THE INFLUENCE OF GELATIN UPON ELECTRO DEPOSITED COPPER

by

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Review of Previous Work

Rosa, Vinal and McDaniel[1] advance what is termed the "theory of discontinuous deposits". They have described deposits from pure solutions of silver nitrate, in which the bare platinum cathode is plainly visible between crystals. They have also described deposits from impure solutions in which the silver seemed to be non-crystalline, but a microscope revealed the deposit to be crystalline. In neither is the cathode completely covered. From the cyanide solutions, however, the silver deposits appear under a powerful microscope to be continuous. "As Ohm's law holds in the electrolyte, it is evident that there is at the surface of the platinum a potential difference opposing the current, which brings the electrolyte in contact with the platinum to a higher potential than that of the electrolyte in contact with the silver, and so the current is turned away from the platinum surface, finding numerous outlets to the platinum cathode through the silver crystals. It is as though the potential difference at the start breaks through the surface film at numerous points, and these

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[1] Rosa, Vinal and McDaniel, The Silver Voltameter, Part II, The Chemistry of the Filter Paper Voltameter and the explanation of Striations. U. S. Bureau of Standards, Vol. 9, Part II, p.277.

initial outlets, which increase in area as the crystals grow, are sufficient, unless the current density is suddenly increased."

"The surface potential differences taken in connection with the specific resistance of the electrolyte and the current density determine the distance apart of the crystals. In a very concentrated solution the specific resistance is less, and hence the fall of potential corresponding to the surface differences of potential occurs in a greater distance. Hence the crystals will be farther apart than in a normal solution. On the other hand, in a very weak solution of higher specific resistance the fall of potential is steeper and hence the given potential difference will occur in a shorter distance. Hence the crystals will be nearer together and more numerous, and hence also the crystals very small. Heating the solution increases its conductivity, and therefore has the same effect as increasing the concentration; that is, the crystals are further apart and of larger size."

These authors give the following explanation for the formation of striations on their deposits. "When the current starts the deposit begins at many isolated points, the distance between crystals being hundreds of times the linear dimensions of the crystals themselves at the end of the first few seconds. The stream lines along which the current flows are thus concentrated at the cathode end, upon these incipient crystals, no current flowing to the bare platinum

after the first instant. The upward current of liquid along
the crystal surface due to the smaller density of the impov-
erished electrolyte at the cathode, carries the chain of ions
which lie along a given stream line upward out of its normal
course, so that the current tends to reach the upper surface
of the crystal. Watching this process under the microscope
one sees the small crystals which appear at the start grow
upward so that after a time instead of a large number of
silver crystals of approximately equal dimensions in differ-
ent directions one sees a great number of elongated deposits,
the longest dimension being vertical. These tend to grow
into one another, so that after a time striations have dev-
eloped, that is, there are ridges of silver of more or less
equal distance apart, separated by intervals of bare platinum."

"Observations shows that the number of striae per centi-
meter is approximately proportional to the current density,
or the distance between striae is inversely proportional to
the current density. In the same way, the initial distance
between crystals in a nonstriated deposit is inversely pro-
portional to the current density, or the number of crystals
per square centimeter is proportional to the square of the
current density. This explains why a small current gives
coarser crystals than a larger current for a given weight
of deposit, for doubling the current multiplies the number
of crystals by four, and hence reduces the average weight
of each crystal to one-half."

Frolich[1] states that the increase in cathode potential is easily explained when it is considered that his measurements were made in acid solutions, where we have to deal with positively charged gelatin ions. The gelatin on account of its positive charge, migrates to the cathode where it accumulates and offers additional resistance to the transportation of the inorganic cations up to the cathode surface, thereby explains the increase in cathode polarization as due to the increase in concentration of gelatin at the cathode surface. This increase in concentration is the result of migration of the positive gelatin ions to the cathode. The positive character of these ions prevent their migration away, and the rates of convection and diffusion are negligible, hence we have the accumulation of a gelatinous film near the surface of the cathode. The resistance to the flow of copper ions is increased, and as a result we have an increased in electrode polarization.

Blum and Hogaboom[2] in reviewing the effect upon electro-deposition of various factors, cover current density, concentration and agitation, temperature, conductivity, metal ion concentration, hydrogen ion concentration, addition agents, structure of base metal, metal distribution and throwing power.

[1]Frolich, The Amphoteric Character of Gelatin and its Bearing on Certain Electro-Chemical Phenomena, Trans.Am.Elec.Soc, Vol. 46, 67, 1924.

[2]Blum and Hogaboom, Principles of Electroplating and Electroforming, McGraw-Hill Book Co., 1924.

Marie and Buffat[1] found that cathode deposits from copper sulfate electrolytes containing gelatin, were heavier than the theoretical deposit. These authors attributed this excess weight to gelatin and mechanically held copper sulfate.

Blum[2] in discussing the effects of colloids in the electro-deposition of metals states that one effect of colloids upon the structure of electro-deposited metal is to reduce the tendency for the formation of trees, or projections upon the surface. Addition agents are frequently used to permit use of higher current densities than normal. Apparently addition agents decrease the tendency for the growth of existing crystals, and increase that for the formation of new crystals.

Blum states also that the presence of addition agents especially those that are colloidal increase cathode polarization. Carbon disulfide which is used as a brightener in silver cyanide solutions decrease the cathode polarization.

Common positively charged colloids employed in acid solutions also increase the anode polarization, but to a less extent than at the cathode. Colloids that are negatively charged tend to migrate toward the anode and to produce the greatest polarization there. Whatever the form in which the colloid exists, it must in most cases migrate to the

[1] Marie and Buffat, Jour.Chim.et Phys, 24; 470, 1927.

[2] Blum, Colloids in the Electro-deposition of Metals, Colloid Sumposium Monograph, Vol. 5, 301, 1928.

cathode, and there increase the cathode polarization in order to affect the structure of the deposit. The most important agencies in colloidal solutions that contribute to the replenishment of metal ions at the cathode are diffusion and convection.

If the colloid actually reaches the cathode surface through migration or other means, it may be included within the cathode deposit by means of (1) co-discharge of colloid particles and metallic ions; (2) the discharge of complex ions containing the metal and colloid; (3) adsorption of the colloid upon the face of the metal deposit; or (4) the mechanical inclusion within the deposit.

Taft and Messmore[1] have given examples of the excess weight as a function of the concentration of copper sulfate in the electrolyte, concentration of gelatin and hydrogen ion concentration.

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[1] Taft and Messmore, Trans. Kans. Acad. Sci., Vol. 32,42,1929.

THE INFLUENCE OF GELATIN UPON ELECTRO DEPOSITED COPPER

The Influence of Gelatin upon the Form of Electro Deposited Copper

One of the effects of gelatin upon electro-deposited copper is that upon the physical form. In general, colloids decrease the size of the individual crystals, and the deposit usually acquires a color markedly different from that of the pure electro-deposited metal.

Gelatin, when in solution, acts as an emulsoid and has its characteristic effect upon the form of electro-deposited copper. Ordinary deposited copper has a light reddish characteristic copper-color, while that electro-plated in the presence of gelatin is frequently darker, in many cases the color grades between that of ordinary copper and a light colored bronze.

The concentration of the gelatin plays quite an important part upon the physical form of the deposit. In the illustrations which follow, the effect of several variables upon the form of the deposit, other than concentration of gelatin, was noted. The surface upon which the deposition was made seemed to play a less important part than one would suspect.

The factors influencing the form of deposit which were observed were concentration of copper sulfate in the electrolyte, concentration of gelatin, hydrogen ion concentration (frequently denoted by pH), brand of gelatin, cathode surface, and length of time during which deposition was continued.

Experimental Procedure

The experimental procedure used in the preparation of the deposits for both the qualitative and quantitative work was very simple. A stock solution of 1.25 molar copper sulfate was prepared by dissolving 312 grams of chemically pure copper sulfate in water and diluting to one liter. A solution of this concentration was very convenient for use in preparing solutions of other molarities. For example, to prepare a 1 molar solution, 80 cubic centimeters of the stock solution and 20 cubic centimeters of water were needed; for the 0.75 molar, 60 cubic centimeters of the copper sulfate and 40 cubic centimeters of

water; for the 0.50 molar, 40 cubic centimeters of copper sulfate and 60 cubic centimeters of water; and for the 0.25 molar, 20 cubic centimeters copper sulfate and 80 cubic centimeters of water gave 100 cubic centimeters of the solution.

Coignet's sheet gelatin was used in the study of the physical form of the deposits, while Eastman Kodak Company's ash-free gelatin was used in all subsequent quantitative work.

Preparation of the gelatin for solution consisted in tearing the sheets into bits and weighing on a watch glass. The gelatin sample was added to the previously prepared copper sulfate solution, and the whole warmed to 50 degrees Centigrade. Solution was a slow process, but was facilitated by slow stirring. After the gelatin was completely dissolved, the 50 or 100 cubic centimeter beaker was placed in a 30 degree thermostat for temperature control. The copper or platinum electrodes had been previously mounted upon an electrode support. This support was simply a board about 1-1/2 inch in cross section and about 20 inches in length. Upon one side of this board were nailed short pieces of copper wire bent into the shape of inverted U's, and to one end of a U was held by a metal clip an anode, and to the other end a cathode. These two electrodes were the anode and cathode of different electrolytes. The cathode of one U and the another of an

adjacent U were placed in the same electrolyte. The U's not only served as electrode supports, but also carried the current from one cell to another. Any number of cells could be placed in series in this manner.

Storage batteries were the source of direct current for the electrolyses. Adjustment of current was made through the use of a potential divider, which will be described in the section on polarization. An ammeter was placed in series with the cells as a current indicator.

After electrolysis was finished, the electrodes were immediately removed from their electrolytes, washed with warm water, then alcohol and dried. Later in the work acetone was used as the drying agent, and was found to be much more effective than the grade of alcohol available.

As a permanent record the cathodes were photographed using Cramer slow contrast plates, 5 by 7 inches. In most cases the cathode handles were clipped to allow for convenient arrangement.

Physical Form of Deposits.

Physical Form as a Function of Concentration of Gelatin.

Figure I shows copper plated at 30°C., with a current density of 1 amp. per dec.^{2} (0.0625 amperes current), for 30 minutes and from 1 molar copper sulfate solutions containing variable quantities of gelatin. The gelatin was Coignet's, prepared in France.

Several types of deposits present themselves upon inspection of the plate. Solutions containing 0.10 per cent of gelatin or less give cathodes containing small "warty" growths or "dots". The number of these dots seems to be roughly inversely proportional to the gelatin content, that is, the greater the proportion of gelatin, the smaller the number of dots. This smaller number of dots seems to go hand-in-hand with dots of greater diameter.

As the gelatin content increases the type of deposit is characterized by vertical raised striations. These striations, when sharp and distinct, are usually very bright and lustrous, as contrasted from the dull and darker colored background.

In the electrode from the cell containing 0.2 per cent gelatin, several striations seem to be composed of dots arranged in a vertical row. Whether or not the other striations were at one time during their development, a series of dots is open to speculation. As concentration of gelatin increases up to 1.33 per cent striations continue to present themselves, although they become fewer in number.

.05% gel.

.10% gel.

.20% gel.

.30% gel.

.40% gel.

.50% gel.

.60% gel.

.70% gel.

.80% gel.

1.00% gel.

1.33% gel.

1.67% gel.

2.0% gel.

Coulometer
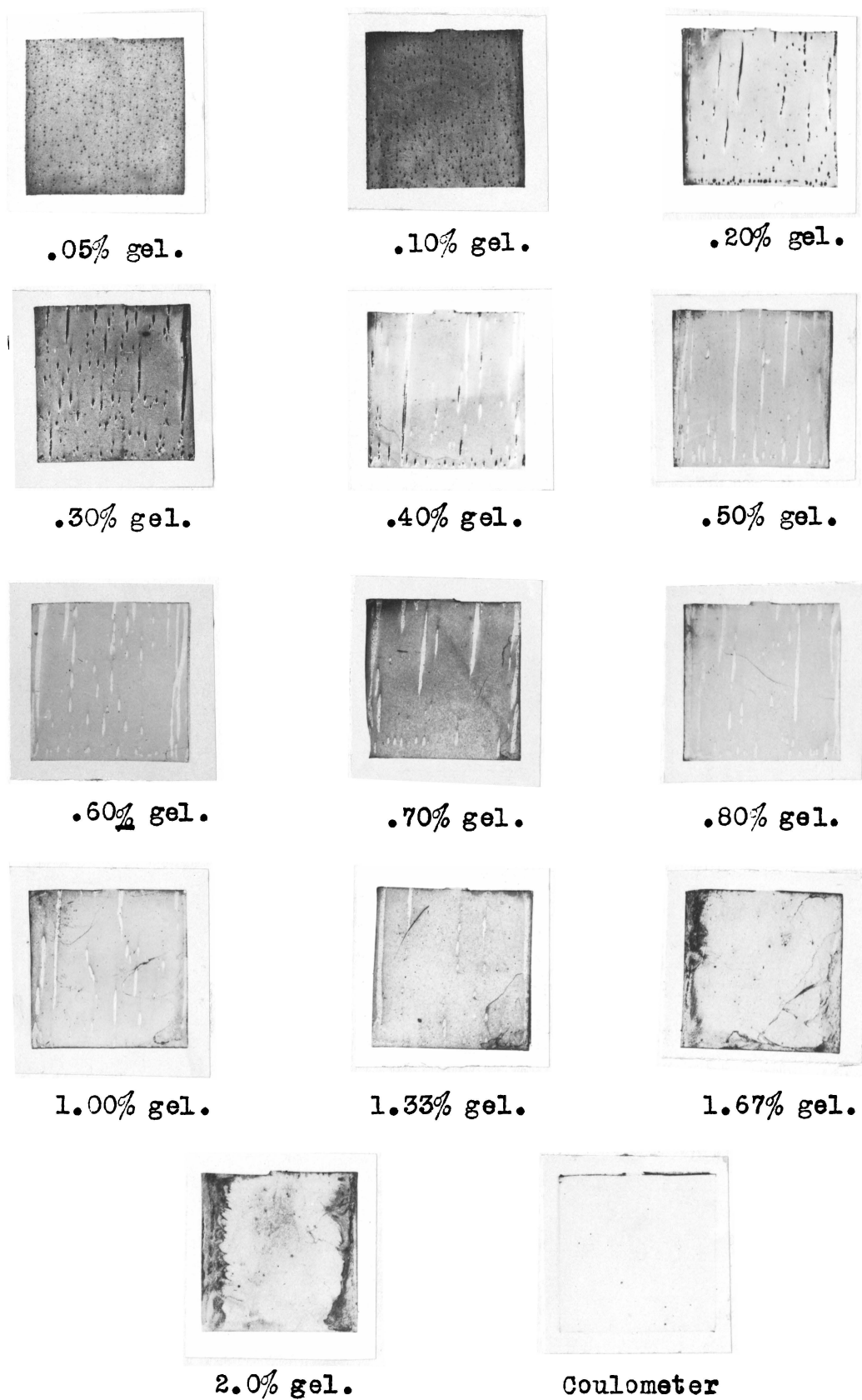
Figure 1

The two electrodes containing 1.67 and 2.0 per cent gelatin contains striations only on their edges.

The cathodes shown in Figure II were prepared under the same conditions as those in Figure I, that is, 1 molar copper sulfate, 30^{0}C. C. D. 1 ampere per square decimeter, with variable gelatin contents. The electrodes from solutions containing 0.10% or less of gelatin give the same general type of deposits as those shown in Figure I. The deposit from .15 to 1.0% gelatin contain the vertical striations, while those of higher gelatin content contain almost no striations. The darkening of the electrodes from the cells containing 1.33% gelatin or more possibly is due to partial reduction of the gelatin. This reduction of gelatin was caused by the setting of the gelatin solution, which thickening in turn prevents free circulation of the electrolyte. When the cupric ions in the vicinity of the electrode had been discharged, the solution was too viscous for a sufficient number to be furnished by convection currents and as a result some gelatin was partially reduced imparting to the cathode a blackish color. The difference in appearance between the coulometer electrodes and the gelatin electrodes is quite marked.

In Figure III are shown electrodes prepared at 30^{0}C, with a C. D. of 1 ampere per dcm^{2} for 30 minutes, but with both concentration of copper sulfate and gelatin as variables. Five concentrations of copper sulfate and three concentrations of Coignet's gelatin were used, each concentra-

.025% gel.   .050% gel.   .075% gel.   .10% gel.

.15% gel.   .20% gel.   .25% gel.   .30% gel.

.40% gel.   .60% gel.   .80% gel.   1.00% gel.

1.33% gel.   1.67% gel.   2.00% gel.   3.0% gel.
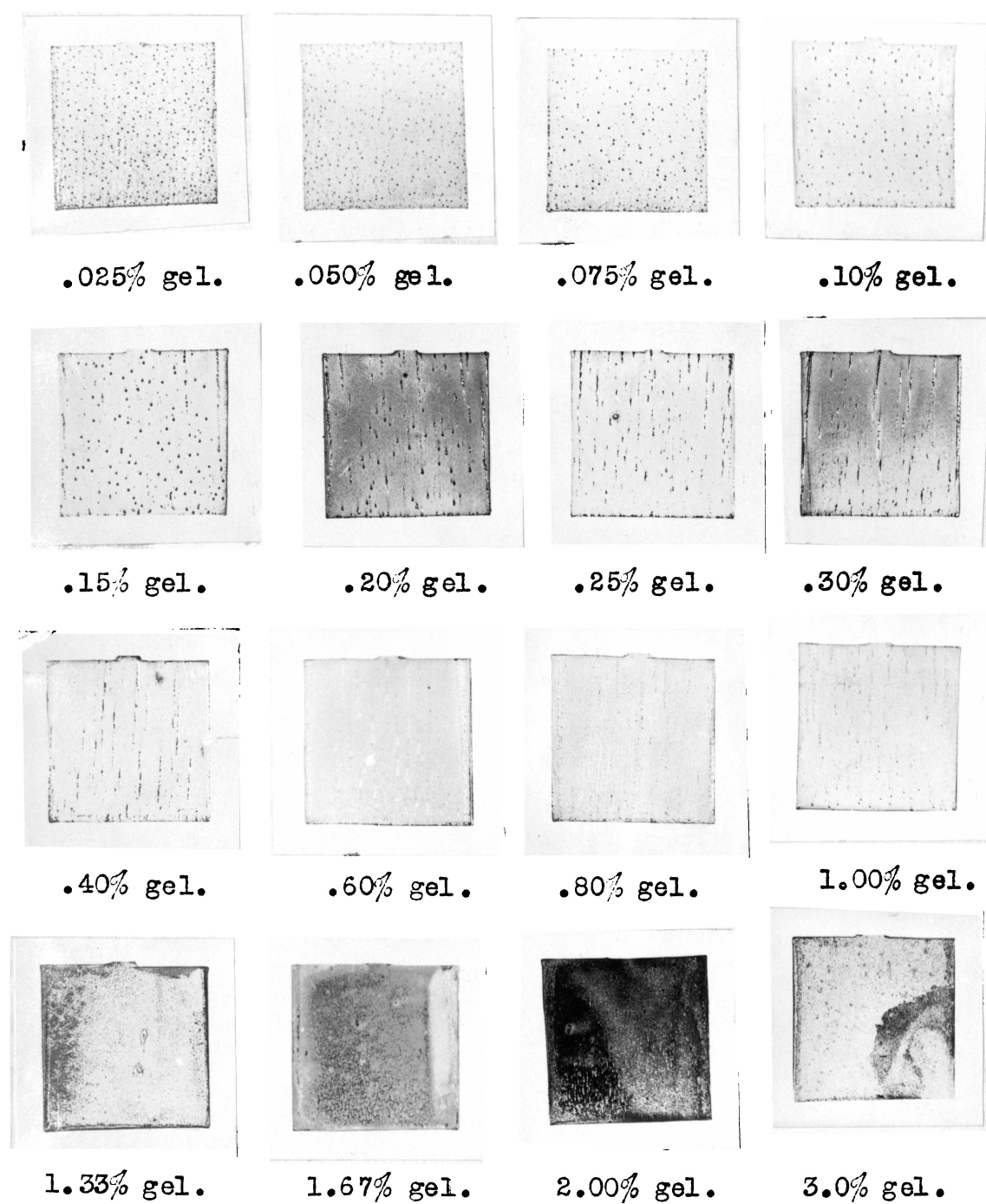
Figure 2.

tion of gelatin being contained in each of the five concentrations of copper sulfate, making a total of 15 cells. The horizontal rows of cathodes are those of constant copper sulfate concentrations and in vertical columns the concentration of gelatin is constant.

Several types of cathodes again present themselves. The cathodes from 1.25 molar $CuSO_4$ and .06 and .50% gelatin are of the same general type, the former has more dots on its surface than the latter. Compared to previously described electrodes from 1 molar $CuSO_4$ it would appear that the increased concentration of copper sulfate tended to decrease the number of dots. The electrode from the solution containing 2.0% gelatin would have contained vertical striations had the electrolyte been sufficiently fluid to have allowed convection currents to have played their part.

The second horizontal row of cathodes from the top are those from 1 molar copper sulfate. The electrode from the 0.06 per cent gelatin appears quite different from the corresponding one described above. It seems to be very difficult to duplicate the physical form of these deposits. The electrode from 2% gelatin is quite similar to the corresponding one from the 1.25 molar $CuSO_4$.

In the next lower row are those cathodes from the 0.75 molar $CuSO_4$. The electrode from the 0.06% gelatin is quite similar to some in Figures I and II. The one from 2% gelatin again is quite similar to the corresponding electrodes from 1.0 and 1.25 molar $CuSO_4$.

The two lower horizontal rows present cathodes of quite different appearance. The dark colored areas are coatings of copper oxide, some portions of which are black some grade from a dark blue to a light blue, then to a red. In each case with 2% gelatin, deposits seem to be quite similar in appearance; it would thus indicate that the gelatin content at 2% concentrations plays a more important part than the change in concentration of copper sulfate.

Physical Form as a Function of Concentration of Gelatin and pH.

Figure IV shows cathodes prepared under the same conditions as those in Figure III, namely from 1.25 molar to 0.25 molar copper sulfate, 0.06 to 2.0% gelatin, C. D. of 1 ampere per dcm^2, 30°C. and for a duration of 30 minutes. Hydrogen ion determinations were made in a duplicate sample from each electrolyte, the results of which are given in Table I. The hydrogen ion determinations were made with the quinhydrone and saturated calomel electrodes.

Table I.
pH Values of Gelatin-$CuSO_4$ Electrolytes.

Conc. $CuSO_4$	% Gelatin	pH
1.25 Molar	0.0625	3.20
1.25 Molar	0.50	3.25
1.25 Molar	2.00	3.35
1.00 Molar	0.0625	3.26
1.00 Molar	0.50	3.33
1.00 Molar	2.00	3.45
0.75 Molar	0.0625	3.41
0.75 Molar	0.50	3.48
0.75 Molar	2.00	3.57

1.25 M
CuSO4

1.00 M
CuSO4

0.75 M
CuSO4

0.50 M
CuSO4

0.25 M
CuSO4

.06% gel.   .50% gel.   2.0% gel.
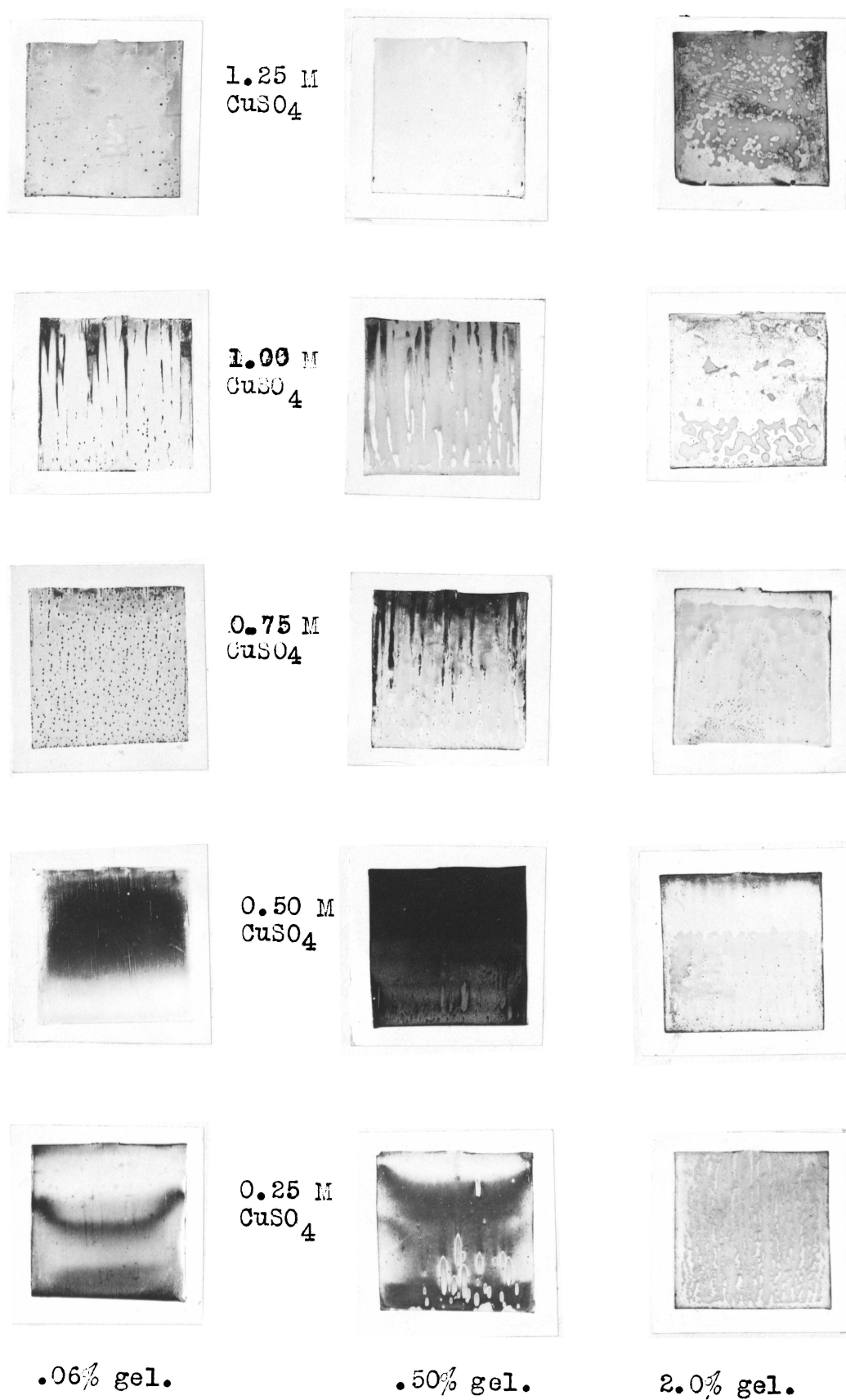
Figure 3

Conc.CuSO$_4$	% Gelatin	pH
0.50 Molar	0.0625	3.57
0.50 Molar	0.50	3.66
0.50 Molar	2.00	3.76
0.25 Molar	0.0625	3.84
0.25 Molar	0.50	3.94
0.25 Molar	2.00	4.01

The cathodes shown in Figure 4 are approximately similar to those in Figure 3, however there are several exceptions. The cathodes from 1.25 molar copper sulfate and .06 per cent gelatin are similar, but that one from 0.5 per cent gelatin in Figure 4 is appreciably darker than the corresponding one in Figure 3. The cathode from 2.0 per cent gelatin in Figure 3 also is darker. The most noticeable difference occurs in the electrode from the cell containing .06 per cent gelatin and 1 molar copper sulfate. Why in one case some of the striations should be broad and comparatively few in number, while in the other case there are few striations and many dots is not simple to explain. These dots are arranged in vertical rows, and had they developed into continuous striations, the latter would have been more numerous.

In the cathode from 0.175 molar copper sulfate and 2.0 per cent gelatin another exception occurs. This electrode in Figure 4 contains a comparatively large number of dots, and these dots are exceptionally large in diameter. The usual cathode from 2.0 per cent gelatin contains comparatively few dots, and these are low and flat and quite large

1.25 molar CuSO$_4$
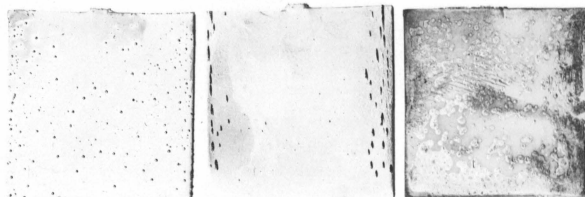
1.00 molar CuSO$_4$
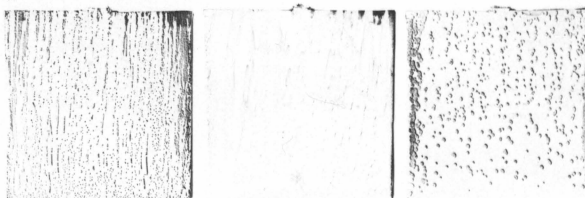
0.75 molar CuSO$_4$

0.50 molar CuSO$_4$

0.25 molar CuSO$_4$
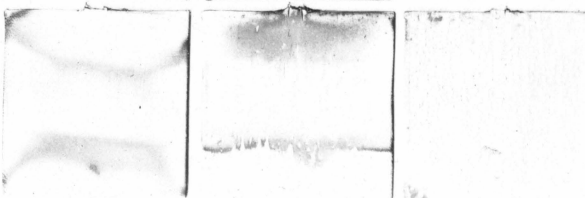
.06% gel.   .50% gel.   2.0% gel.

Figure 4

in diameter. The remainder of the electrodes in the two
plates are quite similar.

These several inconsistencies are not easily to be
explained. All electrolytes were prepared in exactly the
same manner; heating in each case was carried to 50^0 Cent-
igrade for the solution of the gelatin. Stirring was not
vigorous, and all gelatin was dissolved directly by the
respective copper sulfate solutions. Hydrogen ion concen-
trations vary not more than .02 or .03 in terms of pH in a
solution of one definite concentration prepared at differ-
ent times. This small variation is due largely to variat-
ions in the distilled water. It is scarcely reasonable
that differences in pH of a few hundredths would cause such
marked dissimilarity between deposits, when other conditions
are constant.

Table 2 shows the several concentrations of gelatin
and their corresponding pH values.

In the case of 0.0125% gelatin, the change in concen-
tration of gelatin from zero per cent to that value is so
slight that no appreciable change in the hydrogen ion con-
centration occurs.

Figure 5 shows the cathodes prepared from the electro-
lytes whose pH values and gelatin concentrations are given
in the above table. These electrodes are quite similar in
appearance to some previously shown, and also the three
types of deposits are quite definitely illustrated. The
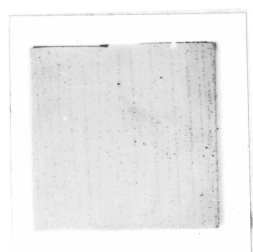
.0125% gel.
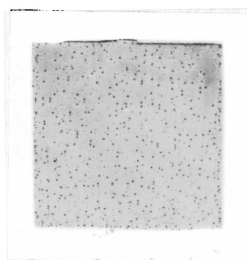
.025% gel.
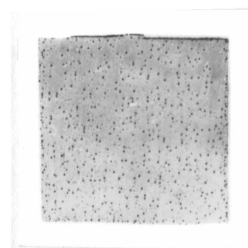
.050% gel.
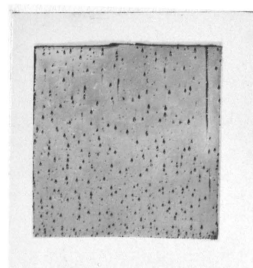
.075% gel.
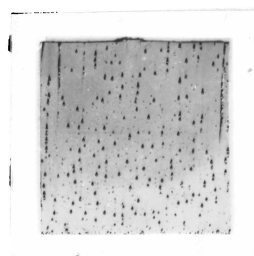
.10% gel.
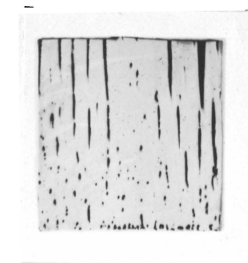
.20% gel.
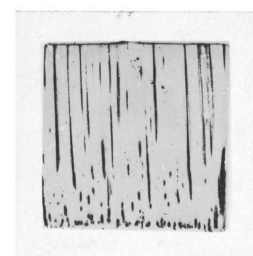
.30% gel.
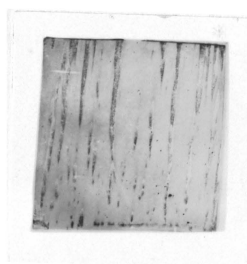
.40% gel.
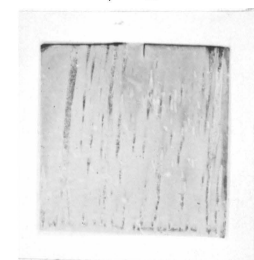
.50% gel.

.75% gel.

