SOME PROPERTIES OF ALUMINUM OXIDE

IN ELECTROLYTIC SOLUTIONS

by

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ABSTRACT

By anodic oxidation, an aluminum plate can be covered with an amorphous or crystalline oxide layer, depending on the electrolyte used. The amorphous layer, obtained in a solution of oxalic or sulphuric acid, has a porous structure. However, the pores do not go right down to the aluminum as has been shown by many investigators, but end in a solic insulating layer, the thickness of which may be determined by capacity measurements.

Corresponding to a given temperature and acid concentration of the electrolytic solution and a given formation current density, there is only one final capacity obtainable. Increasing the concentration, or temperature, or decreasing the current density, increases the final capacity obtainable.

ACKNOWLEDGEMENT

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IN ELECTROLYTIC SOLUTIONS

I - INTRODUCTION

By anodic oxidation an aluminum plate can be covered with an amorphous or crystalline oxide layer, depending on the electrolyte used.

The crystalline layer can be formed in an aqueous solution of a succinate, a citrate or boric acid. The structure of this layer has been identified by Verwey (8) as γ'-Al_2O_3, a cubic face-centered oxygen lattice in which the cations are distributed statistically over all the interstices with the only restriction that 70% of the aluminum ions occupy an octahedron hole and 30% a tetrahedron. Because of the pronounced insulating properties of this layer, the current steadily decreases during formation at constant voltage. Hence the limit to the thickness of a crystalline layer is determined by the spark potential of the electrolyte.

The amorphous layer is obtained in a solution of oxalic, sulphuric or phosphoric acid. This layer has a porous structure, the pores having a diameter of about 10^{-5} cm. and being oriented mainly at right angles to the surface. Dekker and Van Geel (3) showed that if a plate with a porous layer is

then oxidized in boric acid a crystalline structure forms in the pores of the amorphous layer, and that both structures have the same dielectric constant. Higher current density in oxalic acid produces a denser structure of the amorphous coating.

These pores do not go right down to the aluminum as has been shown by many investigators, but end in a very solid layer that seems to be the base of the porous part. This solid layer has insulating properties as can be found from capacity measurements. Anderson (1) suggests a method of formation of the porous layer, basing his theory on measurements of Edwards and Keller (4, 5). According to this theory, the thin basic layer will reach an ultimate thickness for oxidation at constant voltage: the field strength in the insulating layer decreases as the layer grows, so that the rate of growth will gradually decrease until this is equal to the rate of attack of the acid. Now the rate of attack is determined by the concentration of the solution and the temperature; following Anderson's reasoning, one would expect that if one oxidizes at constant current (constant field strength) and hence works with a constant rate of growth, that the basic layer would continuously increase with time, assuming temperature and concentration of the solution are constants. My investigations do not bear out this theory, however.

These oxide layers under conditions of varied temperature, concentration of the acid bath, and current density during formation, have been the subject of this investigation,

with the following reproducible results:

1. Corresponding to a given temperature and acid concentration of the H_2SO_4 bath, and a given constant current density, there is only one final capacity obtainable.

2. Increasing the concentration of the H_2SO_4 bath or using a stronger acid, increases the final capacity obtainable.

3. Increasing the current density decreases the final capacity obtainable.

4. Increasing the temperature of the bath increases the final capacity.

The following facts were also observed:

1. 100% current efficiency during the formation of the oxide could not be obtained with the commercial Al samples at hand (99.5% Al with Fe, Cu, and possibly Si impurities).

2. The thickness of an Al_2O_3 coat in oxalic acid decays exponentially for conditions of no current and no stirring.

3. Corrosion of the plates occurred for current densities above 4 m.a./cm.^{2} in dilute (1.2%) H_2SO_4 solution. The capacity was still measureable in these cases, indicating an oxide layer over the pitted sections; the value of the capacity did not fall on the smooth curve through capacity for lower current densities.

II - APPARATUS

The aluminum sample was cut into 5 cm. square plates with a narrow strip extending above the bath, so that leads could be clipped onto the plate. The plates were cleaned in strong KOH solution and then washed in distilled water.

Since the thickness of the oxide layer is inversely proportional to the capacity, a measure of the capacity is the most direct way of determining that thickness. However, the oxide layer, $\varepsilon = 8$, is not a perfect dielectric, so its capacity, C, is effectively shunted by an ohmic resistance. Therefore an A.C. bridge method of measurement must be used, in which one compensates for the resistance. The bridge operates at 60 cycles and about 2 volts.

