milligram.

Also, calculations were made to ascertain the accuracy of the theoretical deposit obtained with the instruments employed. Model computations for low and high current densities are herein given.

$M = ZIt$ where M = theoretical deposit, Z = electrochemical, I = amperes, and t = time in seconds. The error in M is the summation of the errors in the measurement of Z, I, and t. It was calculated by the fractional method. The computations were made with a consideration of each possible error as represented:

$$M_{(\text{difference in wts.})} \begin{array}{l} = dZ \cdot d(IT) \\ = dZ \cdot dQ \end{array} \left\{ d(\text{planimeter}) \begin{array}{l} dI \\ dt \end{array} \left\{ \begin{array}{l} \dfrac{dv}{dR} \\ \text{curve} \\ \text{plotting} \end{array} \right. \right.$$

The computation of the error in M, due to these factors for a determination at a current density of .0025

amps./sq.cm. for the duration of an hour is as follows.

The voltage was 0.001 v and the potentiometer reading is good to $\pm$ 0.00001 v. Hence, the fractional error of the voltage reading, or $\frac{dv}{v}$ is $\frac{.001}{.00001}$ or 0.01.

The resistance was 0.1 ohm and is good to $\pm$ 0.00004 ohms. Hence, $\frac{dR}{R} = \frac{.00004}{.1} = 0.0004$ ohms.

The error in amperes, or $\frac{dI}{I}$, results from a summation of these.

$$\frac{dI}{I} = \sqrt{\left(\frac{dv}{v}\right)^2 + \left(\frac{dR}{R}\right)^2}$$

$$= \sqrt{(.01)^2 + (.0004)^2} = .01$$

Now, the fractional error of Q is obtainable from the errors in I and t. The time was measured with a calibrated watch. The largest correction necessary to apply over a twelve hour period was ten seconds. Thus, a ten second change occurs in 43200 seconds or an error of $\frac{10}{43,200} = .023\%$ in 12 hours. The determination was for an hour and the error is, therefore, 3600 secs. x .023% = .8 sec./hr. Assuming a maximum discrepancy of 0.2 second in starting and stopping the run, the time estimation is good to $\pm$ 1.0 sec. or t = 3600 $\pm$ 1.0 secs.

The fractional error of Q , or

$$\frac{dQ}{Q} = \sqrt{\left(\frac{dI}{I}\right)^2 + \left(\frac{dt}{t}\right)^2}$$

$$= \sqrt{(.01)^2 + \left(\frac{1}{3600}\right)^2} = \sqrt{(.01)^2 + (.0003)^2} = .01$$

No fall in the voltage at this current density was discernible. Therefore, it was unnecessary to plot I against t and consequently the planimeter was not used.

is obtained from the atomic weight of the element, the valence, and the faraday, or

$$Z = \frac{at.wt.}{2 \times F} = \frac{200.6}{2 \times 96500} = 0.0010395 \text{ grams.}$$

The atomic weight is good to four significant figures and therefore is likewise good to the fourth significant figure. However, since the faraday is an average value, maximum error of one in the fourth figure is assumed as possible. Then $\dfrac{dZ}{Z} = \dfrac{1}{10395} = .00009$

The fractional error of M may now be ascertained since

$$\frac{dM}{M} = \sqrt{\frac{dZ}{Z}^2 + \frac{dQ}{Q}^2}$$

$$= \sqrt{(.009)^2 + (.01)^2} = .01\%$$

Therefore, if the calculated M is 0.0380 grams, the error is $0.0380 \pm 0.0380 \times .01\%$, or $M = .0380 \pm 0.0000$. It is to be concluded, then, that the calculated M (or theoretical deposit) for an hour's determination with a current density of 0.0025 amps./sq.cms. is the exact value, no error being introduced by the instruments used.