1.00% gel.
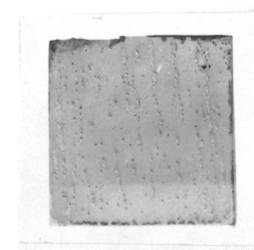
1.50% gel.
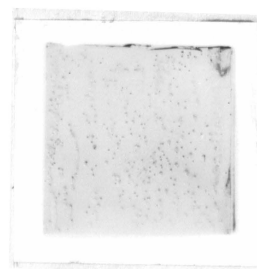
2.0% gel.

2.50% gel.

3.00% gel.

Figure 5
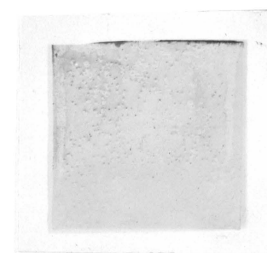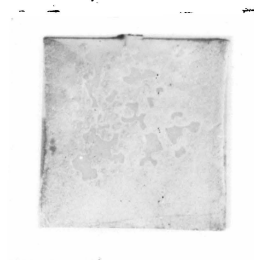
first five cathodes, i.e., those from electrolytes contain-
ing .10 per cent gelatin and less are characterized by the
dots, those from .20 per cent to 1.0 per cent are charact-
erized by the bright to dull lines, and solutions contain-
ing 1.5 per cent and more gelatin have no striations. The
latter deposits are very dull, but in general are light
colored.

<div align="center">

Table 2

Concentration of Gelatin		pH
.0125 per cent		3.30
.0250 " "		3.32
.0500 " "		3.33
.075 " "		3.33
.10 " "		3.33
.20 " "		3.35
.30 " "		3.35
.40 " "		3.36
.50 " "		3.39
.75 " "		3.41
1.00 " "		3.43
1.50 " "		3.45
2.00 " "		3.45
2.50 " "		3.49
3.00 " "		3.50

</div>

Figure 6 shows cathodes prepared similarly to some in
previous plates. Some differences exist, however. The condit-
ions under which these deposits were prepared were 30° Cent-
igrade, at a current density of 1 ampere per square decimet-
er, and for a duration of 30 minutes, the concentrations of
copper sulfate and gelatin being variable.

Again, several types of deposits present themselves
as a result of variation in concentrations of copper sulfate
electrolytes and gelatin. The top horizontal row of cathodes

1.25 molar CuSO$_4$

1.00 molar CuSO$_4$

0.75 molar CuSO$_4$

0.50 molar CuSO$_4$

0.25 molar CuSO$_4$
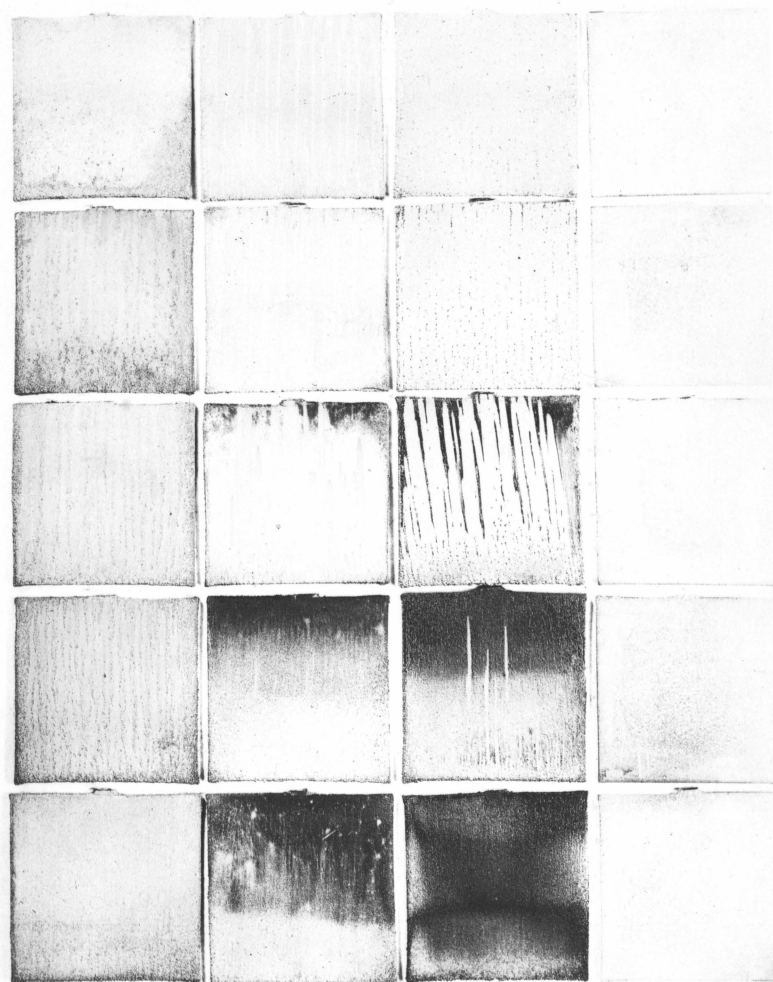
2% gel.   .5% gel.   .06% gel.   0% gel.

Figure 6
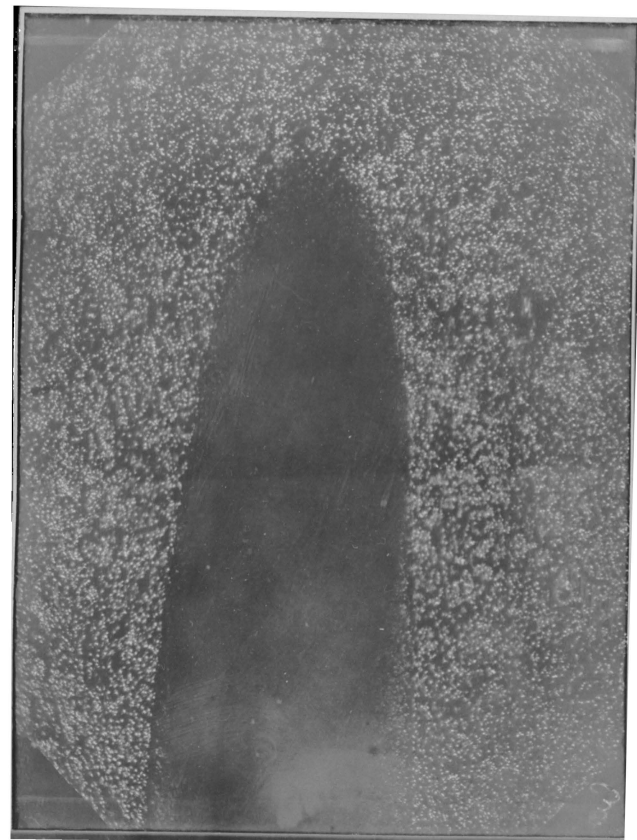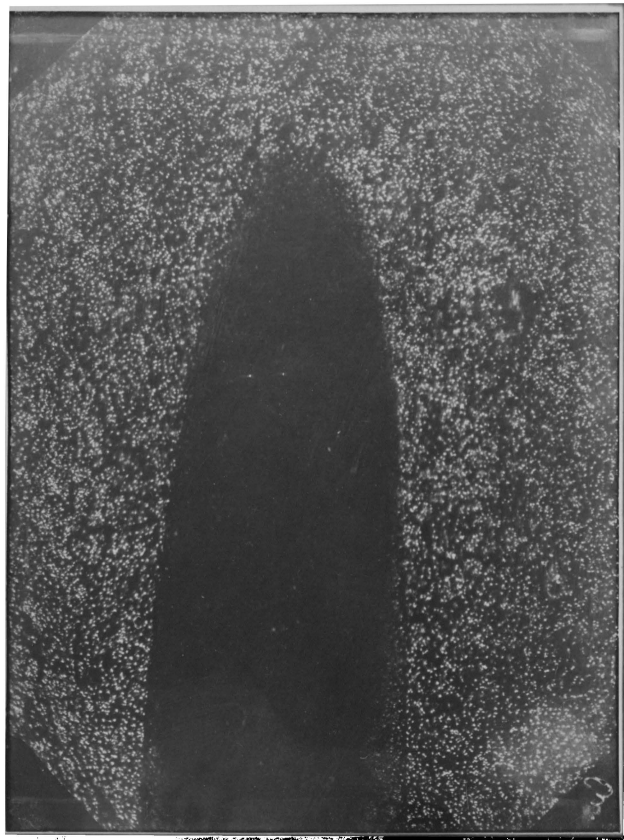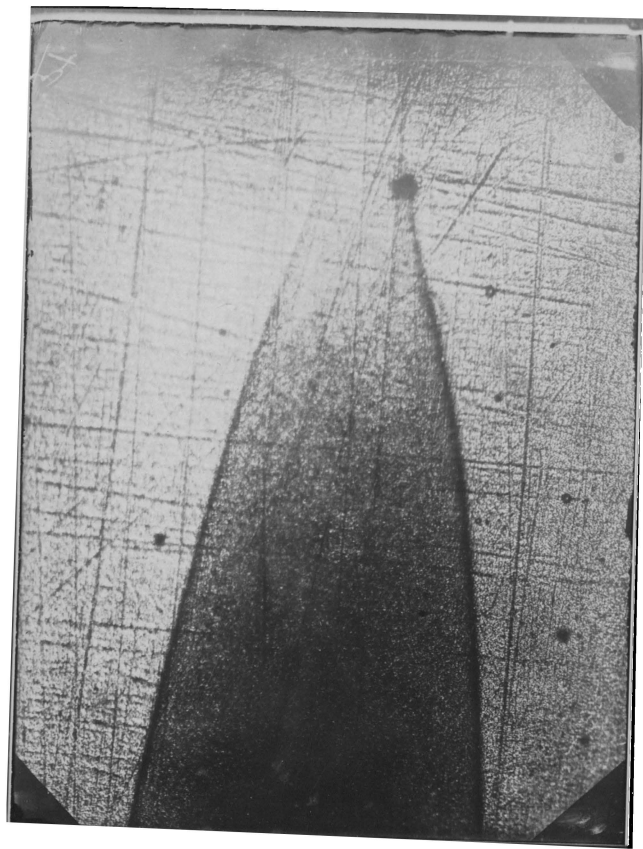
is from the 1-1/4 molar copper sulfate, and the bottom row
from the 1/4 molar solution, and the intermediate rows are
from the corresponding consentrations of copper sulfate.
The vertical columns from left to right contain electrodes
from solutions containing respectively 2.0, 0.5 and .06 and
0.0 per cent gelatin. Many of these electrodes are quite
dissimilar to some shown previously, all conditions of pre-
paration being the same. The small number of comparatively
large dots on electrodes of high concentration of copper
sulfate and low gelatin appear to be absent. In their place,
however, are many more, but much smaller dots. Deposits of
intermediate copper sulfate and gelatin seem to be quite
similar to some previously described. The dark colored de-
posits in the lower center are coated with bluish to red-
dish oxide, and were those prepared from the more dilute
copper sulfate solutions, and those dilute sulfate solutions
did not contain sufficient acid to prevent the oxide format-
ion. The cathode at the lower left contained sufficient gel-
atin to prevent the formation of visible oxide.

The vertical row of electrodes to the right were pre-
pared from solutions containing zero gelatin, or in other
words, from solutions or copper sulfate alone. These elec-
trodes are appreciably heavier than theoretical on account
of their coating of oxide. This coating in all probability
is not just a surface coating but is more or less evenly
distributed throughout the deposit and is very different
from the oxide prepared in the presence of gelatin. These

several deposits are darkened sufficiently as to be easily distinguished from coulometer deposits. One might be led to suspect that the electrodes prepared from .50 and .25 molar copper sulfate and zero gelatin might be bright colored with the oxide but such is not the case. It appears as though low concentrations of copper sulfate and gelatin both are necessary for the preparation of these highly colored deposits.

Hydrogen ion measurements were made on the electrolytes from which the above electrodes were prepared. These values are given in the following table.

Table 5

Molarity of CuSO₄	Conc. Gel. per cent	pH
1.25	0.00	3.02
1.25	0.06	3.09
1.25	0.50	3.16
1.25	2.00	3.25
1.00	0.00	3.16
1.00	0.06	3.25
1.00	0.50	3.33
1.00	2.00	3.41
0.75	0.00	3.31
0.75	0.06	3.41
0.75	0.50	3.49
0.75	2.00	3.58
0.50	0.00	3.47
0.50	0.06	3.60
0.50	0.50	3.68
0.50	2.00	3.78
0.25	0.00	3.75
0.25	0.06	3.88
0.25	0.50	3.99
0.25	2.00	4.06
0.00	0.00	6.15
0.00	0.06	5.62
0.00	0.50	5.47
0.00	2.00	5.38

The addition of gelatin to a copper sulfate solution alters materially the hydrogen ion concentration in some cases. As an example let us consider the pH of the four electrolytic cells containing 1/4 molar copper sulfate. The solution which contains no gelatin, or as we might say, pure copper sulfate has a pH of 3.75. The addition of .06 per cent gelatin raises the pH, which increase indicates the absorption in some manner of the hydrogen ions. The increase of pH obviously means a decrease in acidity, and the decrease in acidity is favorable to oxide formation, which tendency appears logical.

As we pass to the next electrode to the left, which was prepared from copper sulfate containing 1/2 per cent gelatin, we see less oxide than in the previous case. But the hydrogen ion concentration has continued to increase, which increase, of course, means still less acidity. Less acidity should favor increased oxide formation, but the reverse seems to be the case, the electrode from the 2.0% gelatin contains very little oxide. Again the pH has increased, and this increase has failed to favor oxide formation.

Figure 7 shows cathodes which essentially are duplicates of those in Figure 6.

1.25 molar CuSO$_4$

1.00 molar CuSO$_4$

0.75 molar CuSO$_4$

0.50 molar CuSO$_4$

0.25 molar CuSO$_4$

2% gel.   .5% gel.   .06% gel.   0% gel.

Figure 7

Physical form of deposits upon Platinum

For the preparation of all previously described electrolytic deposits, sheet copper was used for backing. To study the effect of platinum as a base for deposition , a number of electrodes were cut from sheet platinum. These electrodes, similar to the copper ones, were 2.5 centimeters on a side, and a handle of platinum 2 centimeters wide was welded to each square.

These platinum electrodes were given thorough cleansing by immersion in hot nitric acid, washing, and finally ignition to redness over a Meeker burner.

The remaining conditions of the experiment were similar to those of several other experiments, namely, variable concentrations of copper sulfate and gelatin, 30° Centigrade, a current density of 1 ampere per square decimeter and for a duration of 1/2 hour. Figure 8 shows the deposits, actual size, prepared under these conditions.

Many of the deposits appear radically different from the corresponding ones plated upon copper bases. The two vertical rows of electrodes at the right are somewhat similar in appearance to many previously prepared. Some minor differences occur, however. The markings in the deposits from zero gelatin in the upper center of the electrodes are due to differences in the surface of the platinum, and these differences were brought about when the platinum handles were welded to the square. The horizontal markings are the

1.25 M
CuSO$_4$

1.00 M
CuSO$_4$

0.75 M
CuSO$_4$

0.50M
CuSO$_4$

0.25 M
CuSO$_4$

2.0% gel.　　.50% gel.　　.06% gel.　　0% gel.
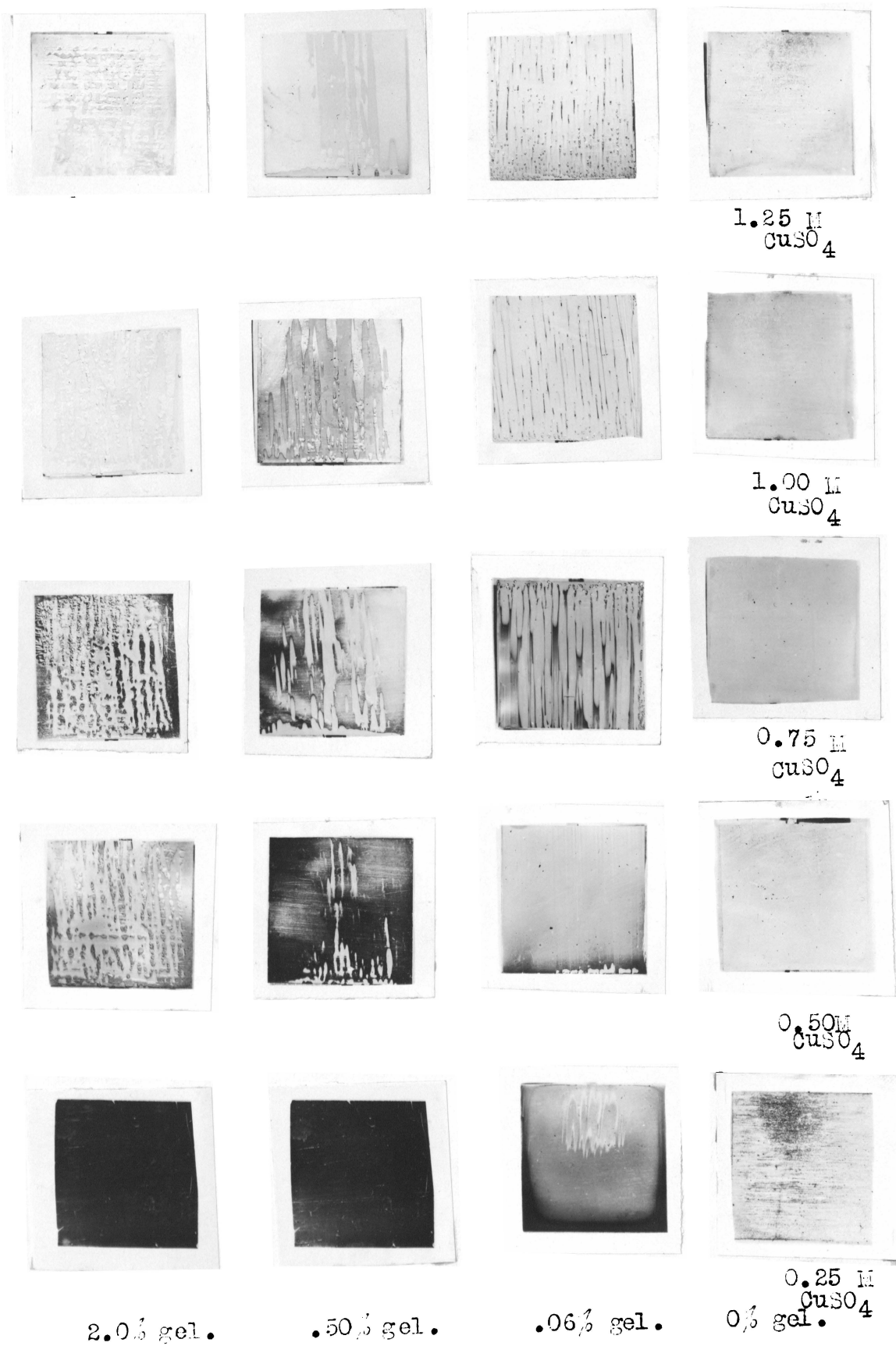
Figure 8

result of roll marks originally on the platinum.

The column of cathodes from .06 per cent gelatin also offers some contrasts to previous deposits. The electrode from 1.25 molar copper sulfate is nearly free from the characteristic dots, and in their places are the vertical striae. The few dots which remain and the striations appear slightly darker in color than the background and as if they had been highly polished. The characteristic oxide appears upon the two electrodes from the more dilute copper sulfate.

Several of the remaining deposits show blistering or loosening and raising of the copper layer from the platinum base. This loosening of the deposit was caused by the tendency to expand, and during this expansion the polished platinum cathode surface was not sufficiently rough to give an adherent deposit. Deposits which had been made over a period of 4 to 5 hours upon platinum electrodes, the surfaces of which had been roughened by abfasion with sea sand, warped convex toward the anode. This warping existing only in the cases of electrolytes which contained 1/2 per cent gelatin or more.

Physical form of deposit as a function of brand of gelatin

For the preparation of all previously described elec-
trodes Coignet's gelatin was used. In Figure 9 are shown
deposits upon copper backing from 1 molar copper sulfate
solutions containing the same quantity, namely 1/2 per cent,
of several brands of gelatin. Time also was a variable in
the preparation of these electrodes, some requiring 1/2
hour and some 1-1/2 hours.

The lower eight electrodes are duplicates of those
on the upper half page, but were prepared at different times.
The electrodes in the left vertical column were prepared
solutions containing 1/2 per cent of the type of gelatin
used by bacteriologists. Those in the next column are the
result of the use of Knox sparkling gelatin, the household
variety; the third column is from Eastman Kodak Company ash-
free gelatin, and the column to the right was from Coignet's.
Coignet's and the Bacto gelatin gave the same type of dep-
osits while those from the Eastman ash-free and Knox were
of the same type, and this type was quite different than
the former.

In each set, the upper row is the result of 1/2 hour
of electrolysis, and the lower rows were prepared during
1-1/2 hours time. In case striations were present, the es-
sential differences in the appearance of the electrodes
which are the result of the different times, was that the
electrodes produced during the greater time had more pro-

.5 hour

1.5 hour

Bacto   Knox   E.K.Co.   Coignet
gel.   gel.   gel.   gel.

.5 hour

1.5 hour

Bacto   Knox   E.K.Co.   Coignet
gel.   gel.   gel.   gel.
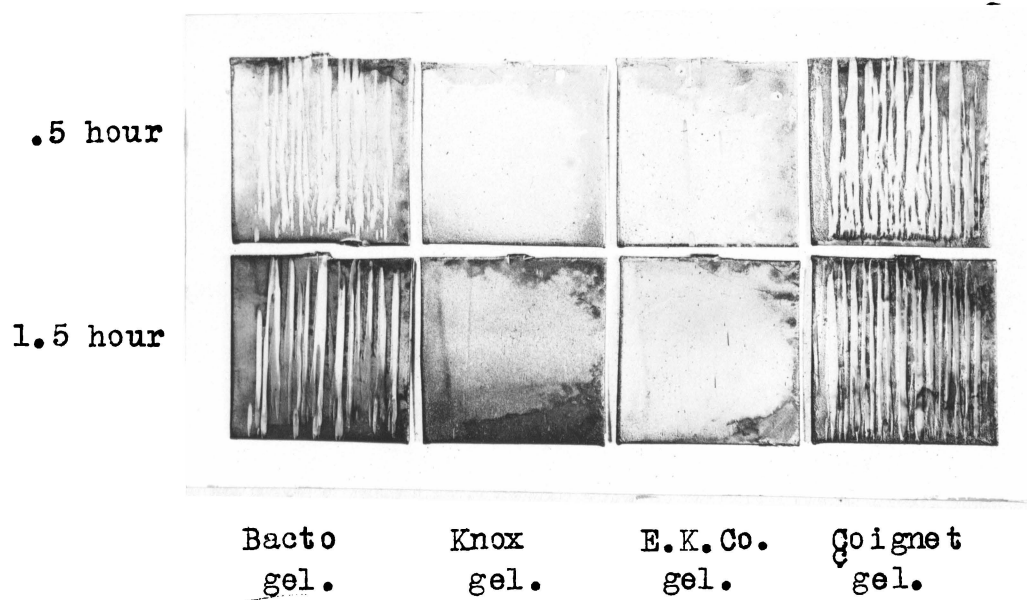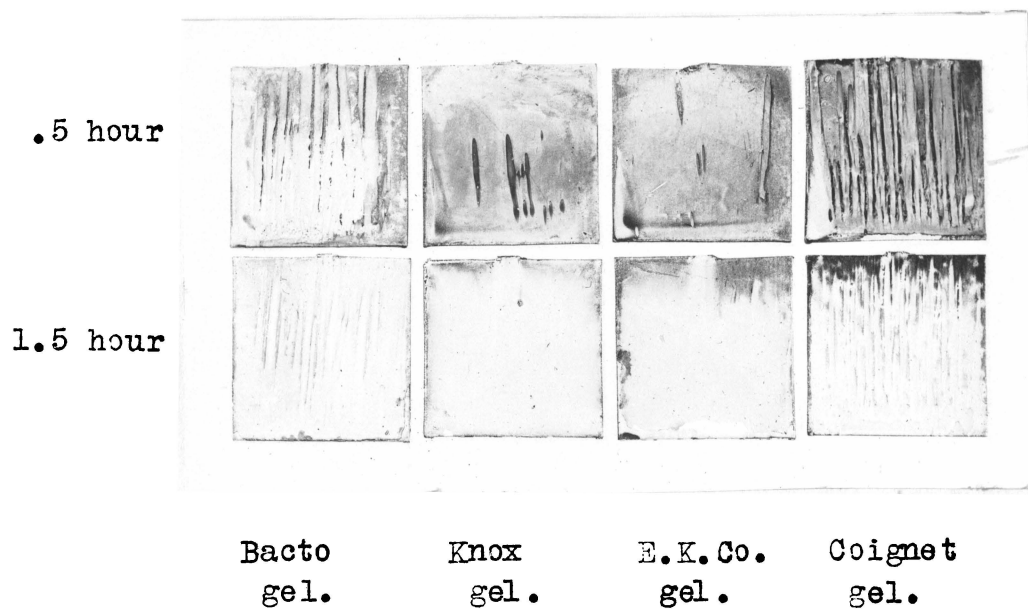
Figure 9

nounced raised striae.

Physical form of deposit as a function of metallic base

All of the deposits previously described had been made upon a base of sheet copper or platinum. To study the effect of another variable upon the type of deposit, several depositions were made upon different bases. Platinum, brass, gold, copper and silver cathodes were used for this purpose. The other conditions of the electrolysis were constant, namely, 1 molar copper sulfate, 30° Centigrade, 1 ampere per square decimeter, and 1/2 per cent Coignet's *Time?* gelatin. Figure 10 shows the result of this experiment.

The cathodes are all quite similar except possibly the one with a platinum base. This electrode gave a finer and smoother deposit than the remainder. A few slight markings, other than the almost normal striations, are the result of roll marks upon the platinum sheet. Another point of dissimilarity that can be mentioned is the unimportant variation in the number of striations. The background of the deposit on platinum was quite smooth, while the others gave fine, but rough deposits.

To make more noticeable any effects not visible to the naked eye, portions of these electrodes were recorded photographically at a magnification of 100 diameters. Figure 11 shows the photomicrographs. The photograph of the deposit on platinum appears to indicate roughness though an absence of dots. In reality this deposit was very smooth. The dark port-

platinum
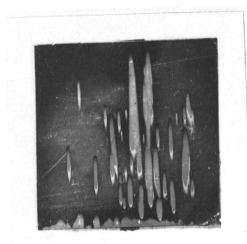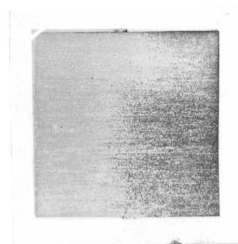
coulometer
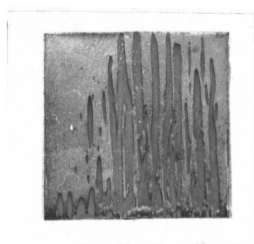
Brass
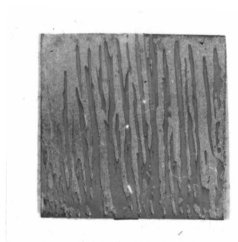
Silver
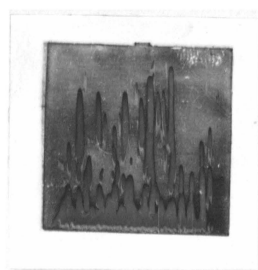
Gold
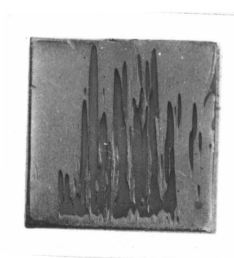
Copper

Figure 10
Copper deposited in the presence of gelatin
upon different bases.
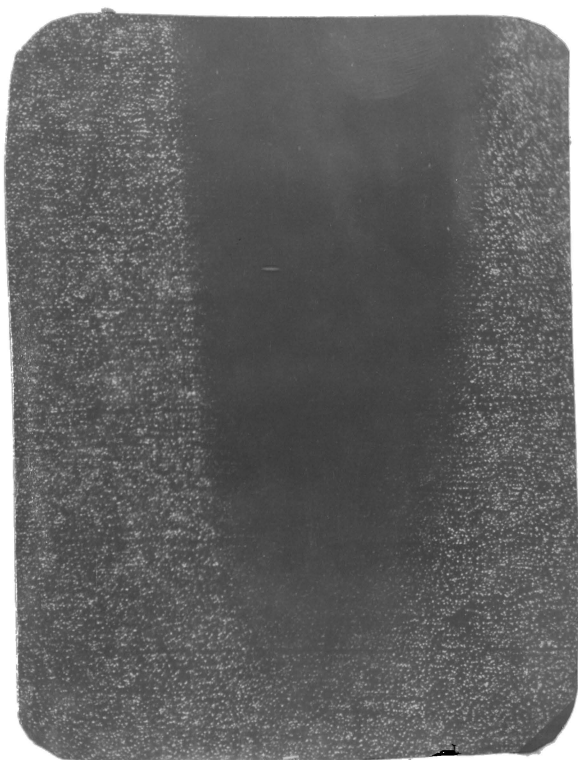
Copper plated upon
a gold base in pres-
ence of gelatin.
x 100
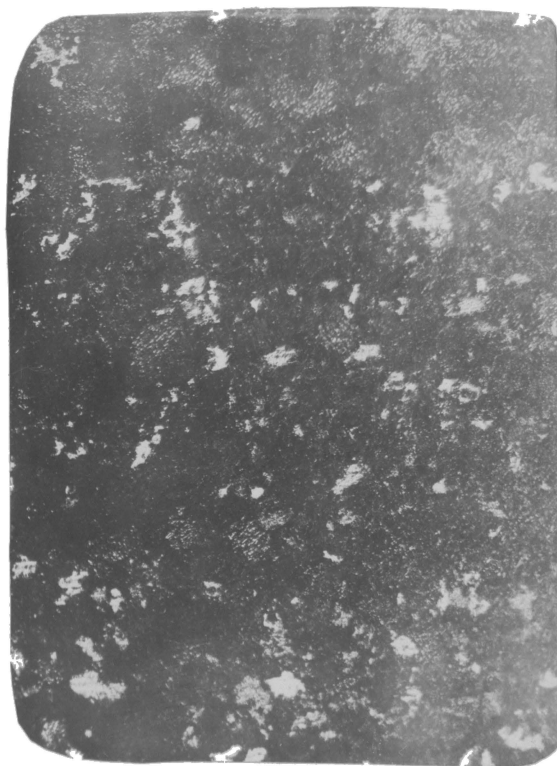
Coulometer deposit1
x 100
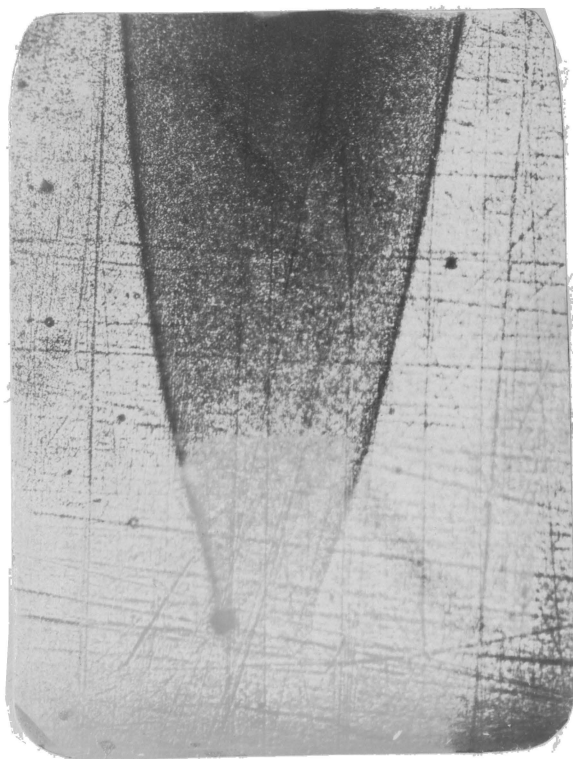
Figure 11

Copper plated upon
platinum in presence
 og gelatin.
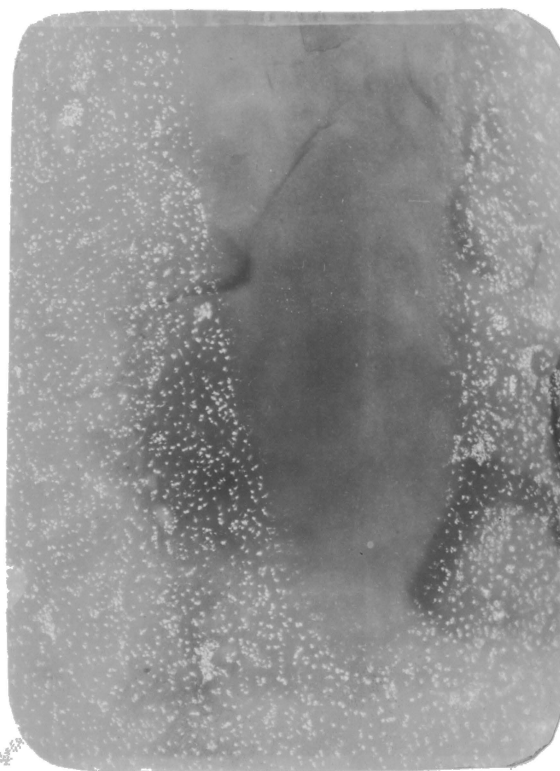
x 100

ᵍopper plated upon
silver in presence
of gelatin.
x 100

Figure 11a
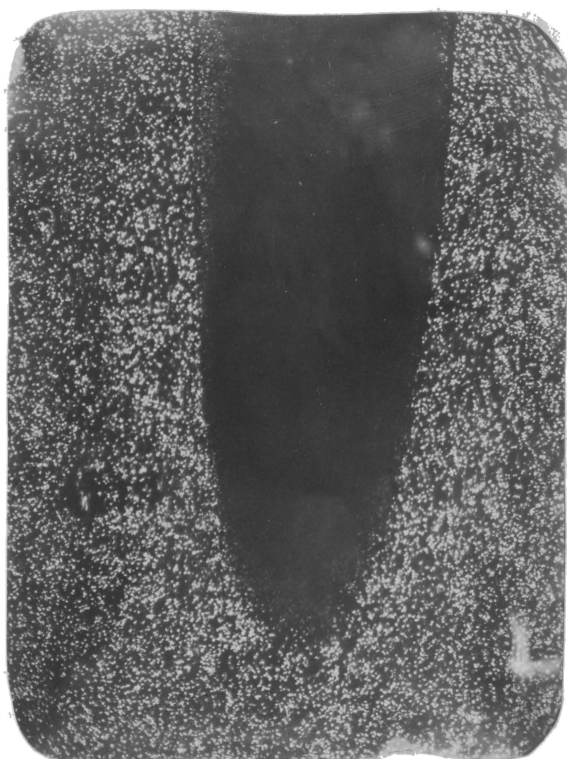
Copper plated upon
copper in presence
of gelatin.
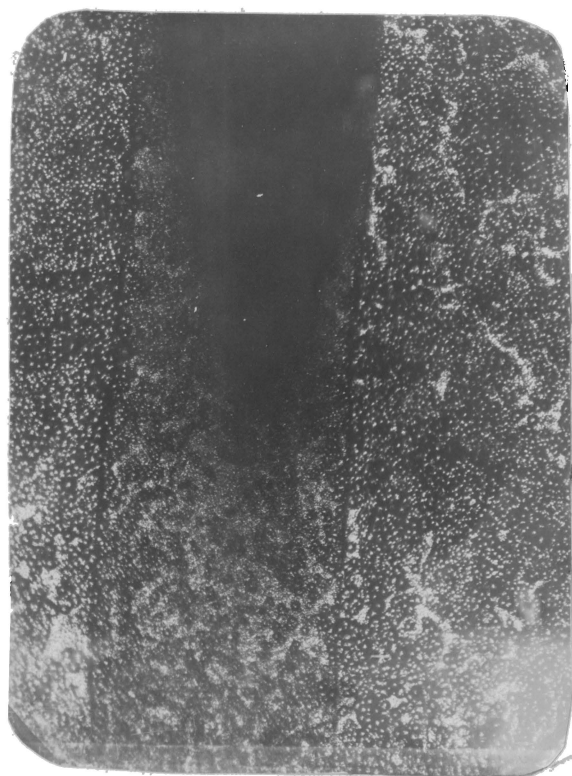
x 100

Copper plated upon
Brass in presence
of gelatin.

x 100

Figure 11b

ion in the center is the bottom end of a narrow striation. The roll marks in the body of the striation barely show, and their absence indicates that the deposited copper on the striation is thicker than on the main body of the electrode. Quite a contrast in color and in the intensity of the light reflected by the deposit is evident.