The plate was hung in a beaker of boric acid opposite sufficient tinfoil, and this group was placed in the A.C. bridge as shown in fig. 1, The bridge consists of a "Philoscope," which gives a resistance ratio, a standard variable-resistance box, and a group of pure capacities.

equivalent to
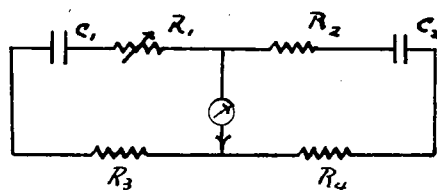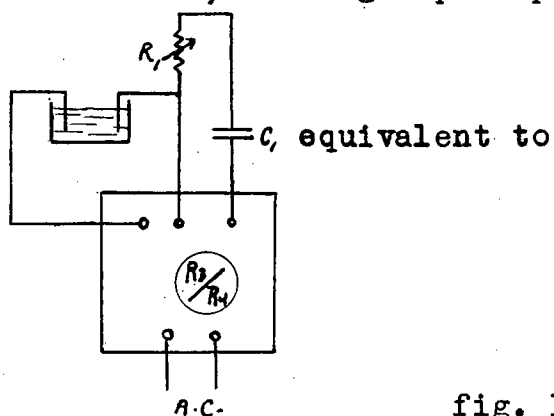
$$\frac{1}{\omega c_1}\bigg/R_3 = \frac{1}{\omega c_2}\bigg/R_4 \qquad \frac{R_4}{R_3} = \frac{C_1}{C_2} = \frac{R_2}{R_1}$$

fig. 1.

Now the total cell is measured as —ww—|ⵏ— but is actually


Al_2O_3 Boric   Tinfoil

However to avoid separation of measured C and R to actual

values, the following was done:

1. The tinfoil capacity was made so high as to be

   negliglible by using 10 sheets of tinfoil folded

   into accordian pleats and connected in series

   around the circumference of the beaker. The

   highest Al_2O_3 capacity measured during the work

   was about 40 microfarads.

   Top view:

   fig. 2.

   — — — foil

   — —Al plate
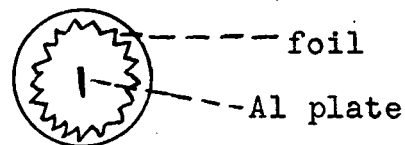
   Let c_1 ≃ capacity of tinfoil and C ≃ the total

   capacity. $$\frac{1}{C} = \frac{1}{c_1} + \frac{1}{40} \quad , \quad C = 40\frac{c_1}{c_1 + 40}$$

   Then c_1 = .98 c_1 + 40 for 2% accuracy

   i.e. c_1 ≃ 2000 microfarads.

   Now to get the experimental value of the foil

   capacity, two sheets of tinfoil were hung in

   boric acid solution, being equivalent to —|ⵏ|ⵏ|—

   Let C_m be the capacity measured by the bridge.

   $$\frac{1}{C_m} = \frac{1}{c_1} + \frac{1}{c_1} = \frac{2}{c_1}$$

   So, $2C_m = c_1$

   When the capacity of an aluminum plate is

   measured, the two sections of foil are connected

   in series and the aluminum placed opposite them.

This doubles the foil capacity, so we have

$$4C_m = C_1 = 2000 \text{ microfarads}$$

$$C_m = 500 \text{ microfarads}$$

Therefore the measured foil capacity should be 500 microfarads or more for better than 2% accuracy.

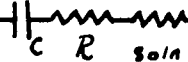In the actual experiment, for two single foils,
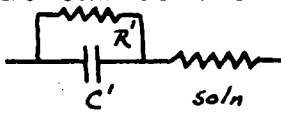
$$C_m = 9.5 \times 2 \times 12.6 = 239 \text{ microfarads}$$

So, for the five pairs used,

$$C_m = 1200 \text{ microfarads}$$

Thus we are assured that the tinfoil capacity is negligible.

2. The solution and foil resistance were measured; upon subtracting that resistance from the resistance measured by the bridge, the correction from series to parallel capacity was found to be negligible.