The longest run was made at a current density of .05 amps./sq/cm. for three hours. The deposit obtained is 2.0

grams. The computation of the maximum error expected
is given. It follows the method above and a discussion
is omitted unless new factors are considered.

$$V = .02700 \pm .00001 \qquad R = .1 \pm 0.00004 \text{ ohms}$$

$$\frac{dV}{V} = \frac{.00001}{.027} = .0004 \qquad \frac{dR}{R} = \frac{.00004}{.1} = .0004$$

$$\text{Therefore} \quad \frac{dI}{I} = \sqrt{\left(\frac{dv}{v}\right)^2 + \left(\frac{dR}{R}\right)^2}$$

$$= \sqrt{(.0004)^2 + (.0004)^2} = .0006$$

- The duration is now 10800 seconds, the error as
above .023% and .2 seconds is again assumed as an error
introduced in starting and stopping the determination.
Then $T = 10800 \pm 2.6$ secs.

$$\frac{dT}{T} = \frac{2.6}{10800} = .0002$$

Again,

$$\frac{d\,Q}{Q} = \sqrt{\left(\frac{dI}{I}\right)^2 + \left(\frac{dT}{T}\right)^2}$$

$$= \sqrt{(.0006)^2 + (0.0002)^2} = .0006$$

At the current density above mentioned, the current
density falls slowly and to obtain the total coulombs
passed, I must be plotted against t, and the area integrated

with a planimeter.

Therefore, $\dfrac{dQ}{Q} = \sqrt{\left(\dfrac{dQ}{Q}\right)^2 + d(\text{planimeter})^2}$

The coulombs obtained by use of the planimeter are 45.6 while those calculated by I x t alone are 1878.99 (0.178 x 10798.8 for this run). The reading on the planimeter is 4.000 and can be reproduced to no greater than 3 in the third decimal (0.003). The fractional error is $\dfrac{.003}{4.0} = .07\%$. This error affects the second decimal in the coulombs calculated from the planimeter integration and is negligible in respect to the much larger number, the error $\dfrac{dQ}{Q}$ of which was computed above.

$$\frac{dQ}{Q} = .0006$$

and $\dfrac{dM}{M} = \sqrt{\left(\dfrac{dZ}{Z}\right)^2 + \left(\dfrac{dQ}{Q}\right)^2}$

$= \sqrt{(0.009)^2 + (0.0006)^2} = .009\%$

Hence, if the calculated deposit (M) is 2.0 grams the maximum error is 2.0 x .009% or $M = 2.0000 \pm 0.0001$ grams. The instruments used introduce an error of a tenth of a milligram under the conditions current density and time considered in this calculation.

Thus, was calculated the maximum error expected to be introduced by the apparatus in the determinations described under experimental work.

EXPERIMENTAL WORK

Preliminary studies (10) were made to ascertain some method by which mercury could be deposited electrolytically in a collectable form at a high current efficiency. Neither a platinum wire nor a platinum gauze was found suitable as a cathode because gaseous evolution occurred (10). A test tube shaped cathode containing a weighed amount of mercury was then employed. Gaseous evolution was stopped but transfer of the mercury to a tared container was accompanied by splashing and a loss of the element. The construction of the cathode as previously described and recommended was then conceived.

Simultaneously with these tests, others were performed to investigate the best method of drying (10). After a run the cathode mercury was washed well by decantation, and then poured into a shallow dish, where as much water as possible was removed by absorption with filter paper. These samples were weighed and placed in an evacuated dessicator containing concentrated sulfuric acid. No consistent results could be obtained and the method was abandoned. Compressed filter cups were then used but again a transfer of mercury from one container to another was necessary. Loss resulted and the method discontinued.

A review of drying data showed that in almost
every instance all but a few tenths of a milligram of
water had been removed by absorption with strips of
filter paper. Therefore, quantitative studies were made
on the method (10). Differences between the original
weight and the weight after wetting and subsequent drying
with filter paper were reduced to a negligible figure,
which could easily be attributed to an inability to
reproduce a given weight.

At the same time, studies were made to determine
the most suitable electrolyte. Solutions of 0.1 N
mercurous salts in 0.1 N HNO_3 were first used. These
gave low deposits and polarized at the anode readily.
The electrolyte used by Wright in the mercury volume
coulometer was then employed and was found to permit a
satisfactory separation of mercury.