The remaining deposits are very similar to one another. They show very plainly that the main portion of the deposit is not composed of normal cubic crystals, but of a multitude of dots similar in appearance to many normally visible. In all cases the striations are very smooth, and lustrous, and appear to contain no dots or rough portions.

The size of the dots vary from deposit to deposit. The coulometer deposit is shown for comparison.

The gold cathode was plated with gold from a potassium auric cyanide solution, and this deposit was fine grained and crystalline. The silver, brass, copper and platinum electrodes were cut from sheet metal.

Summary

In this portion of the work the effect of the following variables upon the physical form of electro-deposited copper has been observed, namely, concentration of gelatin, concentration of copper sulfate, hydrogen ion concentration, brand of gelatin, surface for deposition and time.

Low concentrations of gelatin and low concentrations of copper sulfate tend to give deposits well covered with bright colored copper oxide.

With low and medium concentrations of gelatin and from 0.75 to 1.00 molar copper sulfate the deposits were frequehtly characterized by the presence of bright vertical striations.

Low concentrations of gelatin and 1.25 molar copper sulfate gave deposits with characteristic dots in place of the striations.

High concentrations of gelatin in general gave a deposit containing whitish spots, and the center of these whitish spots appeared to be a normal dot, so characteristic from low gelatin deposits.

Brand of gelatin caused variations only in the number of striations; the bacteriological and Coignet's gelatin making more striations, while Knox Sparkling gelatin and Eastman ash-free gelatin gave a minimum of markings.

Type of deposit might easily have been more a function of concentration of copper sulfate than of hydrogen ion concentration, especially since only comparatively small variations in pH occurred. And again, the pH is a function of the copper sulfate.

Time seemed to be only a subordinate factor, inasmuch as dots or striations formed within a half hour were only increased in size, and possibly only very slightly in number.

The Influence of Gelatin Upon the Cu/Cu^{++}
Electrode Potential

As described in the previous section of this thesis
the addition of gelatin to copper plating baths produce a
very marked effect upon the structure of the deposit. This
effect is not only of a qualitative nature, but is quanti-
tative as well. In a previous paper (loc.cit.) it was shown
that the weight of the cathode deposit in a copper sulfate
electrolyte containing gelatin was always heavier than when
no gelatin was present. It will be shown in another section
that this excess weight is chiefly gelatin.

There are three ways by which the gelatin might be re-
tained in the deposit. In these solutions the gelatin is
probably present as a large and complex cation, which, upon
electrolysis would migrate toward the cathode along with the
faster moving copper and hydrogen ions. When these gelatin
ions reach the cathode, the question arises as to whether
they are actually discharged or whether they migrate to the
cathode and stop mechanically.

The second alternative is mechanical occlusion. A
large gelatin ion or particle may migrate to the cathode,
and at the surface be entirely enclosed by depositing copper.

The third method by which the gelatin may be held is
adsorption by the newly formed crystal faces of copper. The

data which follows, tends to indicate that this last assumption is the correct one. To establish the validity of such an assumption let us reason as follows; the gelatin upon migration toward the cathode tends to accumulate at or near the cathode surface. The copper ions will proceed to the cathode and be discharged. The hydrogen ions from the hydrolysis of the copper sulfate will also migrate to the cathode, and if the potential is below a certain value they will simply accumulate in the cathode region. After electrolysis has continued for some time the concentration of gelatin in the vicinity of the cathode has increased the viscosity of the electrolyte, since gelatin solutions are very viscous as compared to water. Sulfates increase the gelation temperature of gelatin solutions. At the same time the gelatin concentration increases at the cathode, the copper ions adjacent to the cathode are discharged. The increased viscosity tends to make more difficult migration of the copper ions and the result is an increased copper electrode polarization. Bypolarization is understodd to mean the increase in electrode potential necessary to cause deposition of copper above that of the equilibrium potential, the equilibrium potential, E_q, being defined by the relation

$$E_q = E_0 + \frac{RT}{nF} \, Ln \, Cu^{++}.$$

If the reasoning is correct a study of this polarization occurring in the presence of gelatin should throw some light on the mechanism of the electrode process. The polarization of the Cu/Cu^{++} electrode for several concentrations of

gelatin and for various current densities were measured.
The method of polarization measurement was based upon the
ingenious but simple one of Haring[1].

Haring's cell consisted of a rectangular hard rubber
box some over 30 centimeters long and 10 centimeters cross
section. At a distance of 30 centimeters apart were two cop-
per plates which fit vertically into grooves in the cell.
Two copper gauzes were placed into the cell in grooves so
as to divide the cell into three compartments of lcubic
decimeter each. When the end copper plates were connected
with a source of direct current, and using a copper sulfate
electrolyte ordinary electrolysis took place with solution
and deposition of copper. It was feasible to measure the
potential drop from anode to gauze, gauze to gauze and from
gauze to cathode. The potential drop between the two gauzes
measured only the IR drop of the middle compartment. The
potential of either end compartment was the sum of two fac-
tors, the first of which was the ordinary IR drop of the
electrolyte and the second was that due to the dissolving
or deposition of the copper.

If now we measure the potential drop across these
three compartments we have the desired data for our polar-
ization study. The potential of the anode compartment is
the sum of the IR drop across that portion of the cell plus
the potential involved in dissolving the copper. Likewise

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[1] Haring, Trans. Am. Elec. Soc., 49, 417, 1926.

the potential of the cathode compartment is the sum of its
IR drop and the potential necessary to deposit the copper.
This latter potential, that is, that necessary to deposit
the copper, is the potential of polarization and is the quan-
tity we are about to measure.

The cell that was used in these experiments was a
modification of Haring's cell. The box was of wood and about
20 centimeters long by 2.6 centimeters in both width and
depth, all inside dimensions. These dimensions were chosen
so that the length of each compartment would be 5 centimet-
ers. After the box was given several thick coats of an inert
black tar paint, its cross section was very nearly 2.5 centi-
meters by 2.5 centimeters. Two copper sheet electrodes,
2.5 centimeters square were cemented with tar paint into
the cell, 15 centimeters apart. Also two 14 mesh copper
gauzes were cemented into the cell dividing it into three
equal compartments.

Potentials were measured with a potentiometer set,
the diagram of which is given in figure 12. Storage batter-
ies were used as the source of direct current. The potential
divider rheostat was one of the home-made type, using about
160 feet of a nichrome resistance wire. This wire was wound
on a cylindrical drum of 15 inch diameter and 20 inches long.

The capacity of the potentiometer was 2.3 volts, and
many occasions arose in which it was necessary to measure
potentials greater than this value. For this reason two
Leeds and Northrop resistances of 9999 ohms capacity were

POLARIZATION WIRING DIAGRAM
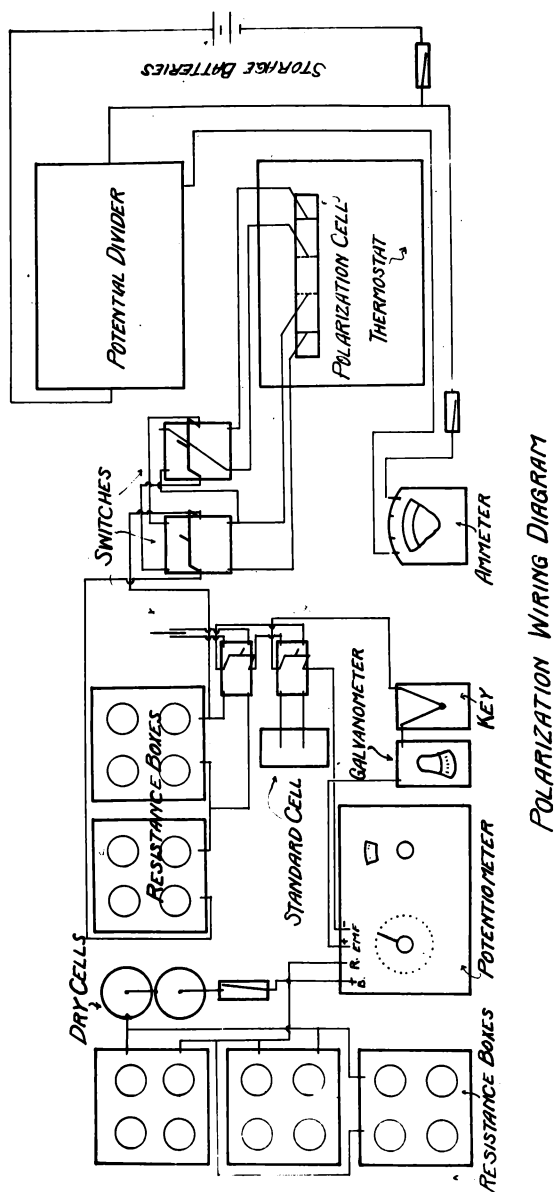
Figure 12.
Potentiometer Diagram

so placed in the circuit that one half the potential of
each cell was measured in place of the entire potential.
And in a few instances the resistance of one box was low-
ered to 4,999 ohms and the potential difference through that
portion of the circuit was measured giving one third the
e.m.f. of the cell.

With these several resistances in the circuit it was
possible that enough current flowed through them to lower
the equilibrium value of the potential. To check this point
a potential of about 2 volts was measured, then after insert-
ing the two resistance boxes at capacity, the half poten-
tial was measured. This latter value was found to be exactly
one half the former value. Then also check readings were
made occasionally when observing the 1/3 potentials. Those
potentials were found to be from .2 to .5 millivolt low.
Errors as small as these are negligible for polarization
measurements involving gelatin, hence the 1/3 potential
values were considered sufficiently accurate.

The polarization measurements were carried out briefly
as follows; the cell, having been previously cleaned was
placed in a glass tank air bath, at 25° Centigrade, plus
or minus $.1^\circ$. The wire connections to the outside circuit
were soldered into place. The electrolyte whose electrode
polarization was to be measured was poured into the cell
until the cell was level full, giving thereby a cross
sectional area of electrolyte very nearly to 6.25 square
centimeters. As soon as the temperature of the electrolyte

became 25°Centigrade the circuit was closed and measurements started. Within approximately one minute after the current began flowing the ammeter was steady at the desired current and polarization readings were taken in the order cathode, middle and anode compartments. After one minute was required in making these observations. Then from 2 to 3 minutes were allowed to elapse and another set of measurements taken. These latter values were frequently one or more millivolts different from the previous readings. Then another 2 or 3 minutes passed and a third set of readings taken. These too, differed from those previously taken. Immediately, then, a higher current was allowed to flow and other sets of readings taken. Measurements were made between current densities of 0.16 and 3.20 amperes per square decimeter.

Table 4 gives the data of the polarization measurements using .5 molar copper sulfate, no gelatin, pH of 3.32 at 25° Centigrade, and copper electrodes.

Table 5 gives also data of polarization measurements using 1/2 molar copper sulfate, no gelatin, pH of 3.32 at 25°Centigrade and copper electrodes. Tables 4 and 5 are results of duplicate experiments.

Table 6 gives the results of measurements using 1/2 molar copper sulfate, 1/2 per cent gelatin, pH = 3.38, at 25°Centigrade, and with copper electrodes.

Table 7 gives the data of measurements using 1/2 molar copper sulfate, .5 per cent gelatin, pH = 3.38 at 25° Centigrade, using copper electrodes. These data and those in Table 6 represent duplicate runs.

Table 4

0.5 Molar $CuSO_4$; No Gelatin; pH = 3.32; Cu Electrodes; T = 25.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F. Cathode Volts	Middle Volts	Anode Volts	Polarization Cathode Volts	Anode Volts
1	0.16	0.1403	0.1243	0.1282	0.0320	0.0078
5	0.16	0.1400	0.1250	0.1301	0.0300	0.0102
9	0.16	0.1387	0.1239	0.1292	0.0296	0.0106
10	0.32	0.2725	0.2513	0.2612	0.0414	0.0198
14	0.32	0.2720	0.2513	0.2617	0.0407	0.0208
18	0.32	0.2722	0.2518	0.2622	0.0408	0.0208
19	0.48	0.4042	0.3773	0.3921	0.0538	0.0296
23	0.48	0.4037	0.3764	0.3917	0.0546	0.0306
27	0.48	0.4038	0.3761	0.3914	0.0554	0.0306
28	0.64	0.5363	0.5013	0.5207	0.0700	0.0388
32	0.64	0.5364	0.5012	0.5210	0.0704	0.0396
36	0.64	0.5348	0.4985	0.5182	0.0726	0.0394
37	0.80	0.6706	0.6260	0.6496	0.0892	0.0472
41	0.80	0.6700	0.6270	0.6502	0.0860	0.0464
45	0.80	0.6691	0.6261	0.6485	0.0860	0.0648
46	0.96	0.8002	0.7502	0.7748	0.1000	0.0492
50	0.96	0.8008	0.7513	0.7757	0.0990	0.0488
54	0.96	0.8009	0.7511	0.7754	0.0996	0.0486
55	1.12	0.9321	0.8741	0.9000	0.1160	0.0518
59	1.12	0.9307	0.8721	0.8973	0.1172	0.0504
63	1.12	0.9299	0.8712	0.8962	0.1174	0.0500
64	1.28	1.0625	0.9956	1.0224	0.1338	0.0536
68	1.28	1.0602	0.9936	1.0204	0.1332	0.0536
72	1.28	1.0582	0.9920	1.0186	0.1324	0.0532
73	1.44	1.1864	1.1118	1.1403	0.1492	0.0570
77	1.44	1.1840	1.1098	1.1382	0.1484	0.0568
81	1.44	1.1830	1.1087	1.1369	0.1486	0.0564
82	1.60	1.3093	1.2266	1.2563	0.1654	0.0594
86	1.60	1.3077	1.2257	1.2548	0.1640	0.0582
90	1.60	1.3056	1.2243	1.2543	0.1626	0.0600
91	2.00	1.6336	1.5303	1.5643	0.2066	0.0680
95	2.00	1.6298	1.5271	1.5603	0.2054	0.0664
99	2.00	1.6290	1.5236	1.5591	0.2108	0.0710

Table 4 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
100	2.40	1.9506	1.8228	1.8614	0.2556	0.0772
104	2.40	1.9444	1.8170	1.8545	0.2548	0.0750
108	2.40	1.9398	1.8118	1.8508	0.2560	0.0780
109	2.80	2.2270	2.0773	2.1192	0.2994	0.0838
113	2.80	2.2191	2.0716	2.1135	0.2950	0.0838
117	2.80	2.2136	2.0663	2.1091	0.2946	0.0856
118	3.20	(1.6412) 2.4618	(1.5260) 2.2890	(1.5601) 2.3401	0.3456	0.1022
122	3.20	(1.6382) 2.4573	(1.5235) 2.2852	(1.5582) 2.3373	0.3442	0.1042
126	3.20	(1.6354) 2.4531	(1.5205) 1.2807	(1.5566) 2.3349	0.3448	0.1084

Table 5

0.5 Molar CuSO$_4$; No Gelatin; pH = 3.32; Cu Electrodes;
T = 25.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
2	0.16	0.1427	0.1218	0.1222	0.0418	0.0008
6	0.16	0.1415	0.1218	0.1231	0.0394	0.0026
8	0.16	0.1419	0.1232	0.1243	0.0374	0.0022
10	0.16	0.1419	0.1240	0.1248	0.0358	0.0016
13	0.32	0.2696	0.2431	0.2482	0.0530	0.0102
17	0.32	0.2696	0.2448	0.2497	0.0496	0.0098
21	0.32	0.2682	0.2446	0.2493	0.0472	0.0094
22	0.48	0.3992	0.3678	0.3768	0.0628	0.0180
26	0.48	0.3973	0.3674	0.3771	0.0598	0.0194
30	0.48	0.3962	0.3667	0.3776	0.0590	0.0218
31	0.64	0.5256	0.4890	0.5043	0.0732	0.0306
35	0.64	0.5245	0.4886	0.5048	0.0718	0.0324
39	0.64	0.5234	0.4882	0.5055	0.0704	0.0346
41	0.80	0.6570	0.6142	0.6353	0.0856	0.0422
45	0.80	0.6562	0.6142	0.6349	0.0840	0.0414
49	0.80	0.6551	0.6138	0.6345	0.0826	0.0414
50	0.96	0.7868	0.7378	0.7607	0.0980	0.0458
54	0.96	0.7861	0.7370	0.7597	0.0982	0.0454
58	0.96	0.7850	0.7360	0.7584	0.0980	0.0448
59	1.12	0.9116	0.8549	0.8798	0.1134	0.0498
63	1.12	0.9093	0.8531	0.8775	0.1124	0.0488
67	1.12	0.9078	0.8515	0.8759	0.1126	0.0488
68	1.28	1.0363	0.9721	0.9987	0.1284	0.0532
72	1.28	1.0342	0.9700	0.9967	0.1284	0.0534
76	1.28	1.0323	0.9678	0.9947	0.1290	0.0538
77	1.44	1.1595	1.0870	1.1155	0.1450	0.0570
81	1.44	1.1580	1.0855	1.1142	0.1450	0.0574
85	1.44	1.1565	1.0840	1.1129	0.1450	0.0578
86	1.60	1.2826	1.2018	1.2328	0.1616	0.0620
90	1.60	1.2814	1.2008	1.2316	0.1612	0.0616
94	1.60	1.2800	1.1992	1.2303	0.1616	0.0622

Table 5 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
95	2.00	1.5722	1.4730	1.5098	0.1984	0.0736
99	2.00	1.5727	1.4718	1.5072	0.2018	0.0708
103	2.00	1.5692	1.4676	1.5040	0.2032	0.0728
104	2.40	1.8628	1.7422	1.7832	0.2412	0.0820
108	2.40	1.8626	1.7406	1.7818	0.2440	0.0824
112	2.40	1.8598	1.7351	1.7782	0.2494	0.0862
113	2.80	2.1595	2.0158	2.0636	0.2874	0.0956
117	2.80	2.1595	2.0110	2.0600	0.2970	0.0980
121	2.80	2.1532	2.0029	2.0550	0.3006	0.1042
122	3.20	(1.6153 2.4229	2.2572	(1.5402) 2.3103	0.3314	0.1062
126	3.20	(1.6104 2.4156	2.2457	(1.5333) 3.2999	0.3398	0.1084
130	3.20	(1.5955) 2.3932	2.2200	(1.5137) 2.2805	0.3464	0.1210

Table 6

0.5 Molar CuSO$_4$; 0.5% Gelatin; pH = 3.38; Cu Electrodes;
T = 25.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
1	0.16	0.2093	0.1297	0.1336	0.1592	0.0078
5	0.16	0.2062	0.1272	0.1325	0.1580	0.0106
9	0.16	0.2070	0.1270	0.1328	0.1600	0.0116
10	0.32	0.3312	0.2518	0.2638	0.1588	0.0240
14	0.32	0.3270	0.2505	0.2620	0.1530	0.0230
18	0.32	0.3291	0.2511	0.2628	0.1560	0.0468
19	0.48	0.4748	0.3792	0.3963	0.1912	0.0342
23	0.48	0.4693	0.3783	0.3946	0.1820	0.0326
27	0.48	0.4643	0.3765	0.3923	0.1756	0.0316
28	0.64	0.6044	0.5040	0.5248	0.2008	0.0416
32	0.64	0.5977	0.5032	0.5235	0.1890	0.0406
36	0.64	0.5989	0.5003	0.5202	0.1972	0.0398
37	0.80	0.7384	0.6292	0.6528	0.2184	0.0472
41	0.80	0.7378	0.6300	0.6528	0.2156	0.0456
45	0.80	0.7357	0.6310	0.6532	0.2094	0.0444
46	0.96	0.9344	0.7558	0.7804	0.3572	0.0492
50	0.96	0.9334	0.7558	0.7806	0.3552	0.0496
54	0.96	0.9310	0.7552	0.7800	0.3516	0.0496
55	1.12	1.0707	0.8768	0.9031	0.3878	0.0526
59	1.12	1.0700	0.8772	0.9038	0.3856	0.0532
63	1.12	1.0680	0.8765	0.9033	0.3830	0.0536
64	1.28	1.2072	0.9997	1.0284	0.4150	0.0574
68	1.28	1.2041	0.9982	1.0272	0.4118	0.0580
72	1.28	1.2018	0.9973	1.0263	0.4090	0.0580
73	1.44	1.3380	1.1194	1.1505	0.4372	0.0622
77	1.44	1.3350	1.1176	1.1492	0.4348	0.0632
81	1.44	1.3325	1.1169	1.1486	0.4312	0.0634
82	1.60	1.4632	1.2348	1.2679	0.4568	0.0662
86	1.60	1.4596	1.2331	1.2660	0.4530	0.0658
90	1.60	1.4574	1.2319	1.2651	0.4510	0.0664
91	2.00	1.7698	1.5143	1.5516	0.5110	0.0756
95	2.00	1.7625	1.5104	1.5476	0.5042	0.0744
99	2.00	1.7596	1.5078	1.5459	0.5036	0.0762

Table 6 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
100	2.40	2.0627	1.7843	1.8258	0.5568	0.0830
104	2.40	2.0548	1.7789	1.8207	0.5518	0.0836
108	2.40	2.0520	1.7742	1.8191	0.5556	0.0898
109	2.80	(1.5772) 2.3658	2.0598	2.1113	0.6120	0.1030
113	2.80	(1.5733) 2.3599	2.0538	2.1079	0.6122	0.1082
117	2.80	(1.5707) 2.3560	2.0503	2.1064	0.6114	0.1022
118	3.20	(1.7354) 2.6031	2.2763	(1.5590) 2.3385	0.6536	0.1244
122	3.20	(1.7325) 2.5987	2.2730	(1.5580) 2.3370	0.6514	0.1280
126	3.20	(1.7290) 2.5935	2.2696	(1.5577) 2.3366	0.6478	0.1340

Table 7

0.5 Molar $CuSO_4$; 0.5% Gelatin; pH = 3.38; Cu Electrodes; T = 25.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F. Cathode Volts	Middle Volts	Anode Volts	Polarization Cathode Volts	Anode Volts
0	0.16	0.2054	0.1255	0.1272	0.1598	0.0034
5	0.16	0.2047	0.1228	0.1225	0.1638	-0.0006
9	0.16	0.2116	0.1266	0.1273	0.1700	0.0014
10	0.32	0.3208	0.2511	0.2537	0.1394	0.0052
14	0.32	0.3212	0.2513	0.2543	0.1398	0.0060
18	0.32	0.3204	0.2503	0.2523	0.1402	0.0040
19	0.48	0.4670	0.3783	0.3826	0.1774	0.0086
23	0.48	0.4612	0.3787	0.3822	0.1650	0.0070
27	0.48	0.4594	0.3780	0.3813	0.1628	0.0066
28	0.64	0.6028	0.5058	0.5115	0.1940	0.0114
32	0.64	0.5982	0.5048	0.5110	0.1870	0.0134
34	0.64	0.5963	0.5038	0.5107	0.1850	0.0138
35	0.80	0.7348	0.6293	0.6382	0.2100	0.0178
39	0.80	0.7302	0.6278	0.6372	0.2048	0.0188
43	0.80	0.7276	0.6248	0.6350	0.2056	0.0204
44	0.96	0.9320	0.7513	0.7627	0.3614	0.0228
48	0.96	0.9300	0.7476	0.7597	0.3648	0.0242
52	0.96	0.9268	0.7430	0.7567	0.3676	0.0274
53	1.12	1.0708	0.8663	0.8818	0.4090	0.0310
57	1.12	1.0675	0.8632	0.8795	0.4086	0.0326
61	1.12	1.0647	0.8608	0.8778	0.4078	0.0340
62	1.28	1.2044	0.9834	1.0015	0.4420	0.0362
66	1.28	1.2007	0.9807	0.9996	0.4400	0.0378
70	1.28	1.1975	0.9780	0.9979	0.4390	0.0398
71	1.44	1.3328	1.0979	1.1191	0.4698	0.0424
75	1.44	1.3270	1.0940	1.1158	0.4660	0.0436
79	1.44	1.3273	1.0910	1.1133	0.4726	0.0446
80	1.60	1.4640	1.2173	1.2414	0.4934	0.0482
84	1.60	1.4597	1.2145	1.2391	0.4904	0.0492
88	1.60	1.4552	1.2115	1.2372	0.4874	0.0514
89	2.00	1.7538	1.4800	1.5084	0.5476	0.0568
93	2.00	1.7451	1.4745	1.5050	0.5412	0.0610
97	2.00	1.7403	1.4715	1.5033	0.5376	0.0634

Table 7 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
98	2.40	2.0807	1.7785	1.8152	0.6044	0.0734
102	2.40	2.0710	1.7732	1.8113	0.5956	0.0762
106	2.40	2.0638	1.7688	1.8077	0.5900	0.0778
		(1.5642)				
107	2.80	2.3463	2.0248	2.0696	0.6430	0.0896
		(1.5580)				
111	2.80	2.3370	2.0183	2.0655	0.6374	0.0944
		(1.5527)				
115	2.80	2.3290	2.0097	2.0624	0.6386	0.1054
		(1.7378)		(1.5468)		
116	3.20	2.6066	2.2602	2.3212	0.6928	0.1220
		(1.7317)		(1.5449)		
120	3.20	2.5975	2.2546	2.3174	0.6858	0.1256
		(1.7259)		(1.5446)		
124	3.20	2.5888	2.2490	2.3169	0.6796	0.1358

The data in Tables 4, 5, 6 and 7 are shown graphically in Plate I.

The two curves nearer the vertical axis represent data contained in Tables 4 and 5, and are the polarization curves of the copper sulfate electrolyte which contained no gelatin. At the origin of these curves a little overvoltage phenomenon presents itself, but other than this deviation the relation of potential to current density is very nearly a straight line function. The larger part of this polarization is concentration polarization. This concentration polarization is the result of the reduction of the concentration of cupric ions in the immediate vicinity of the cathode. The copper sulfate electrolyte is comparatively fluid and convection currents keep a partial supply of cupric ions. For this reason the cathode polarization is only a small fraction of a volt. The duplicate curves are in very good agreement.

The two remaining curves represent the polarization of the cathode from 1/2 molar copper sulfate solution containing 1/2 per cent gelatin, at 25°Centigrade and a pH of 3.38. These curves are quite different than the two from the electrolyte which contained no gelatin. When the first current was passed through the solutions it appeared to be comparatively difficult to get the continuous deposition of copper. The nearly horizontal portion beginning at the origin indicates that it takes a higher potential to force 0.16 amperes per square decimeter through the cell than when no gelatin is present. This increase in potential, without
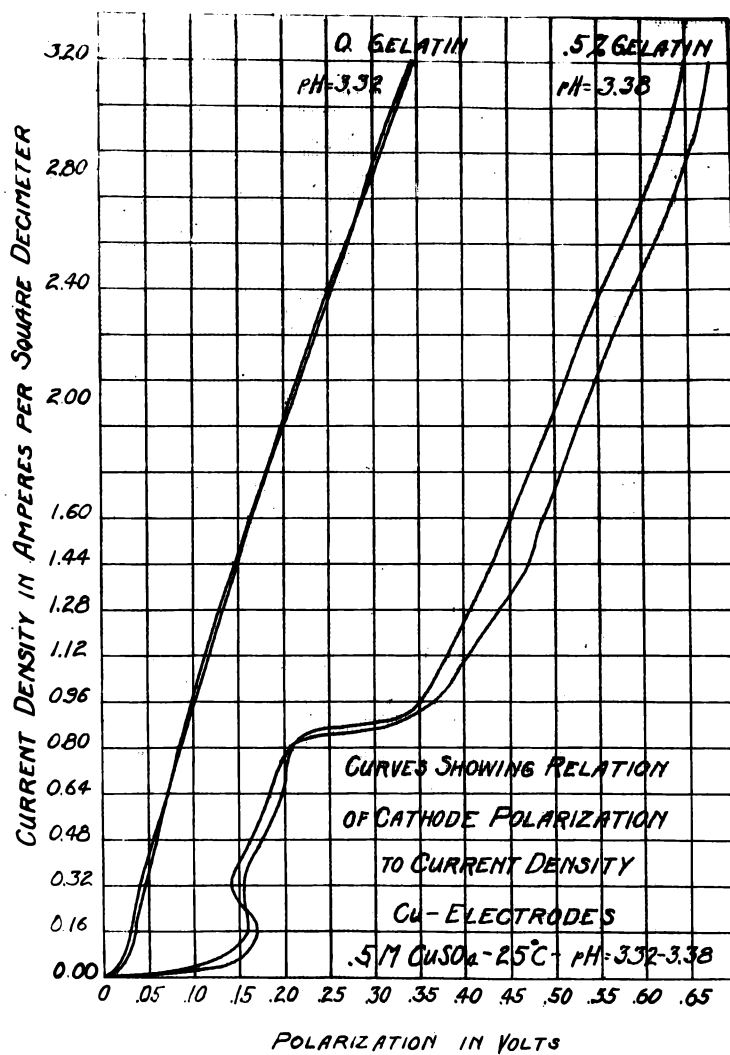
Plate I
Polarization Measurements

doubt, is due to the gelatin solution having a greater viscosity in the cathode region. Once deposition is started, the increase of the current density from 0.16 to 0.32 amperes per square decimeter, involves no increase in potential, in fact, there appears to be a slight decrease.

For several further increases in current density the increase in potential seems to be nearly straight line function, then at a current density of 0.8 amperes, there is a sudden break. This break in the curve again indicates that for a small increase in current density there is a marked increase in the potential necessary to force the current through the electrolyte near the cathode. And again the curves assume their straight line trend.