It can be shown that ⊣⊢—ᴡᴡᴡ—ᴡᴡᴡ— (bridge) and
c R soln
—⊣⊢—ᴡᴡᴡ— (actual case) are related by
c' R' soln

$$C' = \frac{c}{1 + c^2 R^2 \omega^2}$$

The correction, $c^2 R^2 \omega^2$, is that which was found to be negligible in this case.

When the aluminum plate was replaced by a duplicate of tinfoil, the foil and solution resistance came to about 24 ohms. However, the resistance for the aluminum plate measurements was about the same value, varying from 23 to 30 ohms.

That leaves $c^2 \omega^2 (7)^2 = 0.01$ for $c = 40$ microfarads.

The same concentration of boric acid solution was used throughout: a saturated boric acid solution plus sufficient ammonium hydroxide to make the specific conductivity 500 (ohm-cm.)$^{-1}$ at 15° C. The sulphuric acid from which the various concentrations were made was C.P. (96.5%) with specific gravity 1.84.

The oxidizing equipment was arranged as shown:

fig. 3.

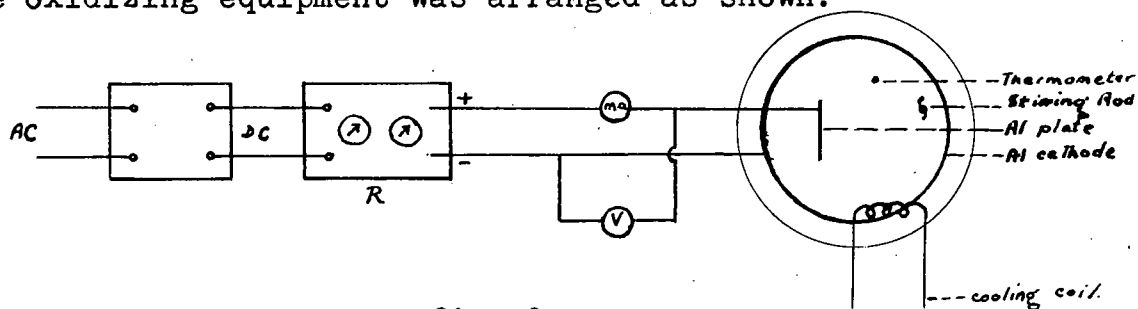R was continuously variable so that either current or voltage could be kept constant as desired. The D.C. supply was checked for A.C. ripple by means of an oscilloscope. A.C. ripple is about 0.2% of volts D.C.

Volts DC	Ripple Measure Gain	Ripple Measure Gain	Ripple Volts AC	% AC/DC
40	.75	.15	.084	.2%
200	2.5	.8	.45	.2%
280	3.5	1.1	.62	.2%

Table 1.

III – EXPERIMENTAL RESULTS

1. Dekker and Van Geel (3) obtained 100% current efficiency when oxidizing high purity aluminum (99.99%) at constant current in boric acid. In our case, with commercial aluminum (99.5%), there was noticeable gas development on the anode, increasing with time, i.e., efficiency decreasing. See Graph 1. No temperature control seemed necessary in this case, since we will show this effect could be due to impurities.

2. Oxalic acid attacks the oxide coat. Since capacity, $C = \dfrac{\varepsilon A}{4\pi d}$, it follows that $\frac{1}{C}$, being proportional to layer thickness d, can be plotted on a time graph to show this attack. A plate was first oxidized at 200 m.a./50 sq. cm. in boric acid, then washed and placed in a saturated oxalic acid solution, which was not stirred. The capacity was measured in the bath at intervals as the coat was dissolving, with results which follow. These results were used to plot Graph 2.

	Minutes	C (µf.)	$\frac{1}{C}$ (µf.)$^{-1}$
	3	6.4	.156
	4	8.6	.116
	6	15.1	.066
Table 2.	7	16.4	.062
	8	17.6	.057
	9	18.9	.053
	14	20.3	.049
	18	21.2	.047
	20	21.4	.047

The graph of $\frac{1}{C}$ against time appears to be an exponential curve.

3. Working at 14.5° C., with a given concentration of sulphuric acid, and keeping constant current density, only one final capacity was obtainable: 5.4% H_2SO_4, and 200 mils per 50 sq. cm.:

	Minutes	C_{series} (μf.)	R_{series} ohms
	1	27.2	25.4
	"	26.2	25.0
	"	27.2	25.0
Table 3.	"	26.7	25.0
	3	26.5	24.8
	5	26.5	24.8
	9	26.5	24.3
	Average:	26.7	0.3 f.