In the preliminary research on the mercury weight
coulometer, the copper coulometer was used to determine
the theoretical current passed. Two copper and two mercury
coulometers were in series in the circuit. The deposits
of copper varied by an average error of .5% and those of
mercury by an average error of .2% (10). Hence, the
precision of the mercury coulometer could not be shown
because of the unreliability of the measurement of the
theoretical number of coulombs passed through the circuit.

The present investigation of the reliability of the mercury weight coulometer consists of a review of the drying method, the establishment of current density limits, temperature studies and maximum time interval observations.

To ascertain the efficiency of the drying method, nineteen samples of mercury were wetted and dried and weighed before and after. The results are:

Tests of Drying of Mercury

	Before Wetting	After Wetting		Before Wetting	After Wetting
1.	47.5808	47.5807	11.	41.5897	41.5898
2.	55.2947	55.2947	12.	51.6423	51.6423
3.	43.3324	43.3323	13.	47.0199	47.0200
4.	48.0506	48.0506	14.	48.0978	48.0978
5.	42.8541	42.8541	15.	47.0927	47.0926
6.	62.0091	62.0089	16.	54.8973	54.8973
7.	49.8780	49.8780	17.	56.3062	56.3062
8.	48.6097	48.6097	18.	51.8729	51.8729
9.	48.7162	48.7162	19.	50.5221	50.5221
10.	49.0979	49.0980			

These experiments show that twelve original and dried weights check exactly, while three dried weights were 0.1 mg. less, one 0.2 mg. less, and three 0.1 mg. more than the original weight. It is concluded then that all but a negligible amount of water can be removed by narrow strips of filter paper.

Solubility tests showed that the cathode mercury should not stand too long in contact with the electrolyte,

unless a current is following. Four tests showed 1.1 mgrms. of mercury to be dissolved in 24 hours.

Removal of the electrolyte by washing with water causes a gray adherent film to form on the mercury. This can be prevented by pipetting off as much electrolyte as possible and washing with two portions of KI solution, which is also pipetted off. The mercury may now be washed by decantation with water. The film does not appear.

The first tests on the reliability of the mercury weight coulometer were performed at a current density of .05 amp./sq.cm. at 25°C for one half hour. Approximately 178 milliamps. flowed through the coulometer; a 150 c.c. beaker was used. Table I shows the results.

TABLE I

	Theoretical Deposit (gms.Hg)	Actual Deposit (Gms. Hg)		% Diff.of Actual	% Diff.of theoretical and Av.
		(1)	(2)		
1.	0.3300	0.3299	0.3300	0.03	0.01
2.	0.3249	0.3252	0.3249	0.09	0.04
3.	0.3265	0.3264	0.3265	0.030	0.01
4.	0.3378	0.3376	0.3378	0.05	0.02
5.	0.3396	0.3395	0.3597	0.05	0.000
6.	0.3373	0.3371	0.3371	0.05	0.05
7.	0.3324	0.3324	0.3328	0.00	0.05
8.	0.3256	0.3228	0.3230	0.12	0.060
9.	0.3385	0.3385	0.3385	0.05	-a-
10.	0.3368	0.3385	0.3385	0.000	0.000
11.	0.3347	0.3364	0.3367	0.08	0.07
12.	0.3345	0.3348	0.3346	0.05	0.000
13.	0.3322	0.3344	0.3347	0.08	0.01
14.	0.3329	0.3325	0.3322	0.090	0.04
15.	0.3353	0.3331	0.3331	0.000	0.06
16.	0.3516	0.3354	0.3354	0.0	0.02
17.	0.3339	0.3315	0.3317	0.030	0.02
			0.3339	0.0	0.00
			Av.	0.04	0.02%

Note a

The next cell polarized at anode in 20 minutes. The electrolyte had been used for five consecutive runs without stirring between determinations. Thus, concentration differences were set up. Possibilities of these occurring were reduced in subsequent runs by thorough stirring before the circuit was closed.

Under these conditions no effective instrumental error is introduced and the error in the theoretical $M = 0.3350 \pm 0.00003$ gms. Hence, the calculated deposit may be considered the precise amount. The average deposit from two mercury weight coulometers in series under these conditions has an accuracy of 0.02%. The absolute error introduced by weighing is 0.03%, and no single run can, therefore, be more accurate than this value.