The ordinary interpretation of potential curves similar to these would be that two static and two dynamic decomposition potentials existed. Decomposition potentials involve measurements of potential across the entire cell, while this work consisted in measuring the potential of polarization. The method is based upon the assumption that a copper gauze which allows free mixing and circulation of the electrolyte, serves as a non-polarized electrode. Hence the potential drop between this non-polarized electrode and the ordinary cathode of the electrolytic cell gives us a value which is the sum of two factors. The first is the IR drop through a certain quantity of the electrolyte and the second is the electrode polarization.

In our polarization curves resulting from measurements

of electrode polarization, we might interpret the abrupt break in the curves from copper sulfate solutions containing gelatin at a current density of 0.8 amperes to indicate a change in electrode process.

In a copper sulfate electrolyte with copper electrodes the only possible reactions are reduction of cupric to cuprous, and the farther reduction of cuprous to the metal, and direct reduction of cupric to the metal. With an ion that is as easily reduced as the cupric, it does not appear reasonable that its reduction should take place through the intermediate cuprous. If partial reduction took place, or in other words if two electrode processes were involved, one above and one below 0.8 amperes current density, then the weights of deposits obtained from current densities of say, .64 and 1.12 amperes, with the same quantities of electricity should be quite different from one another. In another section of this thesis it will be shown from plotted data that the weight of cathode deposit varies uniformly with current densities; and there is no abrupt increase or decrease in the weight of the deposit in the vicinity of 0.80 amperes current density.

From the curvature of the lower segment of the curves and the upper portions, it is obvious that smooth and continuous curves could be drawn. We believe, however, that if gelatin were an emulsoid that did not jel, the portions of the two curves from 0.16 to 0.96 amperes would not exist as they do, and the resulting curves would be very regular.

If these curves actually existed the cathode polarization might be nearly as simple as ordinary concentration polarization.

With such irregular portion in the curve, it remains for these irregularities to be explained. It is reasonable to consider work should be involved in the deposition of the first copper in the presence of the gelatin. Once the ions are moving and deposition has started it does not take much more work to force more current through the electrolyte. In fact there is not much increase in polarization until beyond 0.80 amperes current density. Then apparently due to the more rapid depletion of cupric ions from the electrolyte in the immediate vicinity of the cathode, the tendency is to increase polarization. Increases in polarization are also assisted by the relatively small cathode area which is in contact with the electrolyte; only one side of the cathode is in contact with the solution. The most important factor in this increase in polarization is that during all the time previous gelatin has been accumulating near the cathode, gelation has occurred, and the copper ions have still more difficulty in passing through the solid, hence out increase in largely mechanical polarization. Then at 0.96 amperes the cupric ions apparently penetrated the gel, due to increased voltage. It is possible, also, that the heat of deposition, and the heat effects during migration, might assist at this higher current density to keep the gelatin solution at least partially fluid. When this fluidity exists

polarization increases uniformly with increasing current density.

Tables 8 and 9 contain data of polarization experiments similar to that contained in Tables 4 and 5, with the exception that platinum cathodes and copper plated platinum anodes were used in place of the copper electrodes. The electrolytes contained no gelatin.

Tables 10 and 11 contain data similar to that in Tables 6 and 7, except that platinum cathodes and copper platinum anodes were employed. These electrolytes contained 1/2 per cent gelatin.

Plate II shows graphically the results in the four preceding tables. The two duplicate polarization curves from the electrolytes which contained no gelatin are very similar to the corresponding ones on Plate I. The anode was given a heavy plate of copper in such a manner that no platinum was in contact with the electrolyte. The cathode surfaces, of course, were different.

The two curves representing the polarization of the pure copper sulfate electrolyte are very similar to those of the previous plate. The rounded portions of the duplicate curves represents the potential necessary to cause deposition of the first copper, or an overvoltage effect as it is called. Beyond this point the two curves are very nearly straight lines. At the current density of 3.20 amperes per square decimeter the polarization is 0.28 volts as compared to 0.34 volts when the copper electrodes were used. This variation

Table 8

0.5 Molar $CuSO_4$; 0.0% Gelatin; pH = 3.33; Pt Cathode; T = 25.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F. Cathode Volts	Middle Volts	Anode Volts	Polarization Cathode Volts	Anode Volts
0	0.16	0.1490	0.1253	0.1506	0.0424	0.0106
3	0.16	0.1466	0.1272	0.1530	0.0388	0.0116
6	0.16	0.1477	0.1298	0.1350	0.0358	0.0104
9	0.16	0.1467	0.1291	0.1341	0.0352	0.0100
12	0.16	0.1467	0.1280	0.1331	0.0374	0.0102
14	0.32	0.2828	0.2565	0.2662	0.0526	0.0194
18	0.32	0.2792	0.2558	0.2638	0.0468	0.0160
22	0.32	0.2772	0.2552	0.2620	0.0440	0.0136
24	0.48	0.4175	0.3890	0.3994	0.0570	0.0208
28	0.48	0.4150	0.3881	0.3981	0.0528	0.0200
32	0.48	0.4135	0.3875	0.3972	0.0520	0.0194
34	0.64	0.5506	0.5184	0.5307	0.0648	0.0246
38	0.64	0.5492	0.5185	0.5300	0.0614	0.0230
42	0.64	0.5484	0.5181	0.5299	0.0606	0.0236
44	0.80	0.6868	0.6501	0.6638	0.0734	0.0274
48	0.80	0.6862	0.6495	0.6631	0.0734	0.0272
52	0.80	0.6853	0.6492	0.6630	0.0722	0.0276
54	0.96	0.8198	0.7772	0.7932	0.0852	0.0320
58	0.96	0.8192	0.7762	0.7923	0.0860	0.0322
62	0.96	0.8185	0.7758	0.7915	0.0854	0.0314
63	1.12	0.9524	0.9028	0.9205	0.0992	0.0354
67	1.12	0.9515	0.9018	0.9192	0.0994	0.0348
71	1.12	0.9507	0.9011	0.9183	0.0992	0.0344
72	1.28	1.0846	1.0279	1.0467	0.1154	0.0376
76	1.28	1.0838	1.0268	1.0459	0.1140	0.0382
80	1.28	1.0831	1.0258	1.0452	0.1146	0.0388
81	1.44	1.2113	1.1472	1.1683	0.1282	0.0422
85	1.44	1.2101	1.1455	1.1667	0.1294	0.0424
89	1.44	1.2093	1.1445	1.1658	0.1296	0.0426
90	1.60	1.3428	1.2702	1.2936	0.1452	0.0468
94	1.60	1.3408	1.2685	1.2912	0.1450	0.0458
98	1.60	1.3400	1.2673	1.2900	0.1454	0.0454

Table 8 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
102	2.00	1.671	1.584	1.611	(.1740)	0.054
106	2.00	1.6507	1.5597	1.5852	0.1820	0.0510
110	2.00	1.6493	1.5576	1.5835	0.1834	0.0518
111	2.40	1.9420	1.8326	1.8622	0.2188	0.0592
115	2.40	1.9367	1.8281	1.8577	0.2172	0.0592
119	2.40	1.9335	1.8252	1.8547	0.2166	0.0590
120	2.80	2.2294	2.1031	2.1368	0.2526	0.0674
124	2.80	2.2231	2.0978	2.1312	0.2506	0.0668
123	2.80	2.2188	2.0940	2.1281	0.2496	0.0682
129	3.20	(1.6868) 2.5302	(1.5908) 2.3862	(1.6163) 2.4244	0.2880	0.0764
133	3.20	(1.6813) 2.5219	(1.5867) 2.3800	(1.6157) 2.4235	0.2833	0.0870
137	3.20	(1.6771) 2.5156	(1.5830) 2.3745	(1.6102) -2.4153	0.2822	0.0816

Table 9

0.5 Molar CuSO$_4$; 0.0% Gelatin; pH = 3.33; Pt Cathode;
T = 25.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
1	0.16	0.1455	0.1200	0.1220	0.0490	0.0040
5	0.16	0.1348	0.1181	0.1202	0.0334	0.0042
9	0.16	0.1404	0.1223	0.1253	0.0362	0.0060
13	0.16	0.1405	0.1227	0.1251	0.0356	0.0048
14	0.32	0.2722	0.2494	0.2548	0.0456	0.0108
18	0.32	0.2680	0.2436	0.2507	0.0438	0.0142
22	0.32	0.2663	0.2432	0.2495	0.0462	0.0126
23	0.48	0.3976	0.3681	0.3775	0.0590	0.0188
27	0.48	0.3968	0.3681	0.3768	0.0574	0.0174
31	0.48	0.3968	0.3687	0.3773	0.0562	0.0172
32	0.64	0.5265	0.4912	0.5018	0.0706	0.0212
36	0.64	0.5261	0.4912	0.5015	0.0698	0.0208
40	0.64	0.5252	0.4910	0.5012	0.0684	0.0204
41	0.80	0.6581	0.6162	0.6285	0.0838	0.0246
45	0.80	0.6577	0.6165	0.6289	0.0824	0.0248
49	0.80	0.6561	0.6159	0.6281	0.0804	0.0244
50	0.96	0.7878	0.7398	0.7540	0.0960	0.0284
54	0.96	0.7856	0.7378	0.7519	0.0956	0.0282
59	0.96	0.7853	0.7381	0.7523	0.0944	0.0284
60	1.12	0.9106	0.8558	0.8720	0.1096	0.0324
64	1.12	0.9098	0.8553	0.8717	0.1090	0.0328
68	1.12	0.9090	0.8546	0.8711	0.1088	0.0330
69	1.28	1.0413	0.9792	0.9977	0.1242	0.0370
73	1.28	1.0390	0.9773	0.9961	0.1234	0.0376
77	1.28	1.0377	0.9762	0.9950	0.1230	0.0376
79	1.44	1.1632	1.0934	1.1143	0.1396	0.0418
83	1.44	1.1602	1.0901	1.1121	0.1402	0.0440
87	1.44	1.1583	1.0877	1.1103	0.1412	0.0452
88	1.60	1.2868	1.2078	1.2332	0.1580	0.0508
92	1.60	1.2844	1.2059	1.2316	0.1570	0.0514
96	1.60	1.2825	1.2042	1.2303	0.1566	0.0522

Table 9 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
97	2.00	1.5655	1.4691	1.5000	0.1928	0.0618
111	2.00	1.5609	1.4662	1.4978	0.1894	0.0632
115	2.00	1.5578	1.4643	1.4966	0.1870	0.0646
116	2.40	1.8779	1.7650	1.8032	0.2258	0.0764
120	2.40	1.8719	1.7608	1.8003	0.2222	0.0790
124	2.40	1.8672	1.7574	1.7987	0.2196	0.0826
125	2.80	2.1802	2.0519	2.0995	0.2566	0.0952
129	2.80	2.1742	2.0474	2.0970	0.2536	0.0992
133	2.80	2.1686	2.0429	2.0950	0.2514	0.1042
134	3.20	(1.6075) 2.4112	(1.5144) 2.2695	(1.5532) 2.3298	0.2834	0.1204
138	3.20	(1.6033) 2.4049	(1.5117) 2.2675	(1.5515) 2.3272	0.2748	0.1194
142	3.20	(1.5993) 2.3989	(1.5085) 2.2637	(1.5500) 2.3250	0.2704	0.1226

Table 10

0.5 Molar $CuSO_4$; 0.5% Gelatin; pH = 3.38; Pt. Cathode;
T = 25.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F. Cathode Volts	Middle Volts	Anode Volts	Polarization Cathode Volts	Anode Volts
2	0.16	0.2000	0.1347	0.1533	0.1306	0.0372
5	0.16	0.2004	0.1355	0.1508	0.1298	0.0306
9	0.16	0.2030	0.1335	0.1491	0.1390	0.0312
13	0.16	0.2067	0.1316	0.1472	0.1502	0.0312
16	0.32	0.3418	0.2600	0.2838	0.1636	0.0476
20	0.32	0.3418	0.2612	0.2822	0.1612	0.0420
23	0.48	0.4719	0.3890	0.4145	0.1658	0.0510
27	0.48	0.4712	0.3895	0.4129	0.1634	0.0468
31	0.48	0.4700	0.3897	0.4123	0.1606	0.0452
33	0.64	0.6112	0.5198	0.5452	0.1828	0.0508
37	0.64	0.6078	0.5206	0.5440	0.1744	0.0468
41	0.64	0.6054	0.5208	0.5443	0.1692	0.0470
43	0.80	0.7444	0.6484	0.6741	0.1920	0.0514
47	0.80	0.7401	0.6488	0.6735	0.1826	0.0494
51	0.80	0.7377	0.6481	0.6735	0.1792	0.0508
53	0.96	0.9455	0.7775	0.8040	0.3360	0.0530
57	0.96	0.9434	0.7772	0.8035	0.3324	0.0526
61	0.96	0.9414	0.7767	0.8038	0.3294	0.0542
65	1.12	1.0877	0.9015	0.9308	0.3724	0.0586
69	1.12	1.0864	0.9007	0.9308	0.3714	0.0602
72	1.12	1.0847	0.8994	0.9306	0.3706	0.0624
74	1.28	1.2293	1.0273	1.0606	0.4040	0.0666
78	1.28	1.2277	1.0266	1.0597	0.4022	0.0662
82	1.28	1.2258	1.0256	1.0593	0.4004	0.0674
84	1.44	1.3691	1.1546	1.1904	0.4290	0.0716
88	1.44	1.3668	1.1532	1.1886	0.4272	0.0708
92	1.44	1.3648	1.1516	1.1879	0.4264	0.0726
94	1.60	1.5022	1.2778	1.3162	0.4488	0.0768
98	1.60	1.4992	1.2766	1.3158	0.4452	0.0784
102	1.60	1.4977	1.2761	1.3152	0.4432	0.0782
104	2.00	1.8351	1.5858	1.6296	0.4986	0.0920
108	2.00	1.8303	1.5836	1.6263	0.4934	0.0854
112	2.00	1.8263	1.5813	1.6247	0.4900	0.0868

Table 10 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
114	2.40	2.1191	1.8522	1.8993	0.5538	0.0942
118	2.40	2.1140	1.8497	1.8966	0.5266	0.0938
122	2.40	2.1091	1.8463	1.8939	0.5254	0.0952
124	2.80	(1.5980) 2.3970	2.1145	2.1657	0.5650	0.1024
128	2.80	(1.5941) 2.3911	2.1108	2.1625	0.5606	0.1034
132	2.80	(1.5911) 2.3866	2.1073	2.1606	0.5586	0.1066
134	3.20	(1.8030) 2.7043	(1.6028) 2.4042	(1.6412) 2.4618	0.6002	0.1152
138	3.20	(1.7978) 2.6967	(1.5997) 2.3995	(1.6378) 2.4567	0.5944	0.1144
142	3.20	(1.7943) 2.6914	(1.5980) 2.3970	(1.6363) 2.4544	0.5888	0.1148

Table 11

0.5 Molar CuSO$_4$; 0.5% Gelatin; pH = 3.39; Pt Cathode;
T = 25.0° C.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
1	0.16	0.1985	0.1353	0.1472	0.1264	0.0238
5	0.16	0.1982	0.1336	0.1450	0.1292	0.0228
9	0.16	0.2000	0.1328	0.1432	0.1344	0.0208
11	0.32	0.3540	0.2687	0.2882	0.1706	0.0340
15	0.32	0.3400	0.2601	0.2801	0.1598	0.0400
17	0.48	0.4794	0.3957	0.4217	0.1674	0.0520
21	0.48	0.4779	0.3958	0.4216	0.1642	0.0516
25	0.48	0.4757	0.3957	0.4218	0.1600	0.0522
27	0.64	0.6161	0.5286	0.5579	0.1750	0.0586
31	0.64	0.6131	0.5291	0.5577	0.1680	0.0572
35	0.64	0.6100	0.5292	0.5577	0.1616	0.0570
37	0.80	0.7500	0.6617	0.6926	0.1766	0.0618
41	0.80	0.7482	0.6617	0.6921	0.1730	0.0608
45	0.80	0.7453	0.6612	0.6922	0.1682	0.0620
47	0.96	0.9408	0.7841	0.8166	0.3134	0.0650
51	0.96	0.9385	0.7841	0.8161	0.3088	0.0640
55	0.96	0.9364	0.7836	0.8158	0.2856	0.0644
57	1.12	1.0901	0.9121	0.9467	0.3560	0.0692
61	1.12	1.0885	0.9114	0.9454	0.3542	0.0680
65	1.12	1.0864	0.9104	0.9448	0.3520	0.0688
67	1.28	1.2293	1.0372	1.0738	0.3842	0.0732
71	1.28	1.2268	1.0359	1.0721	0.3818	0.0724
75	1.28	1.2242	1.0348	1.0714	0.3788	0.0732
77	1.44	1.3662	1.1633	1.2018	0.4058	0.0770
81	1.44	1.3634	1.1622	1.2002	014024	0.0760
85	1.44	1.3602	1.1608	1.1933	0.3988	0.0650
87	1.60	1.4853	1.2752	1.3156	0.4202	0.0808
91	1.60	1.4837	1.2741	1.3139	0.4192	0.0796
95	1.60	1.4801	1.2727	1.3129	0.4148	0.0804
97	2.00	1.7989	1.5660	1.6107	0.4658	0.0894
101	2.00	1.7938	1.5630	1.6072	0.4616	0.0884
105	2.00	1.7902	1.5607	1.6053	0.4590	0.0892

Table 11 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
107	2.40	2.1159	1.8636	1.9131	0.5046	0.0990
111	2.40	2.1086	1.8587	1.9071	0.4998	0.0968
115	2.40	2.1021	1.8540	1.9031	0.4962	0.0982
117	2.80	(1.5948) 2.3922	2.1250	2.1790	0.5304	0.1080
121	2.80	(1.5882) 2.3823	2.1170	2.1717	0.5306	0.1094
125	2.80	(1.5845) 2.3767	2.1124	2.1685	0.5286	0.1122
127	3.20	(1.7655) 2.6482	(1.5775) 2.3662	(1.6186) 2.4279	0.5640	0.1234
131	3.20	(1.7596) 2.6394	(1.5732) 2.3598	(1.6143) 2.4214	0.5554	0.1222
135	3.20	(1.7546) 2.6319	(1.5688) 2.3532	(1.6122) 2.4183	0.5574	0.1302

Plate II
Polarization Measurements

69
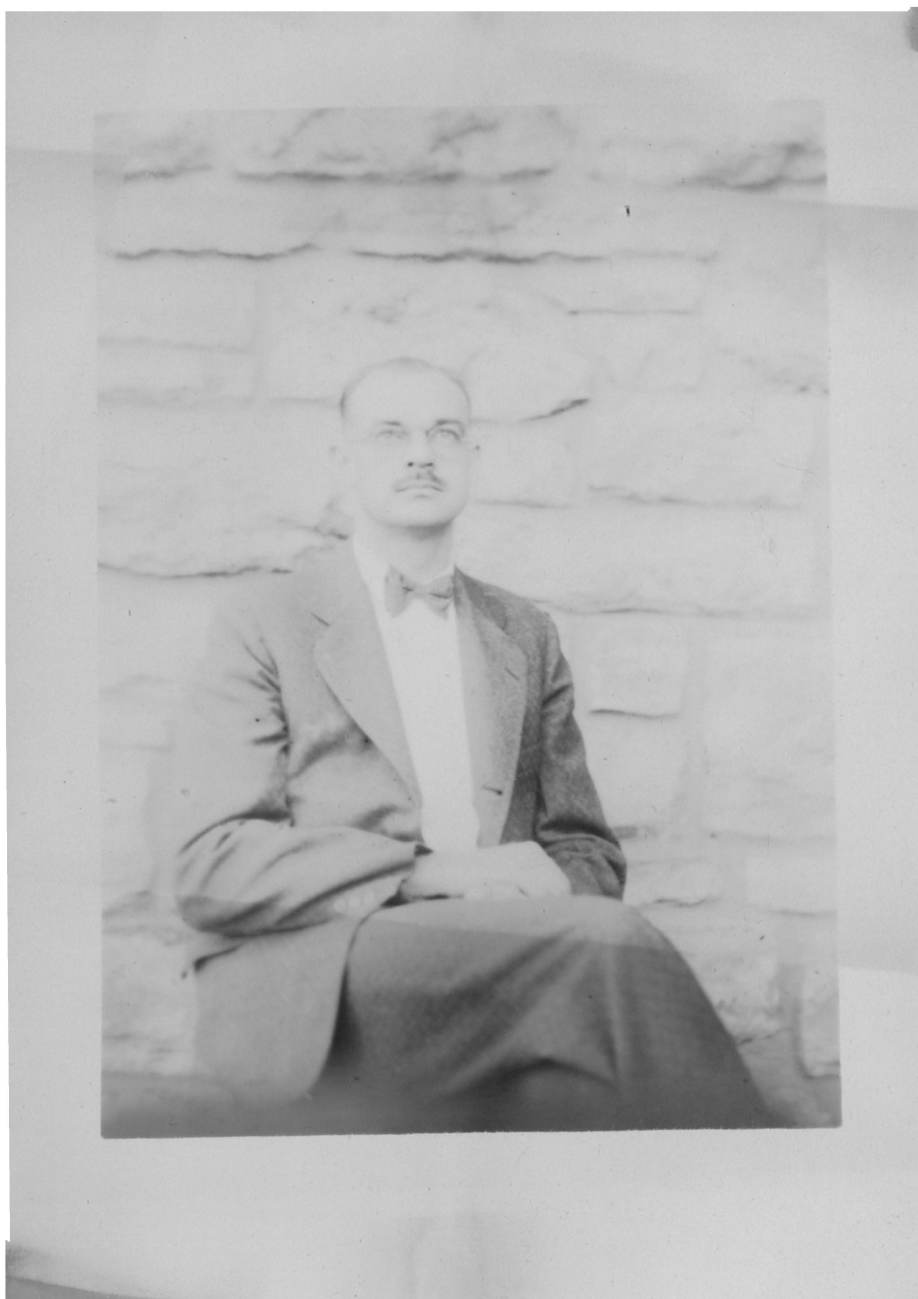
of the two sets of curves seemed to be proportional to the distance from the origin.

The duplicate curves representing the polarization of the Cu/Cu^{++} electrode are quite similar, also, to the two corresponding curves previously described, which contained gelatin. They show approximately the same beginning polarization, although a little less; they have the same region of nearly constant polarization, then the polarization increases very rapidly again at 0.80 amperes, and from 0.96 amperes on the polarization is again very nearly a straight line function. These two curves from the platinum electrode experiments also lie to the left of the corresponding experiments using copper electrodes. Whether or not this latter point has any significance cannot be said, because in either case after electrolysis has begun the nature of the cathodes then is the same, or very nearly so.

These two curves from the gelatin polarization also could be drawn very smoothly if the points at 0.16 and 0.96 current densities were connected by a nearly straight line. The deviation of the actual curves from the very smooth hypothetical one shows again the effect of the gelatin's being a colloid of the type which solidifies to a gel under the proper conditions.

From the curves it is a simple matter to determine the polarization due to the presence of the gelatin. If we assume that the polarization shown by the Cu/Cu^{++} electrode using pure copper sulfate electrolyte as concentration pol-

arization only, than at any current density the difference
between two corresponding polarization values should be the
polarization due to the presence of the gelatin, or as it
is called, mechanical polarization.

A series of experiments was made in which not only
was the current density varied, but also hydrogen ion con-
centration and percentage of gelatin in the 1/2 molar cop-
per sulfate electrolyte. The runs were not all made at a
constant temperature, since the polarization cell was not
placed in a thermostat. In these experiments a copper plated
anode was used and a platinum cathode.

The first polarization measurements in this series
was made on the 1/2 molar copper sulfate electrolyte contain-
ing no gelatin. The hydrogen ion concentration was pH = 3.33,
which value was the pH of the copper sulfate solution as pre-
pared. The laboratory temperature during this run was 28.5^0
Centigrade; Table 12 shows the data and this data is plot-
ted on Plate III.

A run was now made under very nearly the same condit-
ions as the one just previously with the exception that the
temperature was slightly lower, 24^0Centigrade, and the pH
was adjusted by the addition of a few drops of a dilute
sulfuric acid solution, to 2.0. Table 13 shows the polariz-
ation measurements made under these conditions, and the res-
ults plotted on Plate III.

These two curves representing the polarization of
1/2 molar copper sulfate solution which contains no gelatin,

Table 12

0.5 Molar $CuSO_4$;   0.0% Gelatin;   pH = 3.33;   Pt Cathode;
T = 28.5°C.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
4	0.16	0.1346	0.1138	0.1177	0.0416	0.0078
8	0.16	0.1340	0.1142	0.1181	0.0396	0.0078
12	0.16	0.1334	0.1142	0.1182	0.0384	0.0080
17	0.16	0.1333	0.1144	0.1183	0.0378	0.0078
21	0.32	0.2529	0.2248	0.2325	0.0562	0.0154
25	0.32	0.2524	0.2250	0.2329	0.0548	0.0158
29	0.32	0.2519	0.2253	0.2331	0.0532	0.0156
34	0.48	0.3771	0.3417	0.3536	0.0708	0.0238
38	0.48	0.3767	0.3417	0.3537	0.0700	0.0240
42	0.48	0.3764	0.3419	0.3538	0.0690	0.0238
44	0.64	0.5017	0.4573	0.4732	0.0888	0.0318
48	0.64	0.5018	0.4571	0.4730	0.0894	0.0318
52	0.64	0.5017	0.4570	0.4730	0.0894	0.0320
55	0.80	0.6256	0.5707	0.5903	0.1098	0.0392
59	0.80	0.6258	0.5703	0.5900	0.1110	0.0394
63	0.80	0.6257	0.5702	0.5887	0.1110	0.0370
66	0.96	0.7487	0.6824	0.7050	0.1326	0.0452
70	0.96	0.7488	0.6820	0.7042	0.1336	0.0444
74	0.96	0.7487	0.6821	0.7038	0.1332	0.0434
77	1.12	0.8678	0.7908	0.8151	0.1540	0.0486
81	1.12	0.8675	0.7903	0.8144	0.1544	0.0482
85	1.12	0.8671	0.7901	0.8137	0.1540	0.0472
88	1.28	0.9870	0.8992	0.9253	0.1756	0.0522
92	1.28	0.9865	0.8986	0.9248	0.1758	0.0524
96	1.28	0.9862	0.8982	0.9240	0.1760	0.0516
99	1.44	1.1053	1.0046	1.0332	0.1974	0.0572
103	1.44	1.1024	1.0039	1.0325	0.1970	0.0568
107	1.44	1.1016	1.0031	1.0315	0.1970	0.0568
110	1.60	1.2198	1.1108	1.1414	0.2180	0.0612
114	1.60	1.2187	1.1099	1.1402	0.2176	0.0606
118	1.60	1.2175	1.1090	1.1389	0.2170	0.0598

Table 12 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
122	2.00	1.4899	1.3562	1.3919	0.2674	0.0714
126	2.00	1.4890	1.3552	1.3906	0.2676	0.0708
130	2.00	1.4877	1.3541	1.3890	0.2672	0.0698
132	2.40	1.7850	1.6244	1.6652	0.3212	0.0816
136	2.40	1.7823	1.6228	1.6638	0.3190	0.0820
140	2.40	1.7806	1.6207	1.6613	0.3198	0.0812
143	2.80	2.0603	1.8743	1.9204	0.3720	0.0852
147	2.80	2.0591	1.8723	1.9169	0.3736	0.0892
151	2.80	2.0558	1.8709	1.9161	0.3698	0.0904
154	3.20	2.2820	2.0765	2.1261	0.4110	0.0992
158	3.20	2.2804	2.0748	2.1236	0.4112	0.0976
162	3.20	2.2798	2.0737	2.1222	0.4122	0.0970

No.	%CuCl	pH	Temp
1	0	2.00	28.5
2	0	3.33	28.5
3	.1	3.32	23
4	.1	2.00	LAB
5	.5	1.98	25
6	.5	3.34	25
7	1.5	1.99	LAB
8	1.5	3.42	LAB

CURRENT DENSITY IN AMPERES PER SQUARE DECIMETER

CURVES SHOWING RELATION OF CATHODE POLARIZATION TO CURRENT DENSITY Pt. ELECTRODES .5 M CuSO₄

POLARIZATION IN VOLTS
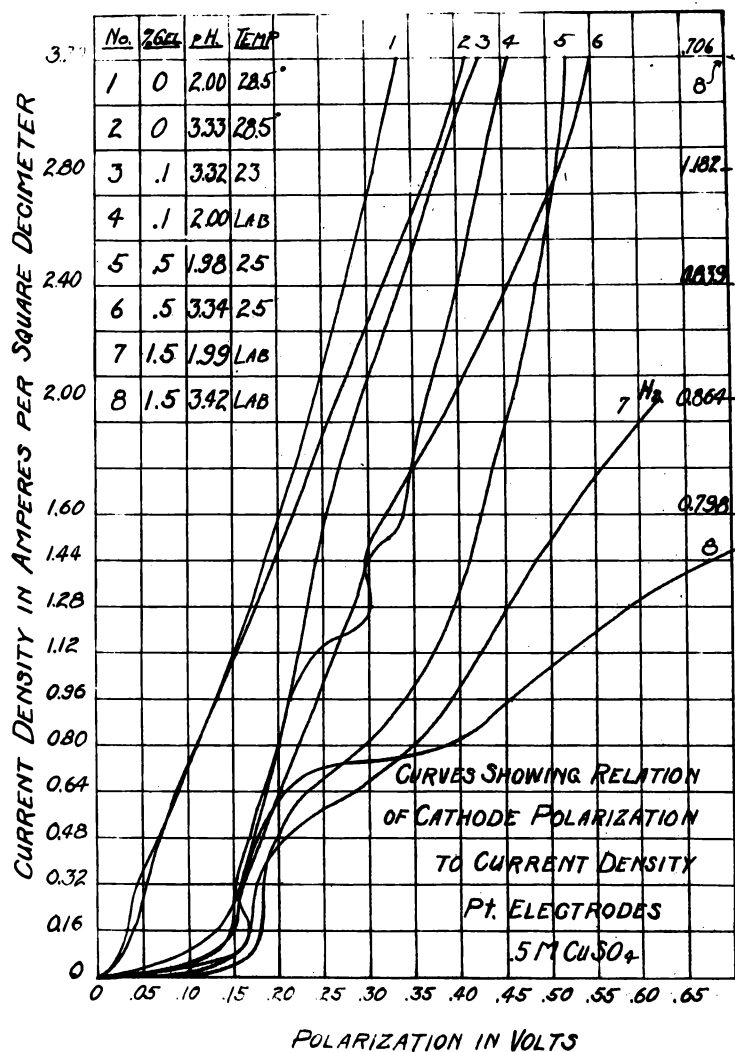
Plate III
Polarization Measurements

Table 13

0.5 Molar $CuSO_4$;   0.0% Gelatin;   pH = 2.0;   Pt Cathode;
T = 24.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F. Cathode Volts	Middle Volts	Anode Volts	Polarization Cathode Volts	Anode Volts
1	0.16	0.1225	0.1030	0.0990	0.0380	-0.0080
5	0.16	0.1210	0.1033	0.0993	0.0354	-0.0080
9	0.16	0.1202	0.1035	0.0996	0.0334	-0.0078
13	0.16	0.1199	0.1035	0.1000	0.0328	-0.0070
16	0.32	0.2338	0.2100	0.2067	0.0476	-0.0066
20	0.32	0.2332	0.2102	0.2072	0.0460	-0.0060
24	0.32	0.2329	0.2104	0.2075	0.0450	0.0058
26	0.48	0.3495	0.3171	0.3138	0.0648	-0.0066
30	0.48	0.3495	0.3167	0.3144	0.0656	-0.0046
34	0.48	0.3497	0.3165	0.3148	0.0664	-0.0034
36	0.64	0.4702	0.4259	0.4242	0.0886	-0.0034
40	0.64	0.4702	0.4260	0.4248	0.0884	-0.0024
44	0.64	0.4701	0.4262	0.4255	0.0878	-0.0014
46	0.80	0.5955	0.5398	0.5390	0.1114	-0.0018
50	0.80	0.5957	0.5397	0.5393	0.1120	-0.0008
54	0.80	0.5954	0.5397	0.5398	0.1114	0.0002
56	0.96	0.7193	0.6519	0.6524	0.1348	0.0010
60	0.96	0.7190	0.6516	0.6525	0.1348	0.0018
64	0.96	0.7184	0.6515	0.6530	0.1338	0.0030
67	1.12	0.8334	0.7563	0.7584	0.1542	0.0042
71	1.12	0.8332	0.7558	0.7587	0.1548	0.0058
75	1.12	0.8321	0.7555	0.7589	0.1532	0.0068
77	1.28	0.9501	0.8624	0.8669	0.1754	0.0090
81	1.28	0.9485	0.8620	0.8668	0.1730	0.0096
85	1.28	0.9471	0.8617	0.8669	0.1708	0.0104
88	1.44	1.0573	0.9625	0.9686	0.1896	0.0122
92	1.44	1.0562	0.9623	0.9686	0.1878	0.0126
96	1.44	1.0544	0.9617	0.9686	0.1854	0.0138
98	1.60	1.1694	1.0664	1.0743	0.2060	0.0158
102	1.60	1.1670	1.0655	1.0740	0.2030	0.0170
106	1.60	1.1653	1.0645	1.0738	0.2016	0.0186

Table 13 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
109	2.00	1.4338	1.3100	1.3212	0.2476	0.0224
113	2.00	1.4300	1.3084	1.3200	0.2452	0.0232
117	2.00	1.4270	1.3068	1.3192	0.2404	0.0248
119	2.40	1.6935	1.5522	1.5671	0.2826	0.0298
123	2.40	1.6887	1.5492	1.5648	0.2790	0.0312
127	2.40	1.6850	1.5468	1.5631	0.2764	0.0326
129	2.80	1.9575	1.7993	1.8183	0.3164	0.0380
133	2.80	1.9518	1.7953	1.8152	0.3132	0.0398
137	2.80	1.9452	1.7917	1.8123	0.3090	0.0412
139	3.20	2.1797	2.0078	2.0313	0.3438	0.0470
143	3.20	2.1710	2.0014	2.0263	0.3392	0.0498
147	3.20	2.1666	1.9981	2.0236	0.3370	0.0510

as a function of current density and pH are quite similar.
The curves are very similar from the origin to the point
corresponding to a current density of 1.12 amperes is
reached. With increasing current density beyond this 1.12
value the effect of variation in pH becomes apparent. As
might be suspected the electrode containing the larger
concentration of hydrogen ion shows the less polarization.
This decrease in polarization may b e due to increased cond-
uctivity and this increased conductivity of course is the
result of the decreased pH.