4. Graph 3 shows sets of final capacities obtained, using current densities from 1 to 8 m.a./cm.^{2}, using oxalic acid and various concentrations of sulphuric acid, but regulating the time of oxidation of the plates so that the same amount of charge passed through each.

Note that no capacity was graphed for current density higher than 4 m.a./cm.^{2} in dilute (1.2%) sulphuric acid solution at 14° C. since the plates in this case corroded visibly. New solution did not change the results. Measurement of the capacity gave a value of the right order, but higher than expected, indicating no shorting of the oxide capacity.

It was found upon increasing the temperature of the solution from 14° to 34° that corrosion did not occur. At 34° the capacity was 18.8 microfarads compared with 16.1 microfarads at 14°. A capacity of about 15 microfarads would

be expected from the graph. Corrosion still occured at 21.5°
C. See Table 5, page 11.

5. Varying the temperature of the bath affected the final
capacity obtainable as shown on Graph 4. Current density of
4 mils/cm.^{2} was used.

T (°C)	C (μf.)	
44	95	
42	86	
37	69.5	Table 4.
30	49.3	
19.5	32.9	
13	26.7	

The capacity for 13° C. was obtained earlier for use in Graph
3.

Table 5.

% H_2SO_4	15%		9%		5.4%		2.3%		1.19%		4.8%		Oxalic acid (saturated)	
Moles/litre	2.71		1.63		.98		.416		.215		.869			
Curr. Dens. ma./cm²	R Ω	C μf.	R Ω	C μf.	R Ω	C μf.	R Ω	C μf.	R Ω	C μf.	R Ω	C μf.	R Ω	C μf.
1	24.1	94.0	24.6	69.9	23.3	57.1	26.1	43.8	26.8	28.7	26.1	58.4	25.0	24.9
2	23.5	66.0	25.0	50.8	25.3	39.1	27.8	26.0	29.3	19.9	26.6	38.1	26.4	15.4
3	23.8	53.3	24.4	40.0	26.2	30.5	27.9	21.8	30.9	17.3	25.0	30.5	27.4	12.1
4	24.3	47.0	25.8	33.0	24.8	26.7	30.3	19.7	29.6	15.9	26.5	25.9	28.6	10.7
8	25.2	34.3	25.5	26.4	25.9	21.6	26.1	17.5	--	--	25.9	21.6	30.3	8.4

Graph 1.

Boric Acid

Voltage vs Time

$I = 40 \ ma/50 \ cm.^2$

Volts →

Time in Minutes →

Graph 2.

$\frac{1}{C}$ vs Time

$\frac{1}{C} \ (\mu f.)$ →

Time in Minutes →

Graph 3.

Capacity vs Current Density

Graph 4.

Final
Capacity
vs
Temperature

C (μf.) →

T in °C →

5.4% H_2SO_4
for 5 min.
4 ma/cm²

Graph 5.

log d →

$\frac{1}{T}$ (°K^{-1}) →

Log (thickness)
vs.
$\frac{1}{T}$
=

GRAPH 6.

Thickness
vs.
Log (Current Density)

GRAPH 7.