An attempted run at a current density of 0.1 amp./sq.cm. resulted in anodic polarization in twenty minutes. Consequently no quantitative determinations were made.

However, at a current density of 0.075 amp./sq.cm. the life of the cell was 49 minutes. Tests were performed to obtain the reliability at this current strength at 25°C. The amperage was approximately 265 milliamps. and results are shown in Table II.

TABLE II

Theoretical Deposit (gms. Hg)		Actual Deposit (Gms Hg)		% Diff.of Actual	% Diff.of theoretical and Average
		(1)	(2)		
1.	0.5022	0.5023	0.5023	0.0	0.02
2.	0.4819	0.4820	0.4821	0.02	0.03
3.	0.5319	0.5321	0.5324	0.05	0.06
4.	0.5072	0.5072	0.5075	0.06	0.02
5.	0.5058	0.5057	0.5057	0.0	0.02
6.	0.5046	0.5047	0.5049	0.04	0.03
7.	0.5023	0.5024	0.5021	0.06	0.01
8.	0.5062	0.5065	0.5062	0.06	0.03
9.	0.4970	0.4970	0.4972	0.03	0.02
10.	0.4999	0.4998	0.5001	0.06	0.01
				Av.0.04	0.02

The instrumental error in this instance is effective
in the fifth decimal only. Therefore, the theoretical
value of the deposition may be considered exact and the
average error shown by two mercury coulometers is .02%.
The error is weighing a mass of 0.5 gms. is .02%. Therefore,
the accuracy of a single determination is equal to that of
the weighing operation.

In an effort to establish the lower limit of the
current density range, measurements were made at current
densities of .005 amps./sq.cm. and .0025 amp./sq.cms. The
results are tabulated in Tables III, IV, and V.

TABLE III

C.D. .005 amps./sq.cm.　17.59 M.A.　Time ½ hr.　25°C.

	Theoretical Deposit	Actual Deposit (1)	Actual Deposit (2)	% Diff. of Actual	% Diff. of Theoretical and Average
1.	0.0382	0.0381	0.0381	0.0	.26
2.	0.0366	0.0367	0.0367	0.0	.27
3.	0.0344	0.0341	0.0342	0.29	.72
4.	0.0344	0.0343	0.0346	0.89	.14
5.	0.0344	0.0340	0.0342	0.58	.86
6.	0.0345	0.0344	0.0345	0.29	.14
7.	0.0345	0.0346	-	-	.28
8.	0.0346	0.0345	0.0344	0.29	.43
9.	0.0345	0.0344	0.0343	0.29	.43
10.	0.0344	0.0343	0.0341	0.58	.58
			Av.	.35	.41

TABLE IV

C.D. .0025 amps./sq.cm.　8.8 M.A.　Time 1 hr.　25°C.

	Theoretical Deposit	Actual Deposit (1)	Actual Deposit (2)	% Diff. of Actual	% Diff. of Theoretical and Average
1.	0.0382	0.0379	0.0378	0.26	0.91
2.	0.0395	0.0393	0.0396	0.75	0.51
3.	0.0382	0.0379	0.0378	0.26	0.91
4.	0.0382	0.0380	0.0381	0.26	0.39
5.	0.0377	-	0.0376	-	0.26 (a)
6.	0.0376	0.0377	0.0377	0.0	0.26
7.	0.0370	0.0366	0.0367	0.26	0.94
8.	0.0370	0.0367	0.0367	0.0	.81
			Av.	.26	.62

TABLE V

C.D.   .0025 amps./sq.cm.   8.8 M.A.   Time 3 hrs.   25°C.