Table 14 gives the results of a similar set of polar-
ization measurements, but in place of the pure copper sulfate
electrolyte, the 1/2 molar copper sulfate containing 0.1 per
cent gelatin was used. The pH was 3.32, and the measurements
were made at approximately 23° Centigrade. The results of
this run are also plotted on Plate III.

A run similar to the previous one was made with all
conditions the same excepting the pH, which now was adjust-
ed with dilute sulfuric acid to 2.00. The results of this
experiment are shown in Table 15. The temperature was that
of the laboratory, approximately 25°C. These results are
also plotted on Plate III. The variation of polarization
is more marked in these two curves than in the previous set.
However, one would suspect the electrolyte containing more
acid to exhibit the least polarization but the reverse
seems to be the case. The explanation of this decrease in
conductivity causing the acid bath which contains a pH of

Table 14

0.5 Molar $CuSO_4$; 0.1% Gelatin; pH = 3.32; Pt Cathode;
T = 23.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F. Cathode Volts	Middle Volts	Anode Volts	Polarization Cathode Volts	Anode Volts
1	0.16	0.1774	0.1183	0.1372	0.1182	0.0378
5	0.16	0.1784	0.1185	0.1341	0.1198	0.0312
9	0.16	0.1806	0.1178	0.1325	0.1256	0.0294
13	0.16	0.1827	0.1172	0.1314	0.1310	0.0284
15	0.32	0.3353	0.2482	0.2678	0.1742	0.0392
19	0.32	0.3296	0.2498	0.2683	0.1596	0.0370
23	0.32	0.3292	0.2500	0.2683	0.1584	0.0366
25	0.48	0.4705	0.3718	0.3938	0.1974	0.0440
29	0.48	0.4637	0.3748	0.3951	0.1778	0.0406
34	0.48	0.4616	0.3756	0.3961	0.1720	0.0410
36	0.64	0.6041	0.5007	0.5248	0.2068	0.0482
40	0.64	0.5999	0.5027	0.5264	0.1944	0.0474
44	0.64	0.5974	0.5036	0.5272	0.1876	0.0472
46	0.80	0.7432	0.6337	0.6610	0.2190	0.0546
49	0.80	0.7398	0.6355	0.6615	0.2086	0.0520
53	0.80	0.7371	0.6355	0.6622	0.2012	0.0514
55	0.96	0.8772	0.7627	0.7918	0.2290	0.0582
59	0.96	0.8735	0.7644	0.7921	0.2182	0.0554
63	0.96	0.8711	0.7652	0.7921	0.2118	0.0538
65	1.12	1.0037	0.8859	0.9152	0.2356	0.0586
69	1.12	1.0011	0.8870	0.9148	0.2282	0.0556
73	1.12	0.9987	0.8874	0.9143	0.2226	0.0538
75	1.28	1.1326	1.0102	1.0393	0.2448	0.0582
79	1.28	1.1299	1.0106	1.0372	0.2386	0.0532
83	1.28	1.1272	1.0108	1.0373	0.2328	0.0530
85	1.44	1.2525	1.1263	1.1543	0.2524	0.0560
89	1.44	1.2497	1.1261	1.1530	0.2472	0.0538
93	1.44	1.2472	1.1260	1.1523	0.2424	0.0526
95	1.60	1.3730	1.2420	1.2698	0.2620	0.0556
99	1.60	1.3700	1.2416	1.2683	0.2560	0.0534
103	1.60	1.3674	1.2410	1.2679	0.2528	0.0538

Table 14 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
105	2.00	1.6837	1.5328	1.5627	0.3018	0.0598
109	2.00	1.6797	1.5310	1.5604	0.2974	0.0588
113	2.00	1.6755	1.5293	1.5589	0.2924	0.0592
115	2.40	2.0052	1.8326	1.8662	0.3452	0.0672
119	2.40	2.0002	1.8301	1.8682	0.3402	0.0642
123	2.40	1.9955	1.8268	1.8592	0.3374	0.0648
125	2.80	2.2796	2.0862	2.1207	0.3868	0.0690
129	2.80	2.2727	2.0819	2.1162	0.3816	0.0686
133	2.80	2.2653	2.0766	2.1115	0.3774	0.0698
138	3.20	(1.6715) 2.5073	2.2956	(1.5546) 2.3319	0.4234	0.0726
142	3.20	(1.6645) 2.4967	2.2885	(1.5524) 2.3256	0.4164	0.0762
146	3.20	(1.6602) 2.4903	2.2834	(1.5504) 2.3256	0.4266	0.0822

Table 15

0.5 Molar CuSO$_4$;   0.1% Gelatin;   pH = 2.0;   Pt Cathode;
T =

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
2	0.16	0.1957	0.1102	0.1240	0.1710	0.0276
6	0.16	0.1903	0.1108	0.1248	0.1590	0.0280
10	0.16	0.1921	0.1098	0.1242	0.1646	0.0288
14	0.16	0.1934	0.1092	0.1235	0.1684	0.0286
17	0.32	0.3033	0.2221	0.2422	0.1624	0.0402
21	0.32	0.2893	0.2159	0.2353	0.1468	0.0388
25	0.32	0.2910	0.2155	0.2346	0.1510	0.0396
27	0.48	0.4237	0.3272	0.3502	0.1930	0.0460
31	0.48	0.4197	0.3284	0.3510	0.1826	0.0452
35	0.48	0.4198	0.3280	0.3515	0.1836	0.0470
39	0.64	0.5425	0.4379	0.4660	0.2092	0.0562
43	0.64	0.5400	0.4384	0.4670	0.2032	0.0572
46	0.64	0.5400	0.4385	0.4672	0.2030	0.0554
48	0.80	0.6710	0.5530	0.5861	0.2360	0.0662
52	0.80	0.6655	0.5536	0.5867	0.2238	0.0662
56	0.80	0.6648	0.5538	0.5868	0.2220	0.0660
58	0.96	0.7858	0.6635	0.7003	0.2446	0.0736
62	0.96	0.7850	0.6633	0.7000	0.2434	0.0734
66	0.96	0.7848	0.6632	0.6999	0.2432	0.0734
68	1.12	0.9033	0.7703	0.8105	0.2660	0.0804
72	1.12	0.9034	0.7704	0.8098	0.2660	0.0788
76	1.12	0.9026	0.7706	0.8097	0.2640	0.0782
78	1.28	1.0243	0.8802	0.9227	0.2882	0.0850
82	1.28	1.0233	0.8805	0.9222	0.2856	0.0834
86	1.28	1.0221	0.8803	0.9222	0.2836	0.0838
88	1.44	1.1417	0.9875	1.0326	0.3084	0.0902
94	1.44	1.1386	0.9872	1.0322	0.3028	0.0900
98	1.44	1.1368	0.9869	1.0322	0.2998	0.0906
100	1.60	1.2545	1.0924	1.1413	0.3242	0.0978
104	1.60	1.2524	1.0922	1.1408	0.3204	0.0972
108	1.60	1.2506	1.0918	1.1405	0.3374	0.0974

Table 15 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
110	2.00	1.5445	1.3567	1.4137	0.3656	0.1140
114	2.00	1.5401	1.3557	1.4115	0.3688	0.1116
118	2.00	1.5371	1.3545	1.4110	0.3652	0.1130
120	2.40	1.8168	1.6118	1.6764	0.4100	0.1292
124	2.40	1.8115	1.6094	1.6738	0.4042	0.1288
128	2.40	1.8075	1.6071	1.6722	0.4008	0.1302
130	2.80	2.0621	1.8433	1.9147	0.4376	0.1428
134	2.80	2.0557	1.8394	1.9115	0.4326	0.1442
138	2.80	2.0515	1.8370	1.9097	0.4290	0.1454
140	3.20	(1.5363) 2.3044	2.0722	2.1521	0.4644	0.1598
144	3.20	(1.5328) 2.2992	2.0692	2.1492	0.4600	0.1600
148	3.20	(1.5292) 2.2938	2.0640	2.1450	0.4586	0.1620

2.0 to give the higher polarization may be due to small changes in temperature.

The polarization due to the presence of some gelatin, at the beginning of the run was similar for these two runs, and these were quite similar to those previously described.

One peculiarity of the curves using this low gelatin content is that the break at 0.8 amperes current density, so characteristic of higher gelatin contents, is absent. The one curve of pH 2.0 shows a very slight break at a current density of 1.44 amperes, but this break is quite meaningless since its magnitude is within the limits of experimental error. The absence of the sudden increase in polarization at about .80 amperes current density indicates also that we have no setting of our gelatin electrolyte, which setting, we previously assumed to be the cause of the rapid increase in polarization. Solutions containing concentrations of gelatin as small as 0.1 per cent, melt at temperatures below that of the room, hence we are working at temperatures above the melting point. Also during the electrolysis the concentration of gelatin is not increased sufficiently to cause setting at the cathode. Experience tells us that copper sulfate solutions containing gelatin must contain from 2.0 to 2.5 per cent of this colloid to give a visible gelation at room temperature. Without doubt enough gelatin is present in 1/2 per cent solutions to give us the characteristic polarization increases.

The next two experiments in this series, whose data

Table 16

0.5 Molar $CuSO_4$;   0.5% Gelatin;   Ph = 1.98;   Pt. Cathode;
T = 25.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
0	0.16	0.1745	0.1005	0.1032	0.1480	0.0054
4	0.16	0.1750	0.0991	0.1022	0.1518	0.0062
9	0.16	0.1838	0.1010	0.1050	0.1656	0.0080
12	0.16	0.1869	0.0994	0.1040	0.1750	0.0092
16	0.16	0.1890	0.0982	0.1031	0.1816	0.0098
20	0.32	0.2922	0.2081	0.2173	0.1682	0.0184
24	0.32	0.2913	0.2079	0.2172	0.1668	0.0186
28	0.32	0.2943	0.2063	0.2161	0.1760	0.0196
32	0.32	0.2970	0.2053	0.2153	0.1834	0.0200
35	0.48	0.4196	0.3192	0.3322	0.2008	0.0260
39	0.48	0.4181	0.3196	0.3328	0.1970	0.0264
43	0.48	0.4193	0.3191	0.3323	0.2004	0.0264
45	0.64	0.5525	0.4332	0.4491	0.2386	0.0318
49	0.64	0.5502	0.4338	0.4497	0.2328	0.0318
53	0.64	0.5500	0.4340	0.4452	0.2320	0.0224
57	0.80	0.6894	0.5423	0.5600	0.2954	0.0354
61	0.80	0.6899	0.5423	0.5600	0.2952	0.0354
65	0.80	0.6900	0.5423	0.5601	0.2954	0.0356
67	0.96	0.8270	0.6540	0.6740	0.3460	0.0400
71	0.96	0.8261	0.6541	0.6741	0.3440	0.0400
75	0.96	0.8257	0.6544	0.6747	0.3426	0.0406
77	1.12	0.9490	0.7610	0.7833	0.3760	0.0446
81	1.12	0.9480	0.7610	0.7836	0.3740	0.0452
85	1.12	0.9469	0.7611	0.7840	0.3716	0.0458
87	1.28	1.0696	0.8696	0.8945	0.4000	0.0578
91	1.28	1.0676	0.8697	0.8948	0.3958	0.0502
95	1.28	1.0663	0.8697	0.8951	0.3932	0.0508
97	1.44	1.1854	0.9765	1.0039	0.4178	0.0548
101	1.44	1.1834	0.9768	1.0040	0.4132	0.0544
105	1.44	1.1816	0.9767	1.0044	0.4118	0.0554
107	1.60	1.2975	1.0820	1.1121	0.4310	0.0602
111	1.60	1.2953	1.0818	1.1121	0.4270	0.0606
115	1.60	1.2933	1.0816	1.1124	0.4234	0.0616

Table 16 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
118	2.00	1.5836	1.3474	1.3837	0.4724	0.0726
122	2.00	1.5791	1.3462	1.3828	0.4658	0.0732
126	2.00	1.5757	1.3452	1.3826	0.4610	0.0748
129	2.40	1.8400	1.5912	1.6348	0.4976	0.0872
133	2.40	1.8348	1.5889	1.6334	0.4918	0.0890
137	2.40	1.8295	1.5870	1.6323	0.4850	0.0906
140	2.80	2.1119	1.8504	1.9013	0.5230	0.1018
144	2.80	2.1050	1.8470	1.8993	0.5160	0.1046
148	2.80	2.0983	1.8434	1.8984	0.5098	0.1100
150	3.20	(1.5472)	2.0640	2.1239		0.1198
154	3.20	2.3208 (1.5445)	2.0615	2.1195	0.5186	0.1162
158	3.20	2.3167	2.0562	2.1158	0.5210	0.1392

are given in Tables 16 and 17 involve polarization of the Cu/Cu^{++} electrode in the presence of 1/2 per cent gelatin. Table 16 shows the results at a pH of 1.98, and Table 17 at a pH of ~~3.42~~ 3.34, and both at approximately 25°C. In each of these two cases the polarization at the beginning of the run is quite characteristic of copper sulfate electrolytes containing gelatin. The polarization at the low current density appears to be independent of the hydrogen ion concentration. The curve of pH 3.34 shows an irregularity beginning at a current density of 0.96 amperes and this without doubt is the result of the partial setting of the gelatin. The increase in polarization is not as great nor as regular as in some previous runs involving this same concentration of gelatin. It is difficult to control conditions suffic- iently close to duplicate accurately results when using gelatin containing copper sulfate solutions.

The curve representing data from the solution of pH 1.98 shows more distinctly the characteristic increase in polarization at a current density of .32 to .48. The in- crease in acidity apparently causes a slight setting of the gelatin, or at least there is a viscosity change at this current density. The presence of the acid probably is the cause for the increased polarization at unusually low cur- rent densities. Acid in greater concentration causes the precipitation of gelatin.

The two remaining experiments of this series involves the use of 1.5 per cent gelatin in the copper sulfate elec-

Table 17

0.5 Molar CuSO4; 0.5% Gelatin; pH = 3.34; Pt Cathode;
T = 25.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
1	0.16	0.1843	0.1130	0.1327	0.1426	0.0394
5	0.16	0.1852	0.1154	0.1338	0.1396	0.0368
9	0.16	0.1868	0.1147	0.1325	0.1442	0.0328
14	0.16	0.1883	0.1144	0.1311	0.1474	0.0334
16	0.32	0.3127	0.2357	0.2581	0.1540	0.0448
20	0.32	0.3121	0.2361	0.2580	0.1520	0.0438
24	0.32	0.3124	0.2364	0.2577	0.1520	0.0426
27	0.48	0.4558	0.3648	0.3908	0.1820	0.0520
31	0.48	0.4536	0.3660	0.3913	0.1752	0.0506
35	0.48	0.4514	0.3671	0.3923	0.1686	0.0504
37	0.64	0.5912	0.4876	0.5174	0.2072	0.0596
41	0.64	0.5849	0.4898	0.5196	0.1902	0.0596
45	0.64	0.5824	0.4906	0.5204	0.1836	0.0596
47	0.80	0.7229	0.6136	0.6485	0.2186	0.0698
51	0.80	0.7184	0.6152	0.6493	0.2064	0.0682
55	0.80	0.7165	0.6162	0.6501	0.2006	0.0678
57	0.96	0.8478	0.7373	0.7754	0.2210	0.0762
61	0.96	0.8466	0.7384	0.7756	0.2164	0.0744
65	0.96	0.8455	0.7388	0.7755	0.2134	0.0734
67	1.12	0.9855	0.8619	0.9022	0.2472	0.0806
71	1.12	0.9845	0.8622	0.9013	0.2446	0.0788
75	1.12	0.9833	0.8625	0.9010	0.2426	0.0770
81	1.28	1.1194	0.9803	1.0205	0.2772	0.0794
85	1.28	1.1203	0.9792	1.0201	0.2832	0.0818
89	1.28	1.1207	0.9790	1.0199	0.3034	0.0818
93	1.44	1.2535	1.1003	1.1429	0.3064	0.0852
97	1.44	1.2511	1.1001	1.1425	0.3020	0.0848
101	1.44	1.2489	1.1004	1.1428	0.2970	0.0848
103	1.60	1.3801	1.2171	1.2627	0.3260	0.0912
107	1.60	1.3785	1.2165	1.2616	0.3240	0.0902
111	1.60	1.3758	1.2158	1.2613	0.3200	0.0910

Table 17 cont'd

Time Min.	Amps, C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
113	2.00	1.6991	1.4959	1.5492	0.4064	0.0988
117	2.00	1.6946	1.4941	1.5453	0.4010	0.1024
121	2.00	1.6900	1.4928	1.5441	0.3944	0.1026
123	2.40	2.0113	1.7748	1.8326	0.4730	0.1156
127	2.40	2.0055	1.7739	1.8299	0.4632	0.1220
131	2.40	1.9992	1.7710	1.8285	0.4564	0.1150
133	2.80	1.5465	2.0570	2.1221	0.5264	0.1302
137	2.80	1.5418	2.0540	2.1172	0.5174	0.1264
141	2.80	1.5373	2.0505	2.1145	0.5108	0.1276
143	3.20	1.7118	2.2842	(1.5687) 2.3530	0.5670	0.1376
147	3.20	1.7053	2.2792	(1.5645) 2.3467	0.5574	0.1360
151	3.20	1.6988	2.2730	(1.5625) 2.4437	0.5502	0.1414

trolyte, one at a pH of 3.42 and the other at 1.99. The data resulting from these two runs are given in Tables 18 and 19 respectively.

The run using the electrolyte of pH 3.42 gives the apparently normal polarization increase, but at the unusually low current density of 0.48 amperes. The curve showing these results in place of changing its course to nearly vertical after this normal polarization increase, continues on with rapid polarization increases with increasing current density. The maximum of polarization is 1.18 volts and occurs at a current density of 2.80 amperes. At the current density of 3.20 amperes the polarization decreases to approximately .705 volts, which decrease is probably the result of both the slight evolution of hydrogen and to the heat effect due to increased resistance. This heating effect has liquified the gelatin in contact with the electrode and allowed a freer passage of copper ions, hence the lower polarization.

The curve giving the results of the same concentration of gelatin but with a pH of 1.99 is still more abnormal. Its first polarization increase occurs normally as compared to the others. Then a second increase comes at a current density of about 0.32 amperes and increases fairly rapidly to 2.0 amperes, at which current density hydrogen was evolved. Thus in solutions of high gelatin content and containing appreciable acidity, hydrogen is evolved with less work than the deposition of copper at current densities of 2 amperes and more.

Table 18

0.5 Molar CuSO$_4$; 1.5% Gelatin; pH = 3.42; Pt Cathode;
T =

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
2	0.16	0.1978	0.1264	0.1498	0.1428	0.0468
6	0.16	0.1991	0.1258	0.1483	0.1466	0.0450
10	0.16	0.2006	0.1252	0.1469	0.1508	0.0488
13	0.32	0.3352	0.2486	0.2756	0.1732	0.0540
17	0.32	0.3326	0.2500	0.2750	0.1652	0.0500
21	0.32	0.3318	0.2511	0.2745	0.1614	0.0468
23	0.48	0.4706	0.3808	0.4082	0.1796	0.0548
27	0.48	0.4706	0.3812	0.4073	0.1788	0.0522
31	0.48	0.4701	0.3815	0.4072	0.1762	0.0514
33	0.64	0.6110	0.5113	0.5408	0.1994	0.0590
37	0.64	0.6122	0.5112	0.5401	0.2020	0.0578
42	0.64	0.6130	0.5107	0.5395	0.2046	0.0576
44	0.80	0.8321	0.6428	0.6753	0.3786	0.0650
48	0.80	0.8338	0.6423	0.6745	0.3830	0.0644
52	0.80	0.8350	0.6415	0.6740	0.3870	0.0650
54	0.96	0.9949	0.7732	0.8085	0.4434	0.0706
58	0.96	0.9980	0.7721	0.8070	0.4518	0.0698
62	0.96	0.9996	0.7714	0.8056	0.4564	0.0684
64	1.12	1.1496	0.8984	0.9357	0.5024	0.0746
68	1.12	1.1530	0.8977	0.9331	0.5106	0.0708
72	1.12	1.1552	0.8968	0.9309	0.5186	0.0682
74	1.28	1.3060	1.0232	1.0596	0.5656	0.0728
78	1.28	1.3102	1.0218	1.0563	0.5768	0.0690
82	1.28	1.3135	1.0204	1.0531	0.5862	0.0654
84	1.44	1.4676	1.1445	1.1785	0.6462	0.0680
88	1.44	1.4732	1.1428	1.1733	0.6608	0.0610
92	1.44	1.4794	1.1411	1.1684	0.6766	0.0546
94	1.60	1.6525	1.2626	1.2889	0.7798	0.0526
98	1.60	1.6571	1.2621	1.2841	0.7900	0.0440
102	1.60	1.6608	1.2618	1.2789	0.7980	0.0340
105	2.00	2.1150	1.5952	1.6123	1.0396	0.0342
109	2.00	2.0585	1.6089	1.6142	0.9992	0.0086
113	2.00	2.0450	1.6132	1.6117	0.8636	-0.0030

Table 18 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
	2.4	(1.5800)				
115	2.40	2.3700	1.8644	1.8588	1.0112	-0.0112
		(1.5530)				
119	2.40	2.3295	1.8749	1.8616	0.9092	-0.0266
		(1.5335)				
123	2.40	2.3002	1.8805	1.8675	0.8394	-0.0260
		(1.7620)				
125	2.80	2.6430	2.1610	2.1503	0.9640	-0.0214
		(1.7250)				
129	2.80	2.5875	2.1650	2.1710	0.8450	0.0120
		(1.7025)				
133	2.80	2.7537	2.1626	2.1878	1.1822	0.0504
		(1.8430)	(1.5728)	(1.5970)		
135	3.20	2.7645	2.3592	2.3685	0.8106	0.0186
		(1.8250)	(1.5728)	(1.6029)		
139	3.20	2.7375	2.3592	2.4045	0.7566	0.0902
		(1.8060)	(1.5707)	(1.6101)		
143	3.20	2.7090	2.3560	2.4151	0.7060	0.1182

Table 19

0.5 Molar $CuSO_4$; 1.5% Gelatin; pH = 1.99; Pt Cathode;
T =

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
1	0.16	0.1940	0.1097	0.1225	0.1686	0.0256
5	0.16	0.1903	0.1102	0.1229	0.1602	0.0254
9	0.16	0.1927	0.1087	0.1214	0.1680	0.0254
12	0.32	0.3175	0.2249	0.2440	0.1852	0.0382
16	0.32	0.3116	0.2260	0.2454	0.1712	0.0388
20	0.32	0.3137	0.2251	0.2440	0.1762	0.0378
22	0.48	0.4411	0.3337	0.3570	0.2148	0.0466
26	0.48	0.4366	0.3348	0.3577	0.2036	0.0458
30	0.48	0.4382	0.3340	0.3572	0.2084	0.0464
32	0.64	0.5760	0.4397	0.4671	0.2726	0.0548
36	0.64	0.5790	0.4382	0.4666	0.2816	0.0568
40	0.64	0.5808	0.4372	0.4666	0.2872	0.0588
41	0.80	0.7291	0.5555	0.5902	0.3472	0.0694
45	0.80	0.7300	0.5548	0.5905	0.3504	0.0714
48	0.80	0.7300	0.5547	0.5905	0.3506	0.0716
49	0.96	0.8621	0.6672	0.7073	0.3898	0.0802
53	0.96	0.8621	0.6673	0.7070	0.3896	0.0794
57	0.96	0.8628	0.6675	0.7069	0.3906	0.0788
58	1.12	0.9880	0.7770	0.8202	0.4220	0.0864
62	1.12	0.9879	0.7770	0.8195	0.4218	0.0850
66	1.12	0.9877	0.7771	0.8192	0.4212	0.0842
67	1.28	1.1120	0.8867	0.9315	0.4506	0.0896
71	1.28	1.1122	0.8868	0.9305	0.4508	0.0874
75	1.28	1.1122	0.8868	0.9301	0.4508	0.0866
76	1.44	1.2375	0.9972	1.0438	0.4806	0.0932
80	1.44	1.2376	0.9964	1.0425	0.4824	0.0922
84	1.44	1.2375	0.9957	1.0421	0.4836	0.0928
85	1.60	1.3603	1.1029	1.1531	0.5148	0.1004
89	1.60	1.3607	1.1020	1.1522	0.5174	0.1004
93	1.60	1.3609	1.1013	1.1518	0.5192	0.1010
94	2.00	1.6668	1.3646	1.4222	0.6044	0.1152
98	2.00	1.6691	1.3614	1.4187	0.6154	0.1146
102	2.00	1.6707	1.3593	1.4172	0.6228	0.1158

The final set of polarization measurements were made with only slight variations in pH and temperature. The data given in Table 20 are the results of polarization measurements using 1/2 molar copper sulfate, 1/2 per cent gelatin, platinum electrodes, at a pH of 3.40 and at 24°C. The temperature was not accurately controlled at this value.

This data is shown graphically in Plate IV as curve 1. The initial increase in polarization is approximately that quite characteristic of many previous measurements. The second increase in polarization occurs at a slightly lower current density than normally. It may be that this slight abnormality may be due to the lower temperature of the cell, since small temperature changes alter very markedly the viscosity of gelatin containing solutions. The deviation from a smooth curve at a current density of 1.60 amperes cannot be explained. Beyond that current density the curve proceeds very uniformly.

The data of the second run of this series is given in Table 21 and is shown graphically as curve No. 2 in Plate IV. In this experiment the acidity is very nearly the same as in the previous run, but the factor varied is temperature. The four degrees increase in temperature played a very noticeable part in delaying the apparent gelation of the electrolyte. The increase in polarization came at a current density of 1.12 amperes, which value is some higher than the corresponding points in the previous plates. Why some of these curves with only very slightly varied conditions

Table 20

0.5 Molar CuSO$_4$; 0.5% Gelatin; pH = 3.42; Pt Cathode;
T = 28.2^0 C.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
1	0.16	0.190	0.1185	0.1200	0.1430	0.0030
5	0.16	0.1791	0.1173	0.1193	0.1236	0.0040
9	0.16	0.1808	0.1160	0.1186	0.1296	0.0052
14	0.32	0.3138	0.2356	0.2452	0.1564	0.0192
18	0.32	0.3118	0.2357	0.2456	0.1522	0.0198
22	0.32	0.3113	0.2355	0.2458	0.1516	0.0206
24	0.48	0.4461	0.3593	0.3722	0.1736	0.0258
28	0.48	0.4410	0.3603	0.3733	0.1614	0.0260
32	0.48	0.4398	0.3607	0.3735	0.1582	0.0256
34	0.64	0.5644	0.4742	0.4885	0.1804	0.0286
38	0.64	0.5613	0.4748	0.4893	0.1730	0.0290
42	0.64	0.5595	0.4753	0.4900	0.1684	0.0294
44	0.80	0.6922	0.5990	0.6152	0.1864	0.0324
48	0.80	0.6863	0.6000	0.6165	0.1736	0.0330
52	0.80	0.6851	0.6003	0.6168	0.1696	0.0330
53	0.96	0.8073	0.7087	0.7271	0.1972	0.0368
57	0.96	0.8033	0.7094	0.7284	0.1888	0.0380
61	0.96	0.8012	0.7096	0.7288	0.1832	0.0384
62	1.12	0.9405	0.8213	0.8422	0.2384	0.0418
66	1.12	0.9297	0.8235	0.8435	0.2124	0.0400
70	1.12	0.9263	0.8240	0.8443	0.2046	0.0406
72	1.28	1.09	0.94	0.967	0.30	0.054
76	1.28	1.0895	0.94	0.9666	0.30	0.054
80	1.28	1.0830	0.9413	0.9674	0.2836	0.0524
82	1.44	1.2318	1.0586	1.0812	0.3464	0.0452
86	1.44	1.2285	1.0583	1.0810	0.3404	0.0454
90	1.44	1.2265	1.0581	1.0804	0.3368	0.0446
91	1.60	1.3503	1.1662	1.1898	0.3682	0.0472
95	1.60	1.3484	1.1655	1.1889	0.3658	0.0468
99	1.60	1.3463	1.1648	1.1881	0.3630	0.0466
100	2.00	1.6433	1.4316	1.4575	0.4234	0.0518
104	2.00	1.6410	1.4308	1.4560	0.4204	0.0504
108	2.00	1.6390	1.4296	1.4589	0.4188	0.0586

Table 20 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
109	2.40	1.9322	1.6975	1.7232	0.4694	0.0514
113	2.40	1.9210	1.6875	1.7120	0.4670	0.0490
117	2.40	1.9096	1.6760	1.7012	0.4672	0.0504
118	2.80	2.2603	2.0006	2.0290	0.5194	0.0568
122	2.80	2.2563	1.9979	2.0265	0.5168	0.0572
126	2.80	2.2512	1.9936	2.0239	0.5152	0.0606
127	3.20	(1.6340) 2.4510	2.1792	2.2107	0.5436	0.0630
131	3.20	(1.6473) 2.5709	2.1970	2.2288	0.7478	0.0636
135	3.20	(1.6431) 2.4646	2.1924	2.2259	0.5444	0.0870
139	3.20	(1.6366) 2.4549	2.1830	2.2175	0.5438	0.0690

Table 21

0.5 Molar $CuSO_4$;   0.5% Gelatin;   pH = 3.39;   Pt Cathode;
T = 28.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
1	0.16	0.1904	0.1267	0.1343	0.1274	0.0152
5	0.16	0.1902	0.1266	0.1336	0.1272	0.0140
9	0.16	0.1926	0.1252	0.1322	0.1348	0.0140
13	0.16	0.1943	0.1243	0.1314	0.1400	0.0142
16	0.32	0.3155	0.2395	0.2511	0.1520	0.0232
20	0.32	0.3139	0.2402	0.2512	0.1474	0.0220
24	0.32	0.3135	0.2404	0.2510	0.1462	0.0212
27	0.48	0.4465	0.3648	0.3793	0.1634	0.0290
31	0.48	0.4442	0.3657	0.3795	0.1570	0.0276
35	0.48	0.4432	0.3661	0.3797	0.1542	0.0272
36	0.64	0.5807	0.4836	0.5014	0.1942	0.0356
40	0.64	0.5730	0.4858	0.5030	0.1744	0.0344
44	0.64	0.5711	0.4861	0.5034	0.1700	0.0346
46	0.80	0.7050	0.6071	0.6286	0.1958	0.0430
50	0.80	0.6998	0.6083	0.6295	0.1830	0.0424
54	0.80	0.6982	0.6086	0.6300	0.1729	0.0428
55	0.96	0.8275	0.7245	0.7473	0.2060	0.0456
59	0.96	0.8233	0.7257	0.7480	0.1952	0.0446
63	0.96	0.8212	0.7258	0.7481	0.1908	0.0446
64	1.12	0.9464	0.8423	0.8652	0.2082	0.0458
65	1.12	0.9460	0.8422	0.8648	0.2076	0.0452
70	1.28	1.1410	0.9554	0.9785	0.3712	0.0462
74	1.28	1.1397	0.9550	0.9778	0.3674	0.0456
78	1.28	1.1389	0.9546	0.9773	0.3686	0.0454
79	1.44	1.2743	1.0736	1.0967	0.4014	0.0462
83	1.44	1.2725	1.0732	1.0957	0.3986	0.0470
87	1.44	1.2712	1.0730	1.0948	0.3964	0.0436
88	1.60	1.3995	1.1878	1.2098	0.4234	0.0440
92	1.60	1.3978	1.1870	1.2088	0.4216	0.0436
96	1.60	1.3965	1.1862	1.2077	0.4206	0.0430
98	2.00	1.7069	1.4685	1.4910	0.4768	0.0450
102	2.00	1.7045	1.4660	1.4893	0.4770	0.0466
106	2.00	1.7022	1.4664	1.4877	0.4716	0.0426

Table 21 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
108	2.40	1.9783	1.7167	1.7423	0.5242	0.0512
112	2.40	1.9747	1.7136	1.7402	0.5222	0.0532
116	2.40	1.9718	1.7117	1.7384	0.5202	0.0534
117	2.80	2.2970	2.0108	2.0398	0.5724	0.0580
121	2.80	2.2922	2.0058	2.0365	0.5728	0.0614
125	2.80	2.2873 (1.6897)	2.0018	2.0338	0.5710	0.0640
126	3.20	2.5345 (1.6860)	2.2308	2.2635	0.6074	0.0654
130	3.20	2.5290 (1.6820)	2.2273	2.2595	0.6034	0.0646
134	3.20	2.5230	2.2232	2.2557	0.5996	0.0650

CURVES SHOWING RELATION OF CATHODE POLARIZATION TO CURRENT DENSITY
.5M CuSO₄-5% GEL.