Thickness
vs.
Root of Capacity^{-1}
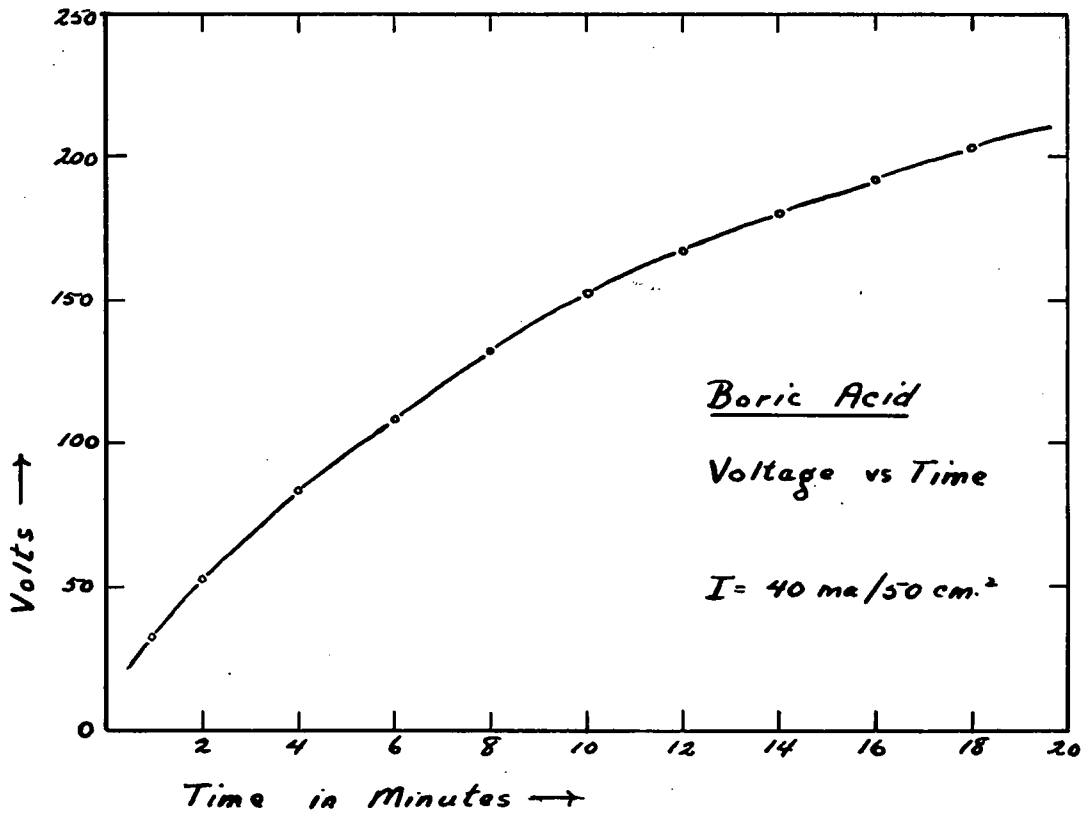