	Theoretical Deposit	Actual Deposit		% Diff.of Actual	% Diff.of Theoretical and average
		(1)	(2)		
1.	0.1043	.1036	.1036	0	.67
2.	0.1043	.1035	.1038	.29	.62
3.	0.1043	.1035	.1036	.09	.71
4.	0.1043	.1034	.1032	.19	.95
5.	0.1043	.1030	.1034	.38	1.05
			Av.	.19	.80

The errors due to the apparatus are not sufficient
to affect the theoretical quantity of mercury deposited.
However, since the numbers are smaller than those represent-
ing deposits in Tables I and II, the percentage error in
Tables III, IV, and V is increased. The weighing error of
the deposits in III and IV is 0.29% and the percentage
difference of check determinations is comparable to this
figure. By prolonging the duration of the tests at C.D.
.0025 amps./sq.cm. the weighing error is reduced to .09%.
Table III shows a minus error of 0.41%, IV of 0.62%, and
V of 0.80%, when the actual deposit is compared with the
theoretical. This low deposit may possibly be explained
by realizing the reaction $Hg^{++} + 1^{(-)} \rightarrow Hg^{+}$ may occur in
preference to $Hg^{++} + 2^{(-)} \rightarrow Hg^{o}$.

A new solution was prepared at (a) because the writer thought that the solution may have become depleted and consequently yield low separations. Since the results with the new solution were in error as much as the previous one, the above explanation seems to be the more likely.

It might be concluded that the error in the coulometer at a C.D. of .005 amp./sq.cm. is 0.4% and at a C.D. of .0025 amps./sq.cm. is 0.8%, which deviations are increased as the duration of the run is prolonged.

Attention was now directed to the determination of the life of the coulometer at the current densities of .075 and .05 amps./sq.cm. At the first current density anodic polarization occurred after 49 minutes. The resulting precipitate would rapidly dissolve after the current was broken. A new solution was prepared and saturated with potassium iodide. The cell life was now one and one-quarter hours. Since it was desired to prevent polarization for at least three hours, mechanical stirrers driven by compressed air were suspended in the coulometer. The results obtained were not very satisfactory and are recorded in Table VI. In Tables VI and VII the coulometer solution is saturated with potassium iodide.

TABLE VI

C.D. .075 amps./sq.cm.   265 M.A.   Time 3 hrs. 25°C.

	Theoretical Deposit (Gms.Hg)	Actual Deposit (Gms. Hg)		% Diff.of Actual	% Diff.of Theoretical & Av.
		(1)	(2)		
1.	3.0582	3.0616	3.0620	0.013	0.11
2.	3.1244	3.1320	-	-	0.24
3.	3.1253	3.1251	3.1258	0.022	0.004
4.	3.0824	3.0821	3.0817	0.013	0.016
			Av.	0.016	0.09

Two other determinations were made prior to those recorded. They are omitted because the watch used stopped from mechanical faults a few hours after the second test. Expected error in weighings is 0.003% and the error incorporated by the instruments is 0.009%, the theoretical mass thus being affected in the fourth decimal. All actual errors are much larger than expected and the use of the coulometer as described herewith is not recommended, if a precision better than 0.1% is desired.

By increasing the anode area, thus decreasing the anodic current density, the coulometer life was two and a quarter hours. The studies performed with the cathode suspended in a 250 c.c. beaker are recorded in Table VII.

TABLE VII

C.D. .075 amps./sq.cm.   265 M.A.   Time 2 hrs.   25°C.

	Theoretical Deposit (Gms. Hg)	Actual Deposit (Gms. Hg)		% Diff.of Actual	% Diff. of Theoretical and Average
		(1)	(2)		
1.	1.8286	1.8281	-	-	0.027
2.	2.0229	2.0243	2.0234	0.004	0.044
3.	2.0105	2.0101	2.0099	0.009	0.024
4.	2.0448	2.0442	2.0448	0.029	0.014
5.	2.0229	2.0228	2.0229	0.004	0.052
6.	2.0123	2.0119	2.0120	0.004	0.017
				Av. .01	.03

The error of the apparatus is .01%. Therefore, referred against this error, the deviation of the coulometer at the specified conditions is .02%.

It was found that the life of the mercury weight coulometer could be prolonged to slightly more than three hours by using a current density of .05 amps./sq.cm. with Wright's electrolyte. Several runs were accordingly made and results slightly greater in error than expected were obtained. The electrolyte was then saturated with potassium iodide, and better agreement resulted.