No.	pH	Temp.
1	3.42	28.2°C
2	3.39	28°
3	3.40	24°

CURRENT DENSITY IN AMPERES PER SQUARE DECIMETER
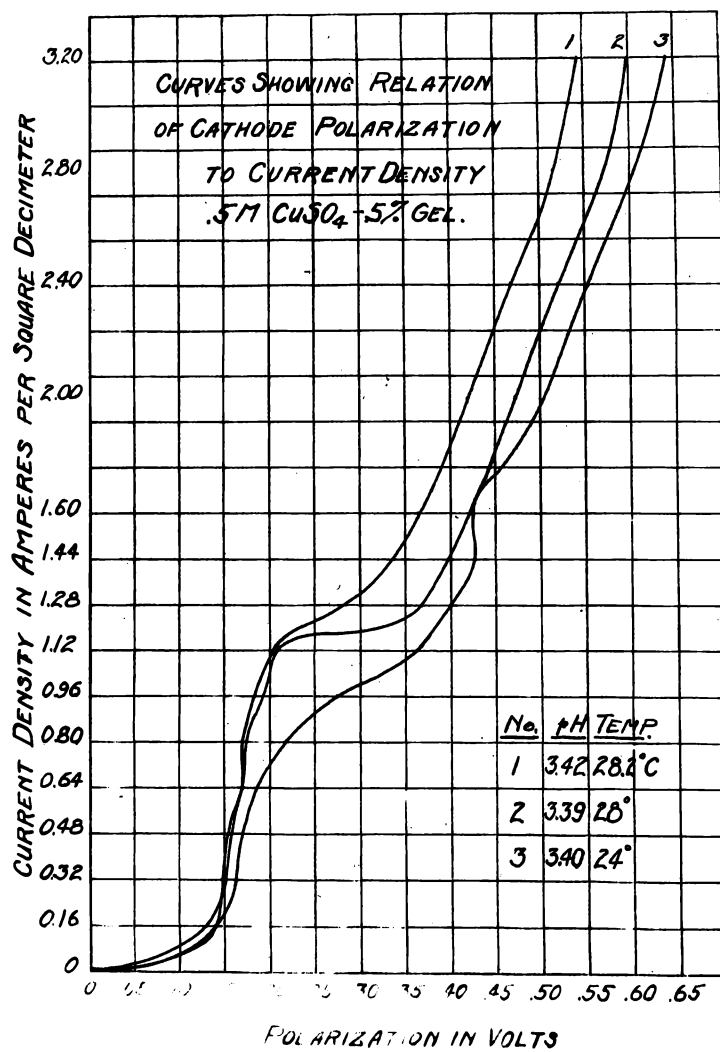
POLARIZATION IN VOLTS

Plate IV
Polarization Measurements

should be so different can only be explained by the fact
that the properties of gelatin solutions change rapidly
with slight changes of temperature, pH and concentration.
In other words the gelatin solutions are quite sensitive
to small changes in conditions.

The data of the third curve shown in Plate IV is
given in Table 22. This table represents data taken under
conditions very similar to that in Table 21, excepting
the small change in pH from 3.39 to 3.42. This curve shows
tendencies very similar to curve 2 in this same plate. The
important point is that the change of .03 in pH causes
almost no variation in the curve over No. 2 curve until
after a current density of 1.12 was reached.

Table 23 gives the data for an experiment of a slight
different character than the previous ones described in
this section. In place of making variations in current density
and measuring the respective polarizations, the current den-
sity was maintained at a constant value of 0.8 amperes per
square decimeter and the polarization measured as a function
of time. The measurements give the data when using 1/2 per
cent gelatin, 1/2 molar copper sulfate and a pH of 3.38;
voltage readings were taken every 2 to 3 minutes. On Plate V
is plotted the data given in this Table 23 as curve 1.

Another experiment of a similar nature was made under
the same conditions as the one just previous. The only dif-
ference being that the pH was 3.37 in place of 3.38, read-
ings were taken at ten minute intervals and the run was con-

Table 22

0.5 Molar $CuSO_4$;   0.5% Gelatin;   pH = 3.40;   Pt Cathode;
T = 24.0°C.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
1	0.16	0.1808	0.1198	0.1281	0.1220	0.0166
5	0.16	0.1883	0.1240	0.1328	0.1286	0.0176
9	0.16	0.1904	0.1230	0.1315	0.1348	0.0170
13	0.16	0.1917	0.1223	0.1308	0.1388	0.0170
15	0.32	0.3290	0.2463	0.2603	0.1654	0.0280
19	0.32	0.3265	0.2467	0.2608	0.1596	0.0282
23	0.32	0.3270	0.2460	0.2609	0.1620	0.0298
25	0.48	0.4694	0.3806	0.4010	0.1776	0.0408
29	0.48	0.4575	0.3727	0.3928	0.1696	0.0402
33	0.48	0.4573	0.3728	0.3935	0.1690	0.0414
35	0.64	0.5993	0.4982	0.5243	0.2022	0.0522
39	0.64	0.5980	0.4985	0.5260	0.1990	0.0550
43	0.64	0.5927	0.5000	0.5281	0.1854	0.0562
45	0.80	0.7463	0.6277	0.6615	0.2372	0.0676
49	0.80	0.7411	0.6292	0.6629	0.2238	0.0674
53	0.80	0.7385	0.6303	0.6638	0.2164	0.0670
55	0.96	0.9220	0.7550	0.7932	0.3340	0.0764
69	0.96	0.8924	0.7510	0.7849	0.2828	0.0678
73	0.96	0.8888	0.7522	0.7855	0.2732	0.0666
76	1.12	1.0630	0.8762	0.9132	0.3736	0.0740
80	1.12	1.0605	0.8771	0.9128	0.3668	0.0714
84	1.12	1.0585	0.8771	0.9132	0.3628	0.0702
86	1.28	1.2046	1.0000	1.0383	0.4092	0.0766
90	1.28	1.2023	1.0001	1.0375	0.4044	0.0748
94	1.28	1.2000	1.0002	1.0370	0.3996	0.0736
96	1.44	1.3404	1.1211	1.1609	0.4386	0.0796
100	1.44	1.3369	1.1210	1.1593	0.4318	0.0766
104	1.44	1.3339	1.1208	1.1581	0.4262	0.0746
106	1.60	1.4591	1.2310	1.2711	0.4562	0.0802
110	1.60	1.4558	1.2307	1.2694	0.4502	0.0774
114	1.60	1.4523	1.2398	1.2680	0.4250	0.0564

Table 22 cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarisation	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
116	2.00	1.7704	1.5119	1.5568	0.5170	0.0898
120	2.00	1.7655	1.5110	1.5532	0.5090	0.0844
124	2.00	1.7620	1.5101	1.5513	0.5038	0.0824
126	2.40	2.0748	1.7910	1.8375	0.5676	0.0930
130	2.40	2.0693	1.7893	1.8347	0.5600	0.0980
134	2.40	2.0637	1.7870	1.8327	0.5536	0.0914
136	2.80	(1.5906) 2.3859	2.0790	2.1291	0.6138	0.1002
140	2.80	(1.5855) 2.3782	2.0740	2.1235	0.6084	0.0990
144	2.80	(1.5821) 2.3731	2.0706	2.1213	0.6050	0.1014
146	3.20	(1.7395) 2.6092	2.2853	(1.5598) 2.3397	0.6478	0.1088
150	3.20	(1.7344) 2.6016	2.2793	(1.5565) 2.3347	0.6446	0.1108
154	3.20	(1.7305) 2.5957	2.2753	(1.5548) 2.3322	0.6408	0.1139

Table 23

0.5 Molar $CuSO_4$; 1/2% Gelatin; pH = 3.37; Pt Cathode; 25.5°C; at constant current density, .08 Amp.per Dcm².

| Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
2	0.8	.7873	.6310	.6581	.3126	N.D.
4		.7921	.6358	.6627	.3126	
6		.7893	.6345	.6613	.3096	
9		.7873	.6337	.6607	.3052	
12		.7898	.6370	.6651	.3056	
17		.7908	.6367	.6658	.3082	
22		.7926	.6373	.6671	.3106	
28		.7944	.6390	.6693	.3108	
33		.7964	.6393	.6697	.3142	
38		.7958	.6405	.6708	.3106	
43		.7928	.6405	.6708	.3046	
48		.7902	.6405	.6708	.2994	
58		.7910	.6432	.6736	.2956	
68		.7893	.6424	.6728	.2938	
78		.7903	.6436	.6740	.2934	
88		.7855	.6413	.6714	.2884	
108		.7820	.6394	.6685	.2852	
138		.7832	.6396	.6678	.2872	
148		.7830	.6389	.6673	.2882	
158		.7820	.6387	.6668	.2866	
168		.7808	.6384	.6666	.2848	
178		.7807	.6387	.6664	.2840	
188		.7800	.6381	.6665	.2838	
198		.7782	.6380	.6667	.2804	
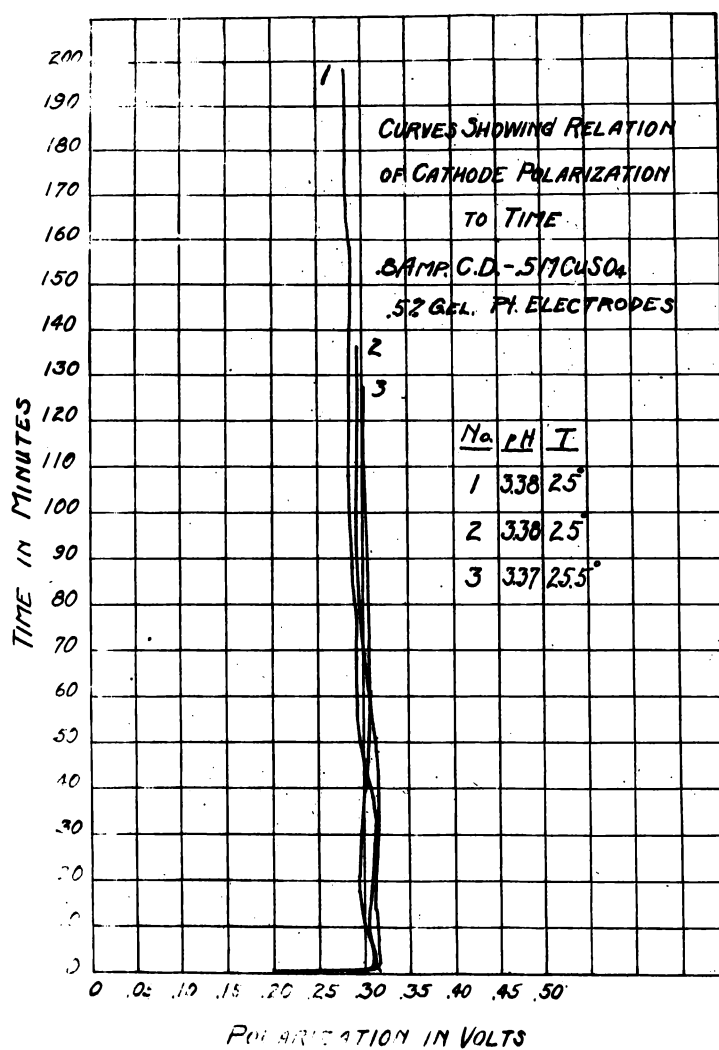
Plate V
Polarization Measurements

tinued over a period of 198 minutes. These results are given in Table 24 and plotted as curve 2 in Plate V.

Table 25 is a run similar to these two above and the results of this one are plotted as curve 3 in Plate V.

Two important points are brought out in these two curves of polarization as a function of time. The first one is that polarization is nearly constant regardless of time within the three hour period. The second is that no break in the curve occurs after a duration of 45 minutes.

During the study of the previous polarization experiments one might suspect that the increase in polarization so characteristic of some of those curves with a current density of 0.8 amperes might have been a function of time. Since these three curves show no abrupt increase in polarization at the end of a 45 minute period, the conclusion is that polarization is independent of time.

Summary

1. The polarization of the Cu/Cu^{++} electrode using 1/2 molar copper sulfate electrolyte, with copper or platinum electrodes at $25^{\circ}C$. increases linearly with current density.

2. The polarization of the Cu/Cu^{++} electrode using 1/2 molar copper sulfate electrolyte containing 1/2 per cent gelatin at $25^{\circ}C$. with copper electrodes, or with platinum electrodes, is much greater than when no gelatin was present.

Table 24

0.5 Molar $CuSO_4$; 1/2% gelatin; pH p 3.38, Pt Cathode; 25.0°C; at constant current density, 0.8 Amp. per Dcm^2.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
1	0.8	.7206	.6215	N.D.	.1982	
2.5		.783	.624		.318	
3.5		.7857	.6284		.3146	
4.5		.7887	.6315		.3144	
5.5		.7880	.6312		.3136	
6.5		.7886	.6313		.3146	
7.5		.7904	.6325		.3158	
8.5		.7921	.6338		.3166	
9.5		.7922	.6338	.6564	.3168	
11		.7924	.6345	.6564	.3158	
13		.7927	.6355	.6568	.3144	
15		.7918	.6359	.6575	.3188	
17		.7912	.6359	.6568	.3106	
19		.7922	.6368	.6578	.3082	
21		.7942	.6383	.6597	.3118	
23		.7936	.6375	.6592	.3122	
25		.7947	.6386	.6604	.3144	
27		.7950	.6387	.6608	.3126	
29		.7947	.6378	.6600	.3138	
32		.7962	.6388	.6613	.3148	
35		.7978	.6400	.6625	.3138	
39		.7983	.6402	.6629	.3162	
42		.7973	.6392	.6622	.3162	
45		.8000	.6418	.6652	.3164	
48		.7990	.6412	.6645	.3156	
51		.8000	.6426	.6660	.3148	
55		.7978	.6426	.6659	.3122	
58		.7980	.6426	.6658	.3108	
61		.7990	.6445	.6676	.3090	
64		.7983	.6448	.6678	.3070	
67		.7976	.6448	.6678	.3056	
70		.7973	.6448	.6677	.3050	
73		.7982	.6467	.6693	.3030	
76		.7974	.6465	.6694	.3018	
79		.7972	.6465	.6692	.3014	
82,		.7963	.6465	.6692	.2996	
85		.7958	.6463	.6690	.2990	
88		.7956	.6463	.6686	.2986	
91		.7952	.6462	.6683	.2980	
94		.7948	.6460	.6680	.2976	
97		.7943	.6463	.6688	.2960	
100		.7949	.6473	.6696	.2952	
103		.7964	.6483	.6706	.2962	
106		.7963	.6483	.6703	.2960	

Table 24 Cont'd

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
109	0.8	.7956	.6479	.6699	.2954	
112		.7950	.6473	.6709	.2954	
115		.7965	6484	.6705	.2956	
118		.7960	.6484	.6705	.2950	
121		.7955	.6482	.6702	.2946	
124		.7968	.6495	.6713	.3946	
127		.7967	.6490	.6708	.2954	
130		.7972	.6493	.6712	.2958	
133		.7977	.6498	.6714	.2958	
136		.8000	.6515	.6730	.2970	

Table 25

0.5 Molar $CuSO_4$; 1/2% Gelatin; pH = 3.38=Pt_2Cathode⨎ 25°C; at constant C. D. = 0.8 Amps. per Dcm^2.

Time Min.	Amps. C. D.	1/2 E. M. F.			Polarization	
		Cathode Volts	Middle Volts	Anode Volts	Cathode Volts	Anode Volts
0.5	0.8	.743	.600	N.D.	.286	N.D.
1.5		.770	.615		.310	
2.5		.7736	.6214		.3044	
3.5		.7756	.6237		.3038	
5		.7756	.6246	.6621	.3020	
7		.7751	.6242	.6596	.3018	
9		.7769	.6258	6586	.3022	
12		.7760	.6266	.6583	.2988	
15		.7771	.6290	.6597	.2962	
18		.7753	.6281	.6583	.2944	
21		.7768	.6290	.6598	.2956	
24		.7773	.6298	.6603	.2950	
27		.7787	.6313	.6615	.2948	
30		.7803	.6317	.6615	.2972	
33		.7832	.6328	.6623	.3008	
36		.7860	.6344	.6632	.3032	
40		.7874	.6350	.6640	.3048	
43		.7871	.6345	.6640	.3052	
46		.7887	.6353	.6646	.3058	
49		.7896	.6368	.6660	.3056	
52		.7901	.6378	.6664	.3046	
55		.7897	.6380	.6661	.3034	
58		.7905	.6386	.6665	.3038	
61		.7935	.6405	.6686	.3040	
64		.7927	.6398	.6678	.3058	
67		.7949	.6417	.6700	.3064	
70		.7944	.6417	.6696	.3054	
73		.7948	.6423	.6702	.3050	
76		.7957	.6427	.6707	.3062	
79		.7988	.6460	.6737	.3056	
82		.7983	.6453	.6728	.3060	
85		.7974	.6443	.6721	.3062	
88		.7986	.6456	.6739	.3058	
91		.7980	.6452	.6732	.3056	
94		.7976	.6458	.6737	.3036	
97		.7992	.6463	.6757	.3058	
100		.7985	.6468	.6757	.3034	
103		.7965	.6455	.6745	.3020	
106		.7972	.6457	.6743	.3030	
109		.7968	.6458	.6750	.3020	
112		.7968	.6462	.6748	.3012	
115		.7978	.6475	.6754	.3006	
118		.7993	.6490	.6780	.3004	
121		.7975	.6472	.6774	.3006	
124		.7972	.6467	.6750	.3010	
127		.7983	.6478	.6753	.3010	

3. The polarization when platinum electrodes were used is approximately equivalent to the polarization when copper electrodes were used, other conditions remaining constant.

4. The first increase in polarization is due simply to increased work involved in depositing copper from solutions containing gelatin.

5. The second rapid increase in polarization, we believe, is due to the partial gelation of the gelatin, and the increased work necessary to get the copper ions to the electrode and discharged.

6. This gelation is the result of increasing concentration of the gelatin in the vicinity of the cathode.

7. The increase in concentration of gelatin in the vicinity of the cathode is the result of migration of the gelatin ions, so to speak, to the cathode and mechanically stopping there, or is the result of migration of the gelatin ions to the cathode, and being adsorbed on the copper crystals of the cathode.

8. Changes in pH alter the polarization curves markedly from those electrolytes which contain gelatin.

9. Electrolytes containing 1/2 molar copper sulfate, 1-1/2 per cent gelatin and a pH of 1.99 evolved hydrogen at a current density of 2 amperes per square decimeter.

10. Temperature changes alter polarization curves greatly.

11. Numerous minor irregularities in polarization curves may be explained by assuming that such variations are the result of slight variations in conditions.

12. Polarization at 25°C. and a C.D. of .8 amperes per square decimeter is practically independent of time over a 3 hour period.

A Study of Excess Weight from Copper-Gelatin Electro-Deposits

Introductory

It has been pointed out previously that copper electro-plated from copper sulfate solutions containing gelatin gives deposits of greater mass than normal. That is, if copper is plated from several cells, which are in series, the weight of the deposit from the electrolyte which contains gelatin will be greater than the weight of the deposit from gelatin-free electrolytes. The difference in mass between the entire deposit and the contained copper has been shown by Marie and Buffat (loc.cit.) to consist of gelatin and sulfate. Their conclusions that the deposit actually contained gelatin was based upon combustion analyses for both carbon and nitrogen.

During this study the gelatin content of the deposits was obtained by difference, after the copper had been determined quantitatively. It was found that in nearly all cases the actual copper content was slightly in excess of that deposited from a coulometer solution. And it is thought that this excess copper was held mechanically or in an adsorbed condition within the deposit. In the electrolyte, since the gelatin migrates toward the cathode, the gelatin must carry a positive ionic or adsorbed charge. If the gelatin carries an ionic charge, some proportion of it is with the sulfate.

This latter statement may be substantiated by the fact that analyses which will soon be given tend to show that more sulfate is present in the deposit than can be accounted for.

In this final section numerous examples will be given, involving this excess weight as a function of variables.

In some of the illustrations in the preceding section on polarization it was found that two polarization increases resulted from some solution which contained gelatin. The first polarization is increased to a normal rate. The second polarization increase is not normal, strictly speaking, is not normal, and may denote that we have two electrode processes, one taking place between a certain potential, and another in conjunction with the first taking place shows above this certain value.

If one or more experiments are carried out at potentials above and below this polarization increase, then the masses of deposits should be quite different, when the potential is less than 0.8 volt and when more than 0.8 volt.

Excess Weight and Current Density

The following experiment shows that we do not have two electrode processes taking place. Seven 2-hour runs were made using 1/2 molar copper sulfate, containing 1/2 per cent gelatin, at a pH of 3.38 and at 25°C. Seven current densities were used, which values were very near those given in Table 26. It was very difficult to continue a run

for a 2-hour period without slight variations in current occurring. In each run were one to two gelatin cells containing 1/2 molar copper sulfate, and one or two coulometers. The coulometer deposits were taken as directly proportional to the quantity of electricity, and since the time factor was constant, the coulometer deposit was directly proportional to the current density. Thus in this experiment all coulometer and gelatin deposits were calculated to the respective current densities shown in the table.

Table 26

Cur. Den.	Coul. Dep.	Gel. Dep.	Exc. Wt.
.32 Amp.	.0471 gm.	.0481 gm.	.0010 gm.
.64	.0942	.0968	.0026
.88	.1296	.1336	.0040
1.28	.1883	.1948	.0065
1.84	.2710	.2852	.0142
2.40	.3536	.3730	.0194
3.20	.4720	.4961	.0241

The curve shown on Plate VI shows graphically the results from the above table, in terms of excess deposit and current density.

The curve in the plate is very regular and smooth, and shows no abrupt breaks. Although an inflection occurs at about the center point, this change in the direction of the curve has no significant meaning other than indicating that the rate of gain in excess weight decreases with increase in current density above 1.6 amperes.

At the current density of 0.80 amperes no change in

Curve Showing Relation
Between Excess Weight
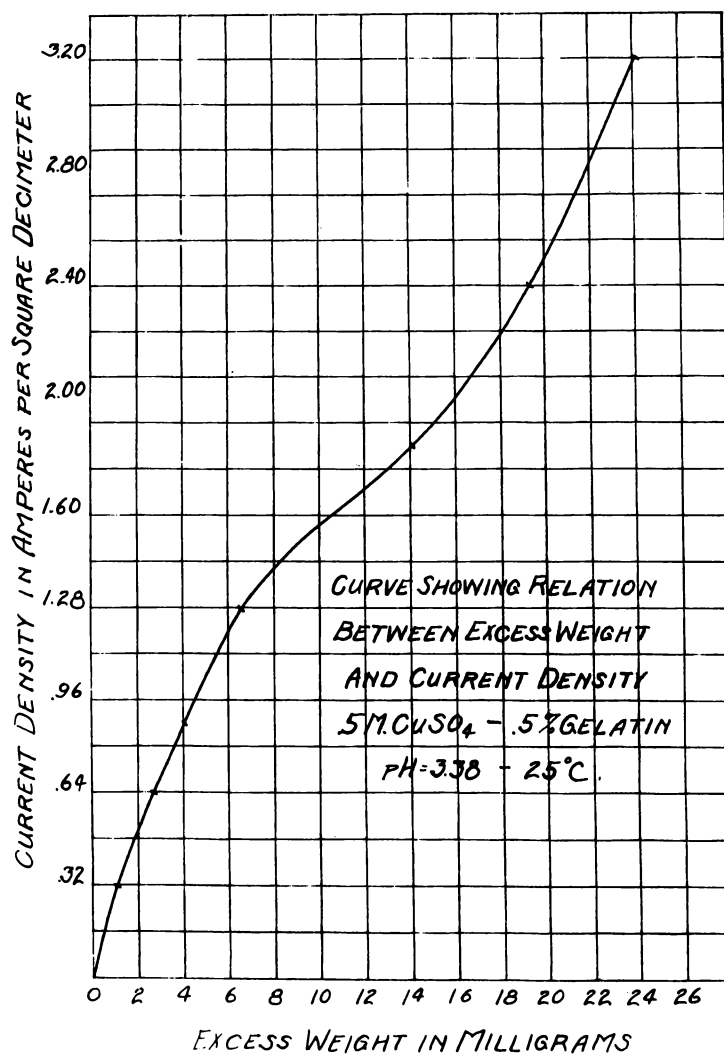And Current Density
.5 M. CuSO₄ - .5% Gelatin
pH=3.38 - 25°C.

Plate VI
Excess Weight Curve

the direction of the curve occurs. It was at this current density that the polarization experiments indicated a change in electrode process might take place. Accordingly at about 0.8 amperes a nearly horizontal segment should be present, but obviously it is not. The uniformity then is interpreted to mean that no change in electrode process occurs at 0.8 amperes current density, with 1/2 molar copper sulfate, and 1/2 per cent gelatin at $25^{\circ}C$.

Relation of Excess Weight and Current at Constant Current Density

Another experiment was made to observe the effect of variation of current but at a constant current density. One run was made using a current of .0315 amperes and two sizes of electrodes. One set of electrodes measured approximately 1.77 centimeters on an edge, giving an area of nearly 3.12 square centimeters. The other set was 2.5 centimeters squared, giving an area of 6.25 square centimeters. The current of .0315 amperes gave a current density of 1 ampere per square decimeter with the smaller electrodes and a current density of 1/2 ampere per square decimeter with the larger electrodes.

Half molar copper sulfate solutions containing variablequantities of gelatin were used as electrolytes with both sizes of cathodes. Also duplicate cells were run with each concentration of gelatin. The copper coulometer electrolytes were maintained at $0^{\circ}C$. to insure a more accurate

measure of the quantity of electricity that flowed. Richards, Collins and Heimrod[1] recommend the use of the copper coulometer at zero degrees Centigrade. Tables 27 and 28 give *bubbled* the results of this portion of the experiment. These two *gas then* tables are shown graphically in Plate VII.

Table 27

Excess Weights from .5 M. $CuSO_4$, .0315 Amps. (.5 Amps. per decimeter squared), 5 hours. Weights in gms. and mgms.

	2.0% gel.		0.5% gel.		.25% gel.	
Dep.	.3899	.3897	.3878	.3884	.3872	.3896 gms.
Ex.Wt.	11.4	11.2	9.3	9.9	8.7	11.1 mgms
Cu	.3803	.3800	.3795	.3793	.3795	.3801 gms.
Ex.Cu.	1.8	1.5	1.0	0.8	1.0	1.6 mgms

	.12% gel.		.03% gel.		Coulometers	
Dep.	.3865	.3864	.3829	.3836	.3783	.3787 gms.
Ex.wt.	8.0	7.9	4.4	5.1	avg. .3785 gm.	
Cu.	.3795	.3796	.3799	.3798	.3780	.3784 gms.
Ex.Cu.	1.0	1.1	1.4	1.3	---	---

Table 28

Same conditions as Table 27, excepting 1 amp. per dcm^2.

	2.0% gel.		0.5% gel.		.25% gel.	
Dep.	.3938	.3942	.3919	.3922	.3919	.3922 gm.
Exc.Wt.	13.2	14.6	12.3	12.6	12.3	12.6 mg.
Cu.	.3799	.3796	.3800	.3798	.3798	.3796 gm
Exc.Cu	0.3	0.0	0.4	0.2	0.2	0.0

	.12% gel.		.03% gel.		Coulometers	
Dep.	.3894	.3895	.3838	.3839	.3795	.3797
Exc.Wt.	9.9	9.9	4.2	4.3	av. .3796	
Cu.	.3799	.3796	.3800	.3798	.3798	.3796
Exc.Cu	0.0	0.3	0.7	0.8		

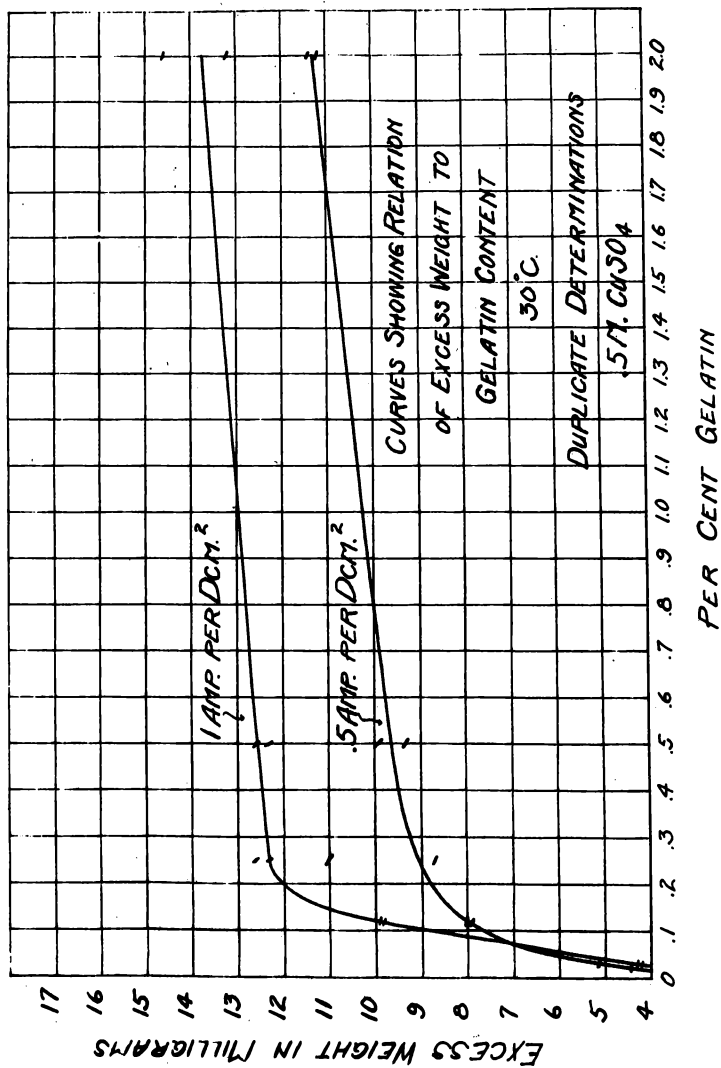[1] Richards, Collins, Heimrod, Proc. Am. Acad.Sci., 35, 123, 1899.

Plate VII
Excess Weight Curves

The curves were plotted from an approximate average of the duplicate determinations. From the curves and the plotted points representing excess weight as a function of concentration of gelatin, it may be seen how far some deviate from a smooth curve. The weight of the redeposited copper in each of these sets of duplicates agrees with one another very well. The failure of the original deposits to agree with each other in mass must then be due to difference in gelatin content. The four electrolytes containing 2.0 per cent gelatin in this double run were identical. They were prepared as follows; one hundred and sixty cubic centimeters of a stock solution of 1.25 molar copper sulfate was diluted to half molar with 260 cubic centimeters distilled water. Then to this 400 cubic centimeters of .5 molar solution was added 8 grams of gelatin, the whole heated to 60°C., and the gelatin dissolved with stirring. Nearly two hours warming at 55 to 60° with occasional stirring were necessary to dissolve the gelatin, since the Eastman gelatin was made into fairly thick sheets. After dissolving was complete the solution was cooled to 30°C. and poured into the proper 100 cubic centimeter beakers, two of which were used with the small and two with the large electrodes. The platinum electrodes had been previously cleaned with nitric acid, washed and ignited. The anodes had been previously given a heavy plate of copper from a copper sulfate-sulfuric acid bath. Thus as nearly as pos-

sible all conditions were identical, but still in several cases in this experiment, duplicate deposits failed to agree in weight. Since these deposits contain very nearly the same number of grams of copper, the error must be in the quantity of adsorbed gelatin.

Another run was made quite similar to the one just described. The only variation was the current, which was maintained at a value of .0625 in place of .0312 amperes. The two different sizes of electrodes were used again in this run giving with the large electrodes a current density of 1 ampere, and with the small ones a current density of 2 amperes per square decimeter. The results of this run are shown in Tables 29 and 30, and the approximate average of duplicate excess weights plotted against concentration of gelatin on Plate VIII.