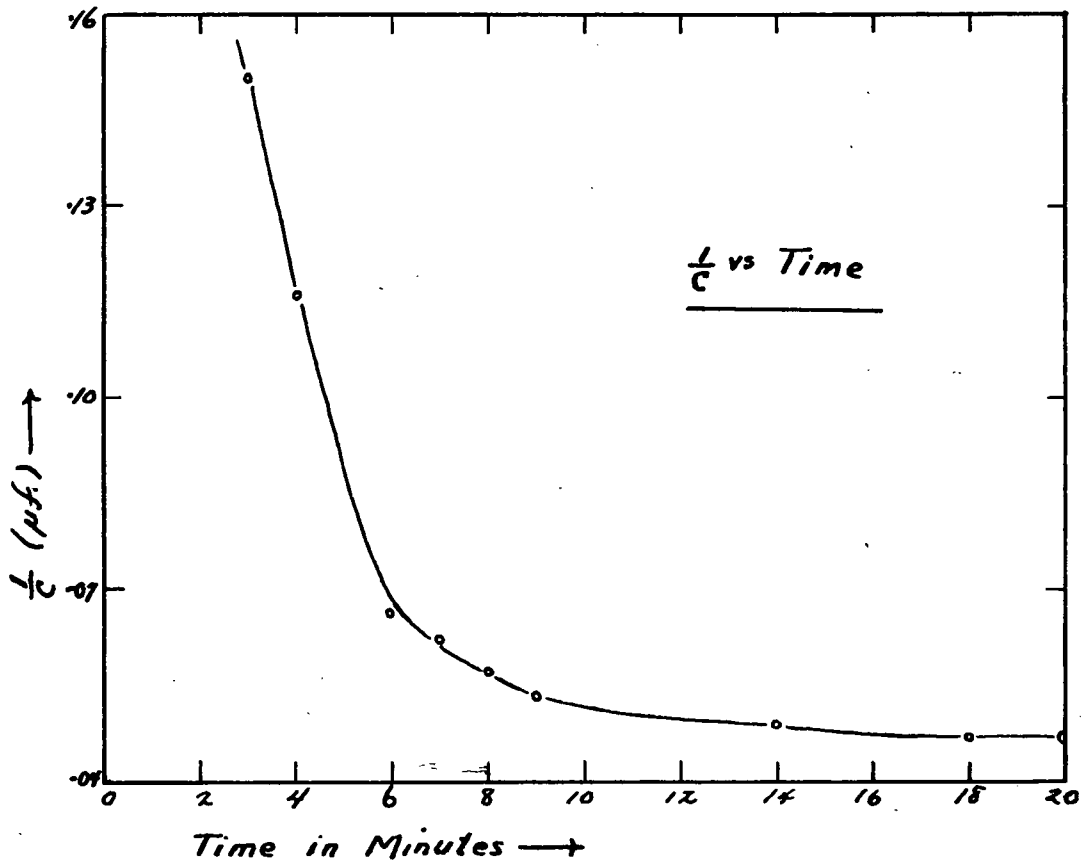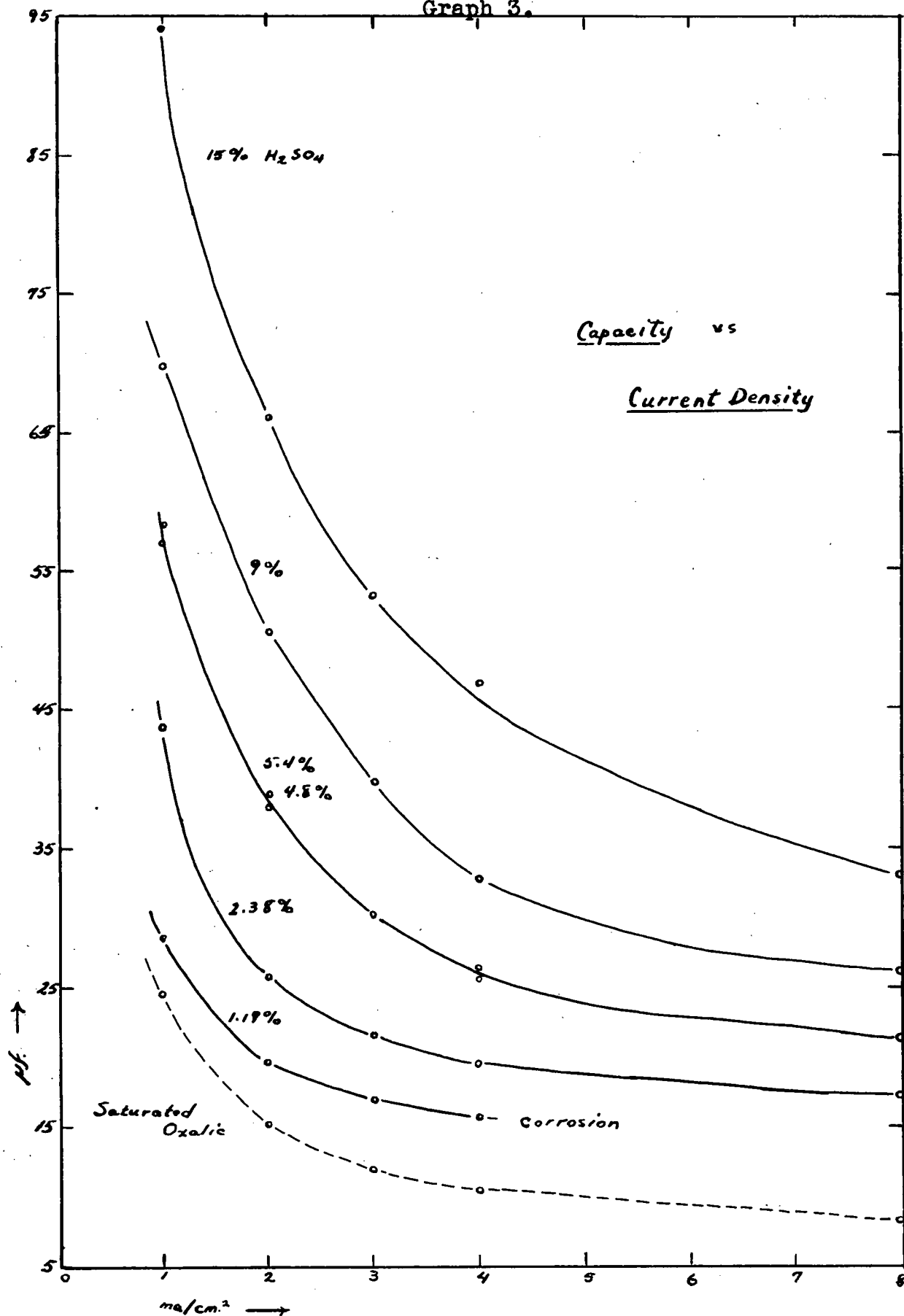