TABLE VIII

C.D. .05 amps./sq.cm.   178 M.A.   Time 3 hrs. 25°C.

	Theoretical Deposit (Gms.Hg)	Actual Deposit (Gms. Hg)		% Diff.of Actual	% Diff.of Theoretical and Average
		(1)	(2)		
1.	2.0006	1.9998	1.9995	0.015	0.037
2.	1.9962	1.9967	1.9968	0.005	0.027
3.	1.9954	1.9948	1.9943	0.025	0.042
4.	1.9317	1.9317	1.9308	0.046	0.023
5.	2.0003	2.0001	2.0003	0.01	0.024
			Av.	.01	.03

Electrolyte Saturated with KI

6.	1.9728	1.9726	1.9727	0.005	0.0075
7.	2.0196	2.0200	2.0199	0.005	0.0170
8.	2.0122	2.0121	2.0122	0.005	0.0024
9.	1.9897	1.9893	1.9896	0.015	0.0120
			Av.	0.007	0.009

The difference between the theoretical and actual deposits is of the same value as that introduced by the apparatus, when the electrolyte is saturated with potassium iodide. However, the error referred to the absolute is approximately .02% when the normal coulometer solution is used. It is concluded then that an error .02% may be expected with the cathode suspended in a 250 c.c. beaker and that this error may be reduced to .009% by saturating the electrolyte with potassium iodide.

To study the effects of temperature on the coulometer, determinations were first made at $35^{\circ}C$ with the cell dimensions that of a 250 c.c. beaker and with the electrolyte saturated with potassium iodide.

TABLE IX

C.D. .075 amps./sq.cm.   265 M.A.   Time $\frac{1}{2}$ hr. $35^{\circ}C$.

Theoretical Deposit (Gms.Hg)	Actual Deposit (Gms. Hg)		% Diff.of Actual	% Diff.of Theoretical and Average
	(1)	(2)		
1. 0.5146	0.5135	0.5135	0.0	0.21
2. .5061	.5053	.5054	0.02	0.14
3. .5099	.5098	.5088	0.19	0.11
4. .5108	.5101	.5098	0.05	0.16
5. .5053	.5042	.5041	0.02	0.22
		Av.	.06	0.17

Electrolyte Without Extra KI

6. 0.5311	0.5308	0.5308	0.0 *	0.05 *
7. 0.5053	0.5053	0.5053	0.0 *	0.0 *
8. 0.5303	0.5302	0.5302	0.0 *	0.02 *
9. 0.5314	0.5311	0.5308	0.006	0.08
10. 0.5253	0.5248	0.5247	0.02	0.10
11. 0.5327	0.5320	0.5317	.05	0.15
		Av. 0.01		.06

New Electrolyte

12. 0.5223	0.5224	0.5220	0.07 *		0.02 *	
13. 0.5125	0.5124	0.5122	0.03 *		0.03 *	
14. 0.5079	0.5079	0.5082	0.05 *		0.03 *	
		Av.	0.05	0.02	.03	.02

TABLE X

Conditions same as Table IX, except Temp. 25°C.

	Theoretical Deposit (Gms. Hg.)	Actual Deposit (Gms. Hg)		% Diff.of Actual	% Diff.of Theoretical and Average
		(1)	(2)		
1.	0.5053	0.5025	0.5026	0.02	.54
2.	0.4448	0.4440	0.4440	0.00	.18
			Av. 0.01		0.36
	Electrolyte Without KI				
3.	0.5093	0.5090	0.5092	0.04	0.03
4.	0.5069	0.5066	0.5065	0.02	0.06
			Av. 0.03		0.05
	New Electrolyte				
5.	0.5137	0.5138	0.5139	0.02	0.03
6.	0.5052	0.5053	0.5049	0.07	0.02
			Av. 0.04		0.02
		Total Av.	0.03		

The results recorded in runs 1 - 5 in Table IX are
very erroneous, in that the instruments introduce no
error and the deviation is expected to be much smaller.
Two determinations (1 and 2, Table X) made at 25°C for
purposes of comparison showed the actual deposit to be
smaller than the theoretical as at 35°C. The electrolyte
had been used for at least six ampere hours and was thought
to be depleted of mercuric mercury.