Table 29

Excess Weights from .5 M. CuSO4, 0.625 amps.(.5 Amps per decimeter squared), 5 hours. Weights in gms. and mgms.

	2.0% gel.		0.5% gel.		.25% gel.	
Dep.	.4020	------	.4012	.4010	.4013	.4002
Exc. Wt	14.1	---	13.3	13.1	13.4	12.3
Cu.	.3889	------	.3892	.3894	.3895	.3892
Exc. Cu.	1.0	---	1.3	1.5	1.6	1.3

	.12% gel.		.03% gel.		Coulometers	
Dep.	.3988	.3989	.3929	.3930	.3878	.3880
Exc.Wt.	10.9	11.0	5.0	5.1	av.	.3880
Cu.	.3897	.3895	.3889	.3890	.3879	.3874
Exc.Cu.	1.8	1.6	1.0	1.1	---	---

CURVES SHOWING RELATION
OF EXCESS WEIGHT TO
GELATIN CONTENT
30°C.

DUPLICATE DETERMINATIONS
.5 M. CuSO₄

2 AMPS. PER DCM.²
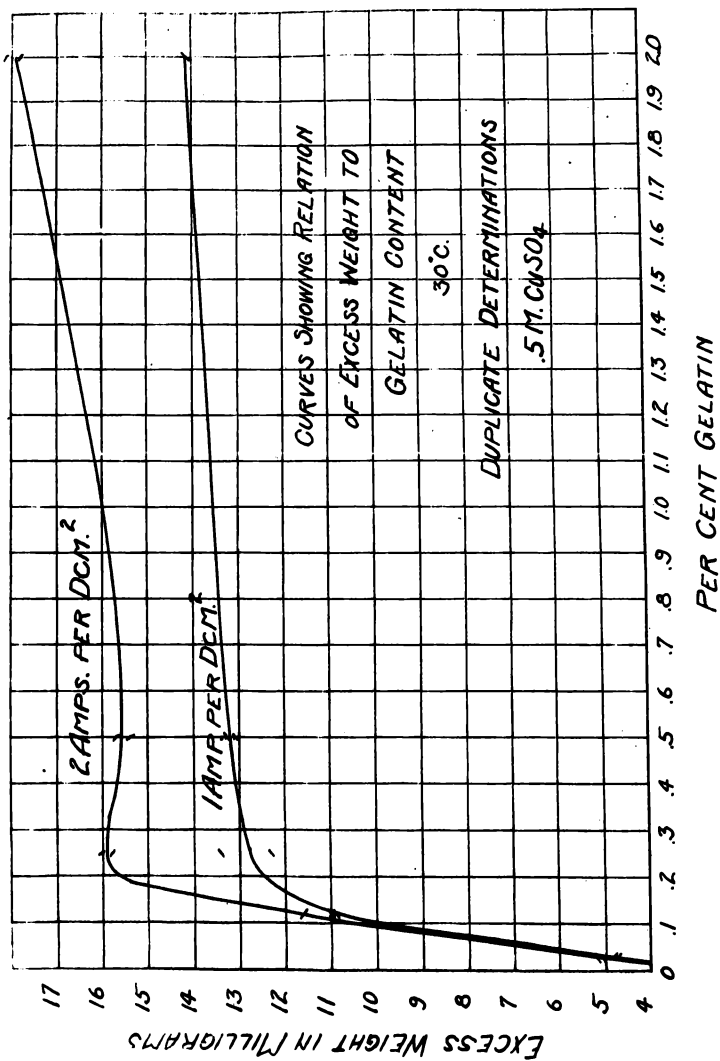
1 AMP. PER DCM.²

EXCESS WEIGHT IN MILLIGRAMS

PER CENT GELATIN

Plate VIII
Excess Weight Curves

Table 30

Excess Weights from .5 M. CuSO$_4$, .0625 Amps.(.5 Amps. per decimeter squared), 5 hours, Weights in gms. and mgms.

	2.0% gel.		0.5% gel.		.25% gel.	
Dep.	.4068	.4064	.4040	.4043	.4046	.4044
Exc.Wt.	18.2	17.8	15.4	15.7	16.0	15.8
Cu.	.3902	.3899	.3895	.3899	.3899	.3898
Exc.Cu.	1.6	1.3	0.9	1.3	1.3	1.2

	.12 % gel.		.03% gel.		Coulometers	
Dep.	.4002	.4002	.3933	.3934	.3887	.3886
Exc.Wt.	11.6	11.6	4.7	4.8	av.	.3886
Cu.	.3897	.3898	.3887	.3894	.3883	.3883
Exc.Cu.	1.1	1.2	0.1	0.8	---	---

The temperature of the coulometer baths was 0°C.

The two curves shown on this plate are quite normal in nearly all respects. The curves showing the excess deposits from 2 amperes per square decimeter seems to pass through a maximum then decline slightly as gelatin concentration increases. This apparent variation is not common, although some curves become nearly horizontal after passing the point corresponding to one half per cent gelatin. This deviation is quite unimportant since its magnitude is only a fraction of a milligram.

In these two runs just described the coulometer deposits were not of the same magnitude, and to make a more definite comparison of the effect of different currents with the same current density, the weights of Table 28 were multiplied by the factor 1.0221. This factor is the ratio of the two coulometer deposits, and these deposits are proportional to the quantity of electricity that flowed

in the two runs of .0312 and .0625 amperes, both at a current density of 1 ampere per square decimeter. The ratio 1.0221 equals $\frac{.3880}{.3796}$. Table 31 shows these calculated results, which are now on a basis for comparison to the results

Table 31

Calculated Excess Weights from .5M $CuSO_4$, .0312 Amps. current, 5 hours, weights in gms. and mgms.

	2.0% gel.		0.5% gel.		.25% gel.	
Dep.	.4015	.4029	.4006	.4009	.4006	.4009
Exc.Wt.	13.5	14.9	12.6	12.9	12.6	12.9
Cu.	.3883	.3880	.3884	.3882	.3882	.3880
Exc.Cu.	0.3	0.0	0.4	0.2	0.2	0.0

	.12% gel		.03% gel.		Coulometer
Dep.	.3980	.3981	.3923	.3924	.3880
Exc.Wt.	10.0	10.1	4.3	4.4	--
Cu.	.3890	.3883	.3887	.3888	
Exc.Cu.	1.0	0.3	0.7	0.8	

shown in Table 29. The weights from the calculated table 31, which represent the current of 0.0312 amperes, are smaller with only one exception, than the corresponding ones from Table 29, which represents .0625 amperes. This exception when studied closely, appears to be an erroneous result; when this result is corrected as nearly as possible, then all weights from the current .0312 amperes are less than those from .0625 amperes.

Since the viscosity of solutions containing gelatin changes rapidly with changes in temperature, an interesting experiment should be the study of the effect of temperature upon the mass of cathodic deposit. In the several tables which follow are given the results of excess weight deter-

Table 32

	Coul		Ogel		.5%
	1.2919		1.2950		1.3581
Red	1.2913		1.2931		1.3001

Table 33

at 25°

Coul	.5%	.5%	Coul
.7817	.8219	.8225	.7819
.7814	.7873	.7873	.7815

minations at several temperatures.

The Effect of Temperature upon Excess Weight

The general procedure in these tests is quite similar
to that previously described. 0.5 molar copper sulfate contain-
ing .5% gelatin was used at the various temperatures. In
several instances a cell was inserted into the hookup which
contained 0.0 per cent gelatin. These cells give erroneous
results due to oxide formation, which results in all instances
give too large deposits. In the tables these results will
be given, however, for comparison purposes. Tables 32 and
33 give the results of two of these runs, at a current den-
sity of 2 amperes per square decimeters

<div align="center">Table 32</div>

Excess Weight from .5 M. $CuSO_4$, C.D. 2 amps., $25^{\circ}C$.

	Coulometer	0 gel.	.5% gel.
Deposit	1.0000	1.0023	1.0512
Exc.Weight	----	2.3	51.2
Redep. Cu.	.9995	1.0009	1.0063
Exc. Cu.	----	0.9	6.3

<div align="center">Table 33</div>

Excess Weight from .5M. $CuSO_4$, C.D. 2 amps., $25^{\circ}C$.

	Coulometer	0.5% gel.		Coulometer
Deposit	1.0000	1.0512	1.0525	1.0000
Exc.Weight	---	51.2	52.5	---
Redep. Cu.	.9994	1.0069	1.0069	.9996
Exc. Cu.	---	6.9	6.9	---

These experiments were continued over a period of
approximately 5 hours and the deposits all calculated to
the basis of 1.0000 gram of coulometer copper at the resp-

at 2°   Coulom   Orig   No Gil   .570

                .7338   .7355   .7794

Redepoint   .7332   .7332   .7390

at 30°

                .7329   .7374   .7650

ReD.   ————   .7359   .7359

ective temperature. The runs whose data are given in these two tables were made on different days; they are duplicate runs but not in the sense of having been made at the same time. The excess weights from the gelatin cells are in very good agreement considering the large amount of the deposit.

Table 34 shows the excess weight data from gelatin cells at 21° and 30°C., half molar copper sulfate and .5 per cent gelatin.

Table 34
Excess weight from .5 M. CuSO$_4$, C.D. 2 amps., 21°C.

	Coulometer	No. Gel.	.5% gel.
Deposit	1.0000	1.0025	1.0623 gms.
Exc.Weight	---	2.5	62.3 mgm.
Redep. Cu.	.9993	.9993	1.0073 gms.
Exc. Cu.	---	-0.7	7.3 mgm.

Excess weight from .5M CuSO$_4$, C.D. 2 amps., 30°C.

	Coulometer	No. Gel.	.5% gel.
Deposit	1.0000	1.0061	1.0438 gms.
Exc.Weight	---	6.1	43.8 mgm.
Redep. Cu.	---	1.0030	1.0030 gms.
Exc. Cu.	---	3.0	3.0 mgm.

Electrolyses at these two temperatures were carried on in series. This table shows quite different excess weights. The electrolyte at 30°C. gave an excess of only 43.8 milligrams compared to 51.2 milligrams at 25° and 62.5 milligrams at 21°C.

Table 35 gives a duplicate determination of the experiment reported in Table 34, with the exception that the cell which contained no gelatin was replaced by a gelatin cell, giving duplicate gelatin cells.

Table 35

21°

	Coulom	.5%	.5%
	.9787	1.0392	1.0387
Re D	.9766* all copper	.9802	.9858

30°

	.9780	1.0188	1.0190
Re D	———	.9826	.9818

Table 36.

21°

	.Coul	.5%	.5%
	1.0152	1.0761	1.0780
Re D	+.———	1.0239	1.0242

39°

	1.0147	1.0459	1.0458
Re D	———	1.0159	1.0175

Table 35

Excess Weight from .5 M. CuSO$_4$, C.D. 2 amps., 21°C.

	Coulometer	0.5% gel.	0.5% gel.
Deposit	1.0000	1.0619	1.0624
Exc. Weight	---	61.9	62.4
Redep. Cu.	----	1.0017	1.0073
Exc. Cu.	---	1.7	7.3

Excess Weight from .5M CuSO$_4$, C.D. 2 amps., 30°C.

	Coulometer		
Deposit	1.0000	1.∅0417	1.∅0419
Exc. Weight	---	41.7	41.9
Redep. Cu.	----	1.0047	1.0039
Exc. Cu.	---	4.7	3.9

In the part of the previous table under 21°, the reason why the first gelatin cell should give such a low value for excess copper, must be that there was only a little copper sulfate entrapped during deposition. The excess weights for both 21° and 30° agree very well with the corresponding values of the preceding table.

Table 36 gives the results of a run similar to the previous one excepting one portion was at 39°C., and the other at 21° as before.

Table 36

Excess Weight from .5 M. CuSO$_4$, 2 amps. C.D., 21°C.

	Coulometer	.5% gel.	15% gel.
Deposit	1.0000	1.0600	1.0619 gm.
Exc. Weight	---	60.0	61.9 mg.
Redep. Cu.	----	1.0085	1.0088 gm.
Exc. Cu.	---	8.5	8.8 mg.

Excess Weight from .5 M. CuSO$_4$, 2 amps. C.D., 39°C.

	Coulometer		
Deposit	1.0000	1.0307	1.0306 gm.
Exc. Weight	---	30.7	30.6 mg.
Redep. Cu.	----	1.0033	1.0027 gm.
Exc. Cu.	---	3.3	2.7 mg.

Table 37

at 39°

Coal		.5 %	.5 %
.9793		1.0071	1.0072
.9783		.9808	.9816

at 21°

Coal			
.9778		1.0368	
.9785		.9869	

Table 38

at 21° Coal		.5 %	.5 %
.9044		.9582	.8574
Red. .9036		.9129	.9116

at 39°

.9031		.9299	.9318
.9011		.9042	.9059

At 39° the excess weight is still appreciably smaller than at 30°, while the one at 21° agrees well with those previously. Table 37 is a duplicate of Table 36.

Table 37

Excess Weight from .5 M. CuSO$_4$, 2 amps. C.D., 39°C.

	Coulometer	.5% gel.	15% gel.
Deposit	1.0000	1.0281	1.0281
Exc. Weight	---	28.1	28.1
Redep. Cu.	----	1.0015	1.0023
Exc. Cu.	---	1.5	2.3

Excess Weight from .5 M. CuSO$_4$, 2 amps. C.D., 21°C.

Deposit	1.0000	1.0572
Exc. Weight	---	57.2
Redep. Cu.	----	1.0072
Exc. Cu.	---	7.2

These excess weight values are both some little smaller than the corresponding ones from Table 36. In Table 38 is still another duplicate run at 21° and 39°, and this table shows results very similar to those in Tables 36 and 37.

Table 38

Excess Weight from .5 M. CuSO$_4$, 2 amps. C.D., 21°.

	Coulometer	.5 % gel.	.5% gel.
Deposit	1.0000	1.0595	1.0587
Exc. Weight	---	59.5	58.7
Redep. Cu.	----	1.0094	1.0081
Exc. Cu.	---	9.4	8.1

Excess Weight from .5 M. CuSO$_4$, 2 amps. C.D., 39°C.

Deposit	1.0000	1.0292	1.0311
Exc. Weight	---	29.2	31.1
Redep. Cu.	----	1.0009	1.0026
Exc. Cu.	---	0.9	2.6

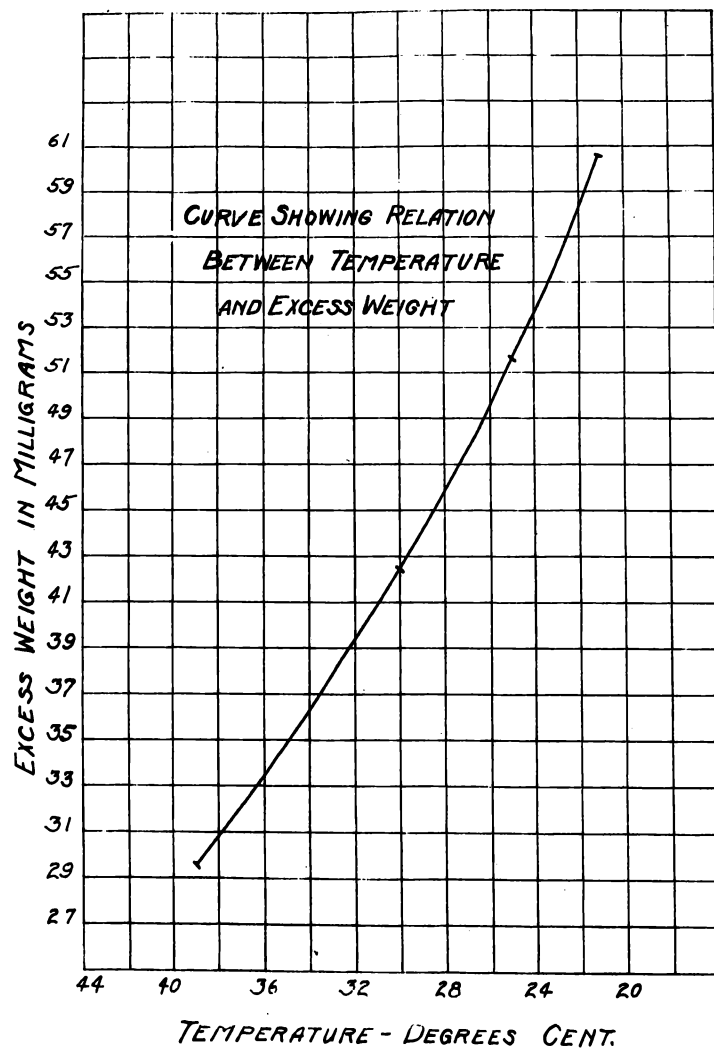CURVE SHOWING RELATION
BETWEEN TEMPERATURE
AND EXCESS WEIGHT

Plate IX
Excess Weight Curve

In summarizing these temperature experiments and preparing them for plotting, the average of all eight determinations at 21° was taken for the point at 21° in the curve on Plate IX. The excess weight at 25° is the average of 3, and the point at 30° is the average of 3, while the higher temperature, 39°, is represented by a mean of 6 determinations.

The curve appears very smooth and uniform, and without break nor inflection, hence excess weight varies uniformly with temperature over the range 21 to 39°.

Excess Weight from 0.0% gelatin solutions

Several of the tables in the study of the effect of temperature upon the magnitude of excess weight contained weights of deposits from solutions which contained no gelatin. These deposits, like those from gelatin solutions, are always heavier than the corresponding coulometer deposit. Two runs were made in which copper sulfate solutions of several concentrations were electrolyzed in the absence of gelatin. Tables 39 and 40 show the results of these two runs; the temperature of the coulometers was 0°C.

Table 39 shows quite a large excess weight for the deposits, especially in the 1.00, 0.75 and 0.50 molar solutions. The 1.25 molar solution might be expected to give a lower excess weight than the more dilute solution, since it has a higher hydrogen ion concentration. And this greater acidity would have a tendency to prevent

Table 39

Excess Weights with 0% gelatin, 9-1/2 hours, 30°C.
Variable copper sulfate.

	1.25 M.	1.00 M.	0.75 M.	0.50 M.	0.25 M.
Deposit	1.2440	1.2448	1.2458	1.2455	1.2438
Exc. Wt.	1.6	2.4	3.4	3.1	1.4
Redep. Cu.	1.2423	1.2439	1.2430	1.2433	1.2422
Exc. Cu.	-0.1	+1.3	0.6	0.9	-0.2

Coulometers 1.2426, 1.2418, 1.2428, av.= 1.2424 gms.

$CD = ?$

Table 40

Excess Weights with 0% gelatin, 10 hours, 30°C.
Variable copper sulfate.

	1.25 M.	1.00 M.	0.75 M.	0.50 M.	0.25 M.
Deposit	1.4865	1.4874	1.4878	1.4891	1.4878
Exc. Wt.	1.2	2.1	2.5	3.8	2.5
Redep. Cu.	1.4848	1.4849	1.4854	1.4881	1.4844
Exc. Cu.	-0.5	-0.4	+0.1	2.8	-0.9

Coulometers, 1.4851, 1.4852, 1.4856, av.= 1.4853.

oxide formation upon the cathode surface. Hydrogen ion measurements have been made on copper sulfate solutions with the following results;

	1.25 M.	1.00 M.	0.75 M.	0.50 M.	0.25 M.
pH =	3.11	3.26	3.37	3.55	3.77

These figures for higher concentrations of copper sulfate show tht an increase in pH gives greater excess weight until the 0.5 and 0.25 molar solutions, when these excess weights, and quite notably the 0.25 M. one gives a decrease in excess weight. In the 1.25 molar solution the acidity may be sufficiently great to prevent the excessive oxide formation. These deposits, in place of presenting a

bright copper color, were darkened somewhat by the oxide.

The redeposition of the copper in most cases shows that there is actually too much copper deposited. However, the larger part of the excess weight, must have been oxygen and this element disappeared when the copper analysis was made.

Excess Weight with Variation of Gelatin and current density

The experiment which follows studies both the variation of current density, but with a constant current, similar to an experiment previously described. The variation in the current density at constant current was accomplished by using plainum electrodes of two sizes. The same current, .0625 amperes were used during the two tests, and since the cathodes were 6.25 and 3.12 square centimeters in area approximately, the current densities were very near to 1.0 and 2.0 amperes per square decimeter. The coulometers werekept at $0^{\circ}C.$ throughout the run to insure a more accurate measure of the quantity of electricity that passed.

Tables 41 and 42 show the results of these variations in current density and gelatin at constant current, using both 1.0 molar and 0.5 molar copper sulfate. In these two tables and plotted on the curves in Plates X and XI are shown the original data. To get them upon a more comparable basis the excess weights of Table 41 are calculated to correspond from the coulometer deposit of .3684 grams to .3792 grams. This calculation may be carried out since excess
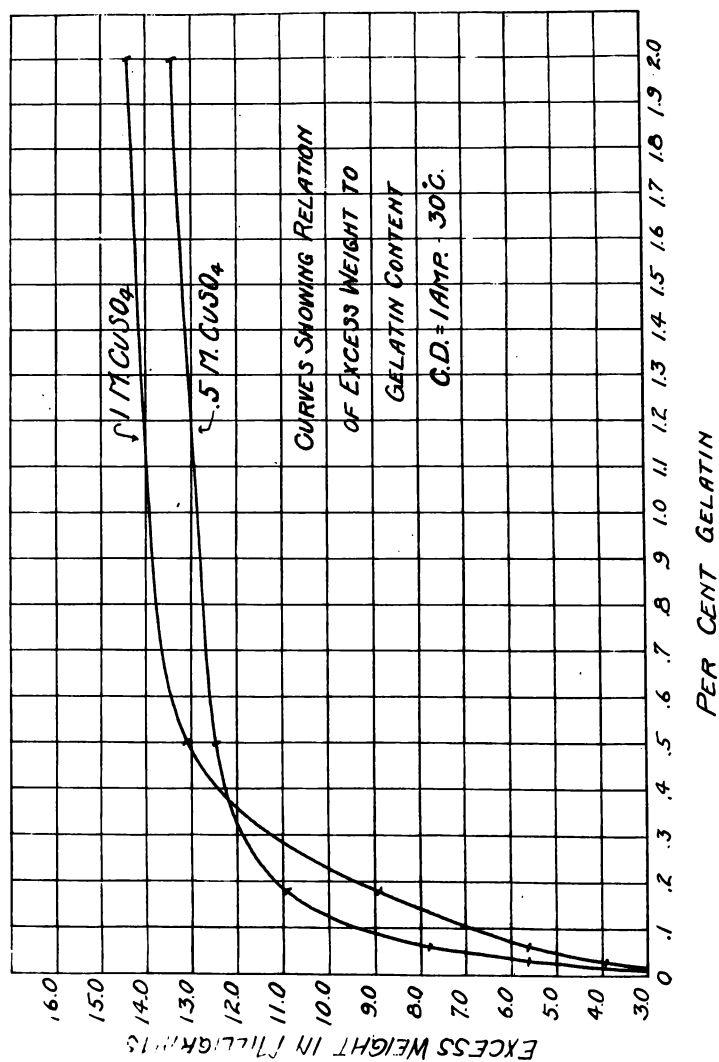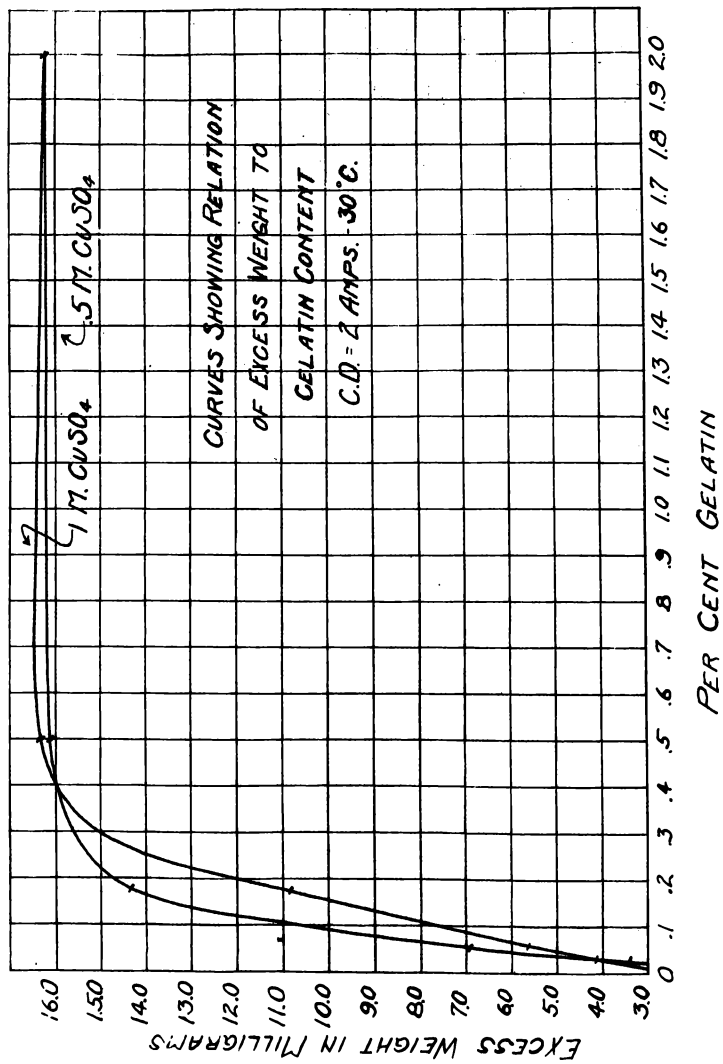
Plate X
Excess Weight Curves

Plate XI
Excess Weight Curves

Table 41

Excess Weights from variable gelatin and $CuSO_4$, at 2 Amps.
C.D.,(.0625 amps current), $30^\circ C$, for 5 hours.

1.0 molar $CuSO_4$

% Gel.	2.0	0.5	0.18	0.06	0.03	0.0
Deposit	.3846	.3847	.3792	.3740	.3725	.3695
Exo. Wt.	16.2	16.3	10.8	5.6	4.1	1.1
Redep.Cu.	.3691	.3701	.3704	.3703	.3700	.3683
Exc. Cu.	0.7	1.7	2.0	1.9	1.6	-0.1

0.5 molar $CuSO_4$

Deposit	.3846	.3845	.3827	.3753	.3718	.3708
Exc.Wt.	16.2	16.1	14.3	6.9	3.4	2.7
Redep. Cu.	.3679	.3694	.3699	.3693	.3685	.3693
Exc.Cu.	-0.5	+1.0	1.5	0.9	0.1	0.9

Coulometers,.3688, .3681, .3684, av.= .3684

Table 42

Excess Weights from variable gelatin and $CuSO_4$, at 1 Amp.
C.D., $30oC$., for 5 hours.

0.5 molar $CuSO_4$

% gel.	2.0	0.5	0.18	0.06	0.03	0.0
Deposit	..3926	.3915	.3901	.3870	.3843	.3863
Exo. Wt.	13.4	12.4	10.9	7.8	5.6	6.9
Redep. Cu.	.3797	.3804	.3806	.3811	.3808	.3834
Exc. Cu.	0.5	1.2	1.4	1.9	1.6	4.2

1.0 molar $CuSO_4$

Deposit	.3936	.3923	.3881	.3848	.3831	.3855
Exc. Wt.	14.4	13.1	8.9	5.6	3.9	6.1
Redep.Cu.	.3817	.3820	.3818	.3825	.3801	.3848
Exc.Cu.	2.5	2.8	2.6	3.3	0.9	5.6

Coulometers, .3797, .3790, .3791, av. = .3792gms.

weight varies very nearly as a straight line function with coulometer deposits. The results of this calculation are shown in Table 43.

Table 43

Excess Weight Calculated from .3684 to .3792 gms coulometer deposit; 30°C, 2 amps. C.D. Variable $CuSO_4$

1 molar $CuSO_4$

Gelatin %	2.0	0.5	0.18	0.06	0.03
Exc. Wt.	16.7	16.8	11.1	5.8	4.2 mgms.
Exc. Cu.	0.7	1.8	2.1	2.0	1.7 mgms.

0.5 molar $CuSO_4$

Exc. Wt.	16.7	16.6	14.7	7.1	3.5 mgms.
Exc. Cu.	-0.5	1.1	1.5	0.9	0.1 mgms.

There seems to be more variation in the excess weights than previous to recalculation. The excess weights at 2 amperes C.D. are greater than those for 1 ampere. This same variation has been borne out in numerous experiments during this work, even in coulometer deposits.

The following experiment was designed to study the excess weights over a wide range of concentrations of copper sulfate and of gelatin. The hydrogen ion concentration of each electrolyte was measured to observe its effect upon the excess weights of cathode deposits. Copper sulfate concentrations of 1.25, 1.00, 0.75, 0.50 and 0.25 molar were used with each of these concentrations, 2.0, 0.5 and 0.06 per cent of gelatin. The pH of each of these resulting solutions was determined along with that of the copper sulfate solution with 0.0 per cent gelatin.

Table 44 gives the results of this experiment.

Table 44

Excess Weights as Functions of $CuSO_4$ concentration and Gelatin concentration, C.D. 1.5-2.0 Amps. 30°C.

Per Cent Gelatin	2.0	0.5	0.06	0.0	
1.25 M.CuSO₄					
pH	3.18	3.14	3.11	3.11	
Deposit	----	1.2958	1.2632	----	gms.
Exc.Wt.	----	49.5	16.9	----	mgms.
Redep. Cu.	----	1.2524	1.2503	----	gms.
Exc. Cu.	----	6.1	4.0	----	mgms.
1.00 M.CuSO₄					
pH	3.28	3.27	3.25	3.26	
Deposit	1.3181	1.2950	1.2657	----	gms.
Exc. Wt.	71.8	48.7	.19.4	----	mgms.
Redep. Cu.	1.2546	1.2509	1.2495	----	gms.
Exc. Cu.	8.3	4.6	3.2	----	mgms.
0.75 M.CuSO₄					
pH	3.44	3.41	3.38	3.37	
Deposit	1.3091	1.2891	1.2671	----	gms.
Exc. Wt.	62.8	42.9	20.8	----	mgms.
Redep. Cu.	1.2542	1.2506	1.2501	----	gms.
Exc. Cu.	7.9	4.3	3.8	----	mgms.
0.50 M. CuSO₄					
pH	3.60	3.58	3.56	3.55	
Deposit	1.3106	1.2922	1.2694	----	gms.
Exc. Wt.	64.3	45.9	23.1	----	mgms.
Redep. Cu.	1.2537	1.2501	1.2483	----	gms.
Exc. Cu.	7.9	3.8	2.0	----	mgms.
0.25 M.CuSO₄					
pH	3.84	3.82	3.80	3.77	
Deposit	1.3371	1.3126	1.2749	----	gms.
Exc. Cu.	80.8	66.3	28.6	----	mgms.
Redep. Cu.	1.2544	1.2534	1.2505	----	gms.
Exc. Cu.	8.1	7.1	4.5	----	mgms.

Coulometer deposits, 1.2459, 1.2464, 1.2464, av. = 1.2464.
Redeposit Cu, 1.2455, 1.2464, 1.2456.

The data of excess weights are plotted in the curves shown on Plate XII.

The curves appear very regular and smooth. The curve

The chart contains the following labels:

- 0.25 M CuSO₄
- 1.00 M CuSO₄
- 0.50 M CuSO₄
- 0.75 M CuSO₄
- 1.25 M CuSO₄
- CURVES SHOWING RELATION of EXCESS CATHODE WEIGHT to GELATIN CONTENT
- PER CENT GELATIN (horizontal axis): 0.05, 0.50, 2.0
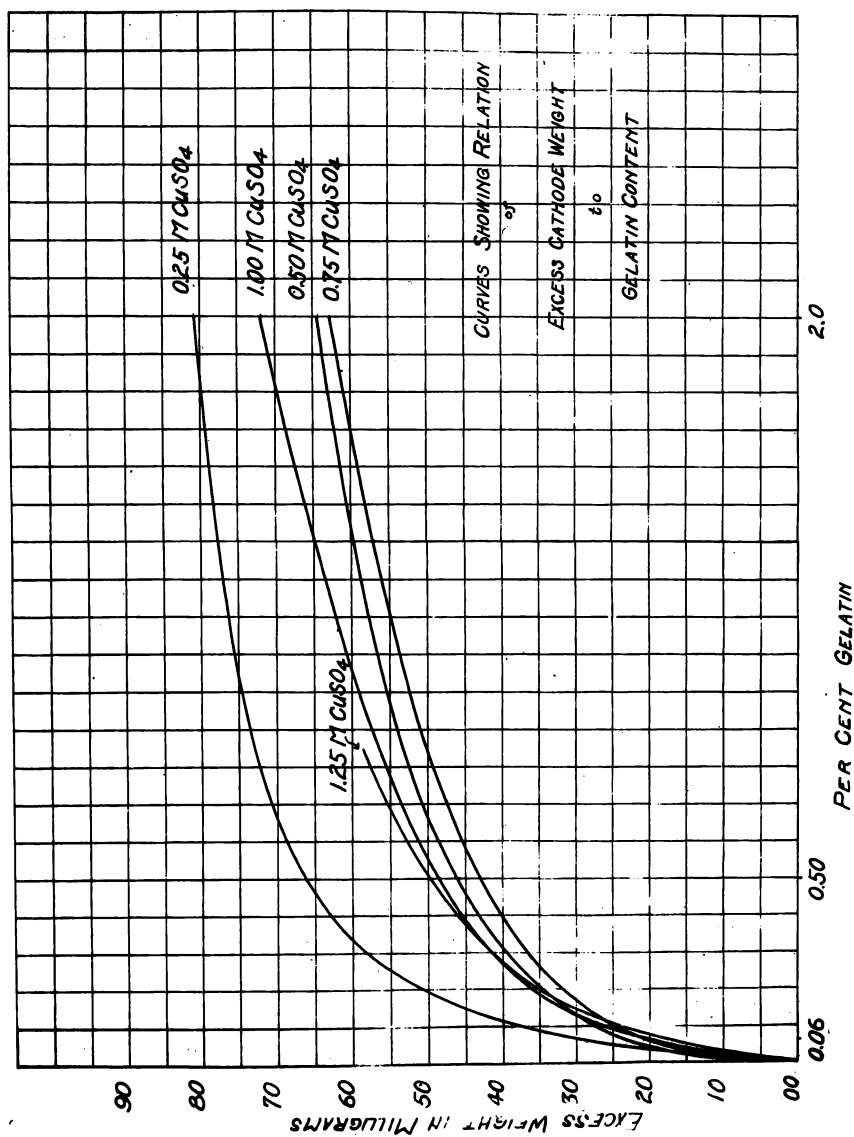- EXCESS WEIGHT IN MILLIGRAMS (vertical axis): 00, 10, 20, 30, 40, 50, 60, 70, 80, 90

Plate XII
Excess Weight Curves

representing excess weights for solution of 0.25 molar copper sulfate is the highest, showing that gelatin adsorption in that solution is the greatest. This concentration of copper sulfate obviously has quite low conductivity, and without doubt an appreciable portion of the current is carried by the positively charged gelatin. Obviously as the conductivity of the copper sulfate decreases the conductivity of the gelatin must increase. The greater conductivity of gelatin with respect to the copper sulfate will cause more gelatin to migrate to the cathode, and this increased gelatin in the cathode region gives more opportunity for adsorption. The result of the entire process is relatively great excess weights.

The 0.50 molar copper sulfate shows much smaller excess weights than the 1/4 molar solutions. Greater conductivity leaves less current to be carried by the gelatin, with the result of less adsorbed gelatin, and in turn lower excess weights. The 0.75 molar copper sulfate shows again slightly smaller excess weights.

The 1 molar solutions show quite a different aspect in regard to excess weights. In place of a further decrease in excess weights, quite a large increase exists. A possible explanation of this increase in excess weight may be that as the concentration of copper ions increases, they may be adsorbed in increasing numbers upon the gelatin particles, and as the copper ions migrate toward the cathode, the gelatin particles travel in that direction also, and the result is increased excess weights.

The excess weight curve representing the 1.25 molar copper sulfate is not complete since the electrolyte containing the 2.0 per cent gelatin became solid, with the result that hydrogen was evolved in place of copper being deposited. Since the resistance in the cell was increased appreciably by gelatin, the current fell from 2 amperes to 1.5 amperes for nearly a half hour period.

In addition to the weights of the deposits and excess weights, the copper content from each cathode was determined analytically, and calculated to terms of copper sulfate. This form is probably the form in which the excess copper exists in the deposits. It is quite reasonable to assume that the gelatin should carry in an adsorbed condition some copper sulfate to the cathode. A second possibility is the simple occlusion of the copper sulfate by the large particles of gelatin as they are adsorbed upon the newly formed crystals of copper. A third possibility is the reduction by gelatin of cupric ions to cuprous ions, thereby giving an excess weight of copper. These data are also included in Table XVII.

The lower set of curves in Plate XIII show the relation of this excess copper sulfate to the gelatin content. In these curves, again the 1/4 molar copper sulfate gave the highest curve for occluded copper sulfate. Close observation shows that these curves are in very nearly the same relation to each other as the total excess weight curves. This relationship would indicate that there is a simple
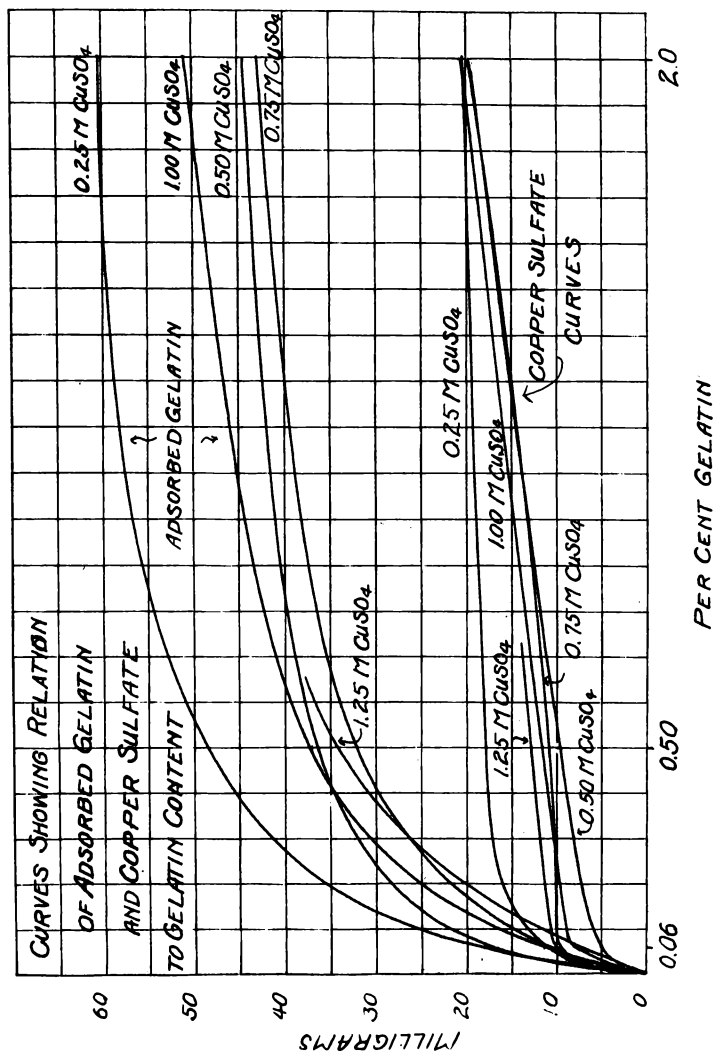
The figure contains the following labels:

CURVES SHOWING RELATION OF ADSORBED GELATIN AND COPPER SULFATE TO GELATIN CONTENT

0.25 M CuSO₄
1.00 M CuSO₄
0.50 M CuSO₄
0.75 M CuSO₄

ADSORBED GELATIN

1.25 M CuSO₄

0.25 M CuSO₄
1.00 M CuSO₄
0.75 M CuSO₄
1.25 M CuSO₄
0.50 M CuSO₄

COPPER SULFATE CURVES

MILLIGRAMS
60 50 40 30 20 10 0

0.06   0.50   PER CENT GELATIN   2.0

Plate XIII
Excess Weight Curves

relation between excess weight and adsorbed copper sulfate.

The second set of curves in this plate show the relation of adsorbed gelatin to the concentration of gelatin in the original electrolytes. The relation of these curves to one another is the same as that of the total excess weight curves on the previous plate. Thus, again, a relation seems to exist between the adsorbed gelatin and the adsorbed or occluded copper sulfate. Thus, in general, the greater the quantity of adsorbed gelatin, the excess copper content will b e larger, and obviously the total excess weight will then be greater.

Hydrogen ion or pH determinations were made upon each electrolyte of the above experiment and the data included in Table 44. The additions of the several concentrations of gelatin do not alter the pH of the copper sulfate solutions appreciably. The general effect of increasing gelatin is to buff or use up a portion of the free acidity.

In any of the concentrations of copper sulfate which were used, increasing the gelatin content decreases the pH, with the net result of a greater excess weight. However, it seems barely reasonable that pH changes of the magnitude of 0.1 to 0.4 would have such an influence as to change the excess weights from 20 to 50, or from 50 to 70 milligrams.

More variation in pH exists as the concentration of copper sulfate changes than when the gelatin content changes from .06 to .50 per cent or even to 2.0 per cent. The source of the acidity is the hydrolysis of the copper

sulfate to form cupric hydroxide and free sulfuric acid.
Curves could be drawn showing the relation of pH to excess
weight, but these are very regular and uniform and are of
no particular value.

Excess Weights plotted as log-log curves.

If this excess weight is strictly an adsorption phen-
omenon, then the logarithm of the excess weight when plotted
againt the logarithm of the gelatin concentration should
give a straight line. Plate XIV which follows shows the
logarithmic curves of excess weights and gelatin contents
given in Table 44.

The logarithmic curves representing .50 and .75
molar copper sulfate solutions appear to be some nearer
straight lines than the remainder. The 0.25 molar solution
curve shows the greatest deviation from this straight line
relation.

Since each of the curves on the plate represented only
three points it was deemed desirable to plot other curves
from an experiment in which more concentrations of gelatin
had been used. Hence, the excess weights and gelatin concen-
tration data were taken from Tables 41 and 42 and plotted
in logarithmic form on Plate XV. None of the curves on
this plate exhibit straight line properties, although port-
ions of curves Nos. 2 and 4 are fairly straight. This would
indicate that the excess weight is approximately a logarith-
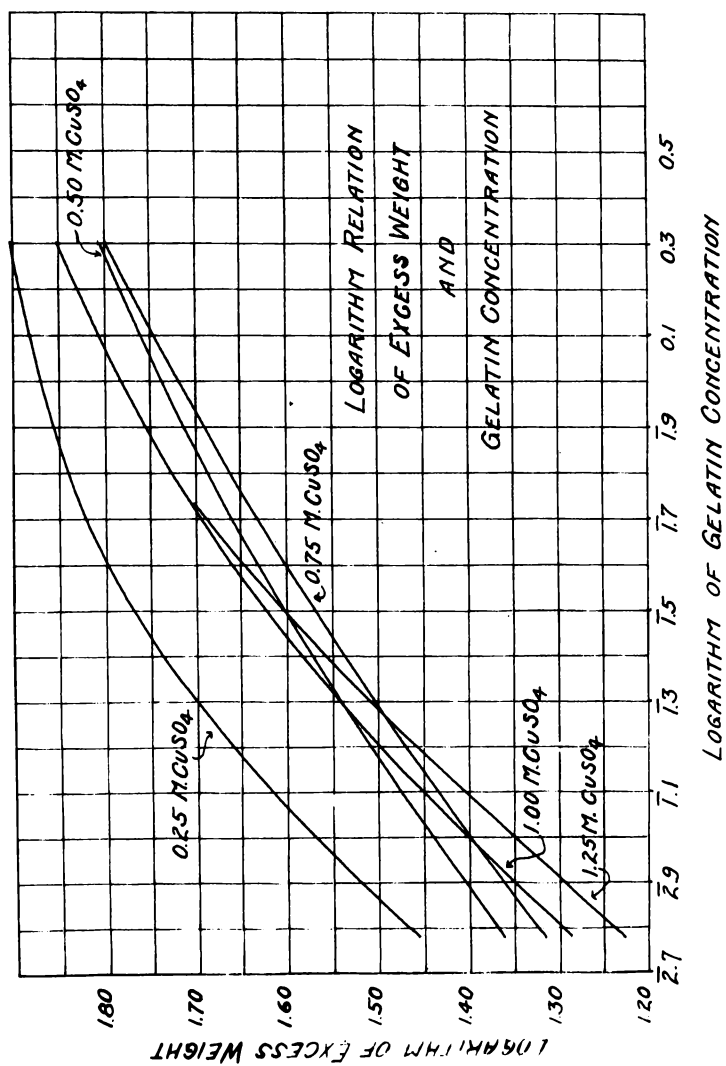mic function, and being of that nature suggests that the

Plate XIV
Logarithmic Curves

Curves Showing Logarithmic Relation of Excess Weight and Concentration of Gelatin

1 - 0.5 M CuSO₄ - 2Amps/DCM²
2 - 1.0 M CuSO₄ - 2 "
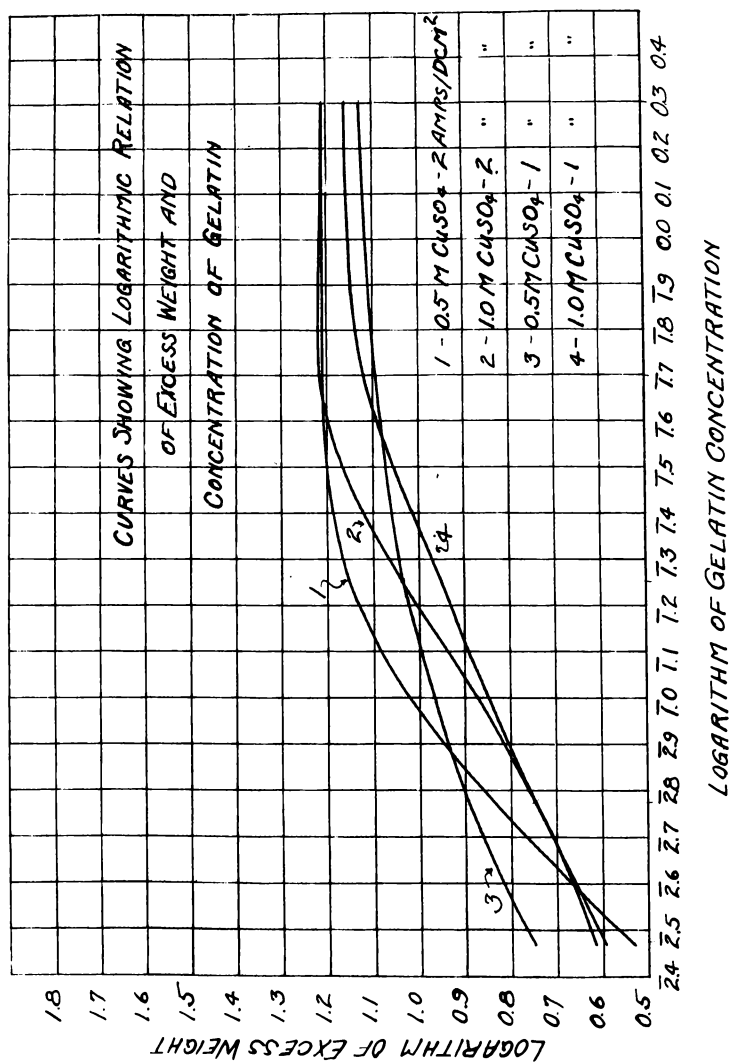3 - 0.5M CuSO₄ - 1 "
4 - 1.0M CuSO₄ - 1 "

Plate XV
Logarithmic Curves

excess weight is an adsorption phenomenon.

In place of the logarithmic values of the excess weight, it should be the logarithm of $\frac{x}{m}$, where x will represent the excess weight in milligrams, and m is the mass of the absorbent. If we consider m as a constant, then out plotting of log x and expecting a straight line is legitimate.

The adsorption relation is $\frac{x}{m} = ks$, where x and m refer to the milligrams gelatin adsorbed and mass of the absorbent respectively; s is the surface, and k a constant. If we keep m constant, then x varies as s. In other words if s remains constant, then the logarithm of the milligrams adsorbed and the logarithm of gelatin concentration should give a straight line. If s increases, then the log-log curve will bend concave upward. Our curves indicate that the specific surface of the deposited copper is decreasing as gelatin concentration increases beyond 0.5 per cent gelatin. The excess weight at the gelatin concentration of 0.5 per cent seems to have reached a saturation value. With increase in gelatin content if the number of milligrams excess weight do not increase, then its logarithm cannot increase, and our log-log curve bends concave downward.

Excess Weight as a Function of Time

For calculation purposes it has been assumed that the excess weights or rather the cathode weights were directly proportional to coulometer deposits. That is, if a coulometer

deposit were 0.5 gram and the deposit from a gelatin containing copper sulfate solution was .5025 grams, then if the run had been continued until the coulometer deposit was 1.0 gram, the gelatin deposit should be 1.0050 grams. This assumption is not strictly true, but deviations are not great. Since coulometer deposits are proportional to time, and if gelatin deposits are approximately proportional to coulometer deposits then the gelatin deposits should be approximately proportional to time, and it is this latter point that the following table and plate were designed to show.

It is not practical to plot actual gelatin deposit weights against coulometer weights, because of the difficulty of choosing a scale. But if the excess weight in milligrams be plotted against coulometer deposits, then the deviation from a straight line relation becomes apparent. In Table #5 are given coulometer deposits ranging in mass from 0.5 to 1.75 grams, and excess weights from about 20 to 87 milligrams. The conditions of the experiment were 0.5 molar copper sulfate electrolyte, 0.5 per cent gelatin, at $25^{\circ}C$, and at a current density of 2 amperes per decimeter squared. These results are plotted on Plate XVI.

Table 45

Excess Weight as Function of Coulometer deposits; $25^{\circ}C$, 1/2 % gelatin, 1/2 molar $CuSO_4$, C.D. 2 Amps.

Coulometer deposit grams	Excess Weight milligrams
.4880	20.9
.5314 (over)	21.9
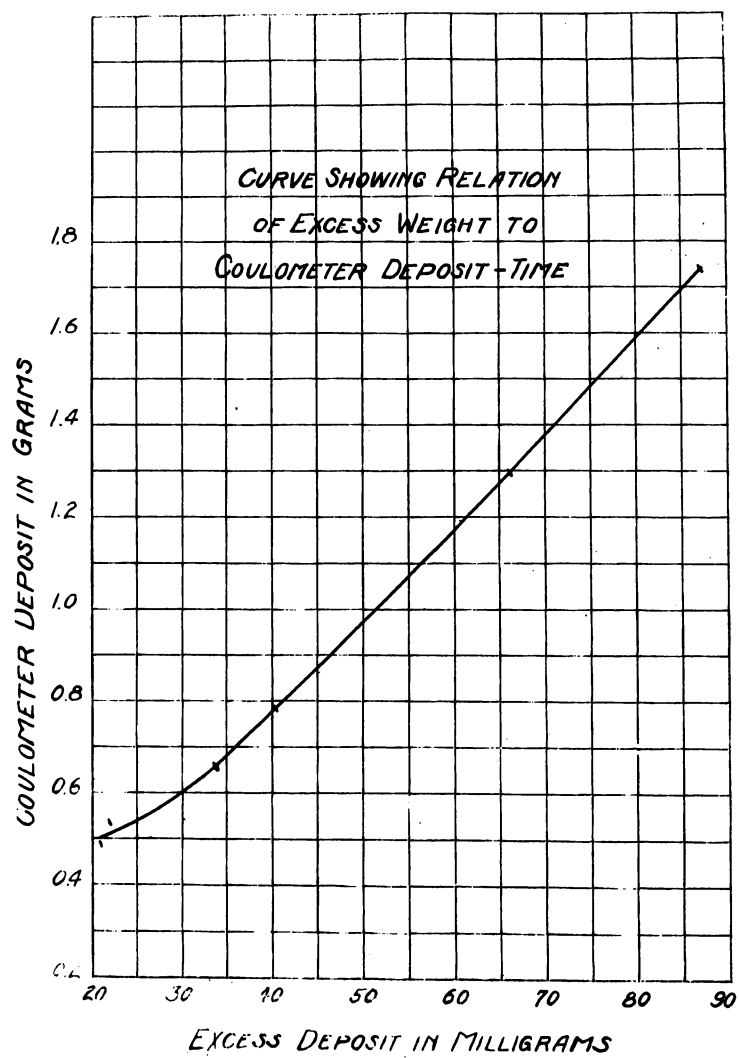
Plate XVI
Excess Weight Curve

Table 45 Cont'd

Coulometer deposit grams	Excess Weight Milligrams
.6585	33.6
.7818	40.4
1.2919	66.2
1.7389	86.9

As will be seen from the curve excess weights of 30 milligrams or over lie on a curve which approaches very closely a straight line. The point representing 21.9 milligrams is entirely off the curve.

Since this curve is so nearly a straight line, no appreciable error has been introduced in assuming the gelatin deposit directly proportional to the coulometer deposit and to time for calculations.

Attempts to determine sulfate in the presence of gelatin

It has previously been assumed that the copper in the gelatin deposit in excess of that contained in the coulometer deposit has been in the form of copper sulfate. Copper analyses and sulfate analyses were made in an attempt to determine whether or not the excess copper and the sulfate were present in equivalent quantities. The first point to be investigated is, after these gelatin containing deposits are dissolved in nitric acid and diluted is whether or not the sulfate can be completely precipitated. The decisive factor, of course, is the gelatin. To determine the feasibility of this precipitation, the following pro-

cedure was followed. Into each of four 400 cubic centimeter
beakers was placed 50 cc of a potassium sulfate solution
which contained about 0.8 grams per liter. Five cubic centi-
meters of nitric acid were added to each. Then into two of
the solutions was dissolved 1/2 gram of Eastman Kodak ash-
free gelatin, at about 60°C. After solution was complete,
the temperature of the four solutions was raised to about
80°C. and 15 cubic centimeters of a hot 10 per cent solution
of Barium nitrate added. Precipitation was slow, but after
some time barium sulfate could be seen settling to the bot-
tom of the beaker. The solutions were allowed to set for
about 16 hours, then filtered twice through Munktell papers.
The precipitates were thoroughly washed, and ignited in
platinum crucibles. The following gives the results of
this initial trial.

	no gelatin		&1/2 gram gelatin	
Barium Sulfate, gms.	.0700	.0701	.0682	.0689

The gelatin presumably protected or hindered complete
precipitation of the barium sulfate. Since these results
were not satisfactory, it was thought that precipitation
might be more complete if the solution after precipitation
were kept hot for several hours. Also 0.5 per cent gelatin
is one gram in 200 cubic centimeters of solution, and this
is a much larger proportion than ordinarily occurs in the
gelatin containing cathodes. Accordingly 15 milligrams
of gelatin were used in each of the gelatin containing

solutions. Two beakers contained potassium sulfate with
15 milligrams of gelatin each, and two contained only the
potassium sulfate. Precipitation was carried out in a man-
ner similar to that before. After precipitation, the sol-
utions were kept near the boiling point for about 2-1/2
hours, and allowed to cool slowly for 1-1/2 hours, after
which time they were filtered twice through Munktell papers.
The following are the weights of the precipitated barium
sulfate;

	No gelatin		15 mgms gelatin	
Grams BaSO$_4$	.0636	.0644	.0633	.0622

Again, the results are not what were desired. The
filtrate from the four precipitations were allowed to stand
over night, during which time more barium sulfate precipi-
tated out.

Another attempt was made to obtain complete precipi-
tation by allowing the barium sulfate and solution to stand
in a warm place for 36 hours. The remainder of the procedure
was the same as before. The following are the results of
this third precipitation;

	No gelatin		15 mgms gelatin	
Grams BaSO$_4$	.0986	.0989	.0966	.0977

This experiment also failed to precipitate all the
sulfate. Thus, an entirely different method had to be used
to determine the sulfate content. Triplicate gelatin cath-
odes were prepared, along with one coulometer electrode.

These deposits were dissolved in nitric acid, and evaporated cautiously to dryness and ignited. This ignition destroyed the gelatin. The copper oxide mass was then dissolved in nitric acid and diluted to 200 cubic centimeters and the remainder of the sulfate determination carried out as before with the following results;

	Copper-gelatin deposits			Coulometer
Gms. Deposit	.5537	.5530	.5530	.5314
Gms. BaSO$_4$	.0092	.0088	.0088	.0001

The conditions under which the electrodes were prepared were 0.5 molar copper sulfate, 1/2 per cent gelatin, pH = 3.38, at 25°C. and a current density of 2 amperes. It is impossible to determine copper and sulfate both from the same sample, since during the ignition and decomposition of the copper nitrate, considerable quantities of copper are lost. Hence, it will be necessary to prepare duplicate gelatin deposits, determine copper on one and sulfate on the other.

Analyses of deposits for sulfate and copper

Accordingly, in the following experiment duplicate gelatin containing electrodes were prepared, one of which was used for copper analysis and the other for sulfate analysis. The conditions under which the deposits were prepared were 1/2 molar copper sulfate, 30°C., .0625 amperes, with gelatin and current densities as variables. The temperature of the coulometers were 0°C. The method of sulfate

analysis has been described and the method for copper analysis will be given soon. Table 46 gives the results of the experiment.

Table 46

Copper and Sulfate analyses; from electrodes prepared from .5 M $CuSO_4$, 1 Amp. C.D., .0625 Amperes, $30^{\circ}C$.

	2.0% gel.		0.25% gel.		.03% gel	
Dep.	.3952	.3944	.3930	.3938	.3825	.3823
Exc.Wt.	17.5	16.7	15.3	16.1	4.8	4.6
	Cu	$BaSO_4$	Cu	$BaSO_4$	Cu	$BaSO_4$
grams	.3800	.0053	.3789	.0051	.3787	.0024
Exc. Cu.	2.3		1.2		1.0	
$BaSO_4$		5.3		5.1		2.4 mgm.
$CuSO_4$ from Exc.Cu	5.7		3.0		2.5	
$CuSO_4$ from $BaSO_4$		3.6		3.5		1.6

Similar conditions as above, excepting 2 Amps. C.D.

	2.0 % gel.		.25% gel.		.03% gel.	
Dep.	.4024	.4025	.3956	.3956	.3829	.3829
Exc.Wt.	24.4	24.5	17.6	17.6	4.9	4.9
	Cu	$BaSO_4$	Cu	$BaSO_4$	Cu	$BaSO_4$
grams	.3804	.0107	.3794	.0096	.3787	.0050
Exc.Cu	2.4		1.4		0.7	
$BaSO_4$		10.7		9.6		5.0
$CuSO_4$ from Exc.Cu	6.0		3.5		1.7	
$CuSO_4$ from $BaSO_4$		7.3		6.6		3.4

Coulometers			
1 amp. C.D.		2 Amps. C.D.	
.3775	.3780	.3780	.3779

As can be observed from the table the agreement in the copper sulfate calculated from the copper and from the barium sulfate is not as good as might be desired. The general tendency seems to be that the sulfate was present in the copper deposit in greater quantity than the excess copper. The three analyses of deposits from the 2 amperes per square decimeter portion of the table indicate that more sulfate is present in the deposit than can be accounted for by the copper. In the 1 ampere C.D. part only one analysis of the three points in that direction.

If this excess sulfate actually exists, it must be interpreted that some sulfate has been adsorbed by the gelatin and the gelatin in turn adsorbed by the deposited copper during deposition. Since the two electrodes did not agree in their sulfate analyses with the remaining four, itiwas deemed necessary to repeat these two, with conditions, of course, as nearly similar to the previous run as possible.

Three deposits of each of the two concentrations of gelatin were prepared, two were analyzed for sulfate and the remaining one for copper. The temperature of the coulometers was $0^{\circ}C$. The following table gives these results.

Table 47

Repetition of part of Table 46.

Deposit	2.0% gel			Coulometer
	.3894	.3886	.3886	- .3740
	BaSO$_4$	BaSO$_4$	Cu	Cu
	.0028	.0020	.3754	.3740
Exc. Cu.			1.4 mgm.	
Cu as CuSO$_4$			3.5	
BaSO$_4$	2.8	2.0		
BaSO$_4$ as CuSO$_4$	1.9	1.4		

Deposit	.03 % gelatin			Coulometer
	.3768	.3790	.3788	.3741
	BaSO4	BaSO$_4$	Cu	n.d.
Exc. Cu.	.0006	.0004	.3750	
Exc.Cd as CuSO$_4$			1.0 mgm.	
			2.5	
BaSO$_4$	0.6	0.4		
BaSO$_4$ as CuSO$_4$	0.4	0.3		

The duplicate determinations agreed very well with each other considering the small quantities involved. But the agreement with the previous results in Table 46 are not so satisfactory. However, in both cases the excess copper is more than equivalent to the sulfate.

Moisture in the Eastman gelatin

The gelatin used in all of these excess weight experiments was Eastman Kodak Company ash-free gelatin. Since all gelatin of commerce contains some moisture, a moisture

determination was made upon a sample of the gelatin. Five grams of gelatin were weighed into a small evaporating dish, and the whole heated in a moisture oven at 110°C for 24 hours. The following are the results of the determination.

$$
\begin{array}{llr}
\text{Wt. gel.} & 5.0000 \text{ grams} \\
\text{After drying} & \underline{4.4030} \quad " \\
\text{Loss} & .5970 \text{ grams, } = 11.94 \text{ \% moisture.}
\end{array}
$$

Analysis of anode coating

During the preparation of many of the excess weight experiments, a coating was formed upon the anode. In electrolytes of 0.5 and 2.0 per cent gelatin this coating was comparatively heavy, so heavy, in fact, that it peeled off occasionally. This deposit appeared much more abundant upon copper anodes which had not been previously plated. Anodes which had been previously plated showed only a darkening and on rare occasions slight peeling.

This coating contained copper, and dissolved in nitric acid to a blue solution with the evolution of a gas.

Two samples of this coating were analyzed for their copper content with the following results;

	No. 1	No. 2
Wt. of sample	6.6 mgms	7.1 mgms.
Wt. Cu, det.	5.5	5.6
Per cent Copper,	83.3	78.8

These compositions would indicate more of a cupric than cuprous compound. Cupric oxide contains nearly 79.8 per cent copper.

Method for copper analysis

During the earlier part of the excess weight work difficulty was experienced in making the copper analyses. The procedure followed was; dissolve the copper deposit from the platinum electrode with about 2-1/2 cc nitric acid diluted to about 20cc with water. After solution was complete, it was evaporated to dryness and ignited to destroy the gelatin. Solution was again affected with nitric acid, water, ammonia added until the blue color remained and one cubic centimeter excess added. Then nitric acid was added until just acid and again 1 cubic centimeter in excess was added. The solution was now electrolyzed using a revolving copper gauze electrode and a platinum wire anode.

When the above procedure was followed coulometer deposits which were being analyzed lost from 4 to 5 per cent of their copper. The loss, it was found occurred when the first solution had been evaporated to dryness and was ignited to destroy the gelatin. When the nitrate was decomposing to oxide some copper was carried away, and since the gases escaping imparted the characteristic copper color to the flame, the loss was discovered.

The necessary step was then to prevent this loss of copper. Since copper sulfate does not easily decompose, the nitrate was converted to the sulfate by the addition of sulfuric acid. As soon as this step was adopted in the procedure, the copper determinations were much improved. But

still errors about 1 milligram in magnitude occurred. It was noticed also, that some corrosion of the stem of the revolving electrodes, at the surface of the solution occurred. The excess nitric acid was, without doubt, responsible for this corrosion. In order to eliminate this error, new electrodes were made using ordinary copper gauze and gold wire for the stems.

With these two steps incorpprated into the analysis some very good results were obtained. However, three platimum gauze electrodes were made and these were used in place of the gold stem ones. The advantage of the platimum cathodes being self-evident.

The platimum electrodes had also the advantage of lightness since they weighed from 3-1/4 to 4-3/4 grams, as compared to 12 grams of the gold stem electrodes.

After slight modifications in the determination the following procedure was adopted with excellent results; Place the deposit to be analyzed in a 250 or 400 cubic centimeter beaker and add 40 to 50 cc water containing about 3 cc nitric acid. Solution was allowed to take place slowly to prevent slight losses of copper. Just enough sulfuric acid was added to convert the copper to the sulfate. For a .4 gram sample, approximately .5 cc acid was used. The whole was now ovaporated to dryness slowly to prevent boiling and spitting of the copper sulfate when the solution had nearly evaporated. When dry, the beaker is held over the open flame of a Meeker burner to remove the excess

sulfuric acid and to destroy the gelatin. When cool the
copper sulfate is taken up with about 10 cc water, about 1
cc nitric acid added, then ammonia until neutral and about
1 cc in excess. This ammoniacal solution is then neutralized
with nitric acid and from 10 to 15 drops sulfuric acid added,
and diluted to from 150 to 200cc. This solution is now ready
for electrolysis. One 40-watt light globe allows sufficient
current to pass to give a bright very adherent deposit. As
soon as the copper color has disappeared from the solution
a second light globe is placed in parallel with the first,
the combined result being to completely remove the last
traces of the copper. The solution may be tested conven-
iently for copper by adding a few drops of the solution
to hydrogen sulfide water. If a brown to black color ap-
pears electrolysis is not complete. Free sulfur will also
appear, but since this is white, no confusion should result.

The following are some coulometer deposits which were
analyzed for copper as just described to show the accuracy
which may be expected when the procedure is carefully fol-
lowed.

Coulometer deposit	.3740	.3878	.3797	.3790 gms.
Redeposit	.3740	.3879	.3797	.3788 gms.