There was then employed as electrolyte a portion
of the usual solution which had already been used. A
determination was made at 25°C (Table X 3) to ascertain
the condition of the electrolyte. The coulometer was
then tested at 35°C and three good results (IX 6,7,8)
were recorded. The deviations then rose rapidly and
the electrolyte was again tested at 25°C. The error
(X 4) was abnormal and a new electrolyte prepared.
Tests were then recorded at both 35°C (IX 12,13,14) and
25°C (X 5,6) and average deviations calculated. At 35°C
for tests 6,7,8,12,13,14 the actual deviates from the
theoretical by 0.02% and at 25°C tests 5 and 6 by 0.02%.
The deviations between the actual deposits and their
average from the theoretical are within the limits of
weighing. It is concluded that temperature has no effect.

Several tests have been made with the usual solution
diluted with an equal volume of water for runs of a half
hour. Deviations were of the same magnitude as those
obtained with the ordinary electrolyte. It is, however,
recommended that whole strength be used since conductivity
is much better. The data shows that care need not be taken to
adjust the concentration of the electrolyte.

CONCLUSIONS

The data obtained by actual experimentation supports the conclusions: (1) Current densities ranging from .075 to .005 amps./sq.cm. may be used. (2) For half-hour runs at C.D. from .075 - .05 amps./ sq.cm. the accuracy for a single determination is equal to that of the weighing operation. (3) If the electrolyte is saturated with KI, runs may be made at a C.D. of .075 amp./sq.cm. with an error of .02% and at a C.D. of .05 amps. for three hours with an error equal to that of the weighing operation. (4) The ordinary electrolyte may be used for longer periods at a C.D. of .005 amps./sq.cm. with an error of 0.4% and a C.D. of .0025 amps./sq.cms. of .8%. (6) Variations in room temperature have no effect.

RECOMMENDATIONS

The following recommendations for use of the mercury weight coulometer are made.

1. The electrolyte should be a solution of 225 grams of HgI_2 and 750 grams of KI per liter for determinations at a C.D. .075 - .05 for a half hour. The solution, if saturated with KI will prolong the life of the coulometer to at least an hour. If a 250 c.c. beaker is substituted for the 150 c.c. beaker, the cell life at a C.D. of .075 amps/sq.cm. is at least two and a quarter hours and at a C.D. of .05 amps./sq. cm.three hours. The coulometer will run at current densities of .005 and .0025 amps./sq.cm. for over three hours but the precision is lowered.

2. Current densities from .005 to .075 amps./sq.cm. may be used with excellent results. The maximum error for any single determination in the current density range .05 - .075 is .02%. The error at a current density of .005 amps./sq.cm. 0.4%. This last figure is likely to increase as the duration increases.

3. Two coulometers should be connected in series and the depositions averaged.

4. Clean, pure mercury must be used.

5. A Parr weighing bottle should contain the cathode mercury. Approximate dimensions are: 2 cms. in depth and dia. of $2\frac{1}{2}$ cms.

6. Splashing of the mercury must be prevented.

7. Wash the cathode with potassium iodide solution, then with water by decantation. Care should be taken in the washing operations to prevent drawing of mercury into the pipette.

8. To absorb all the moisture on the mercury use narrow strips of filter paper as the absorbent.

9. The strongest current passed was 280 M.A. By enlarging the surface of both the anode and cathode and increasing the volume of the coulometer, higher currents would be permitted to pass through the cell.

SUMMARY

1.   The theoretical principles and variables concerning electrodeposition are discussed.

2.   A discussion of the mercury weight coulometer as studied is given. A theoretical dissertation, description of the coulometer and materials, and manner of operation are included.

3.   The method of measuring the current is given.

4.   A discussion of errors is included.

5.   The experiment data supporting the conclusions reached are recorded.

6.   Recommendations for use of the mercury weight coulometer are given.

7.   Between the current density range of 0.05 - 0.075 amps./sq.cm. for determinations up to three hours, the maximum error is .02%. As the current density is decreased, the error increases and may become as high as .4%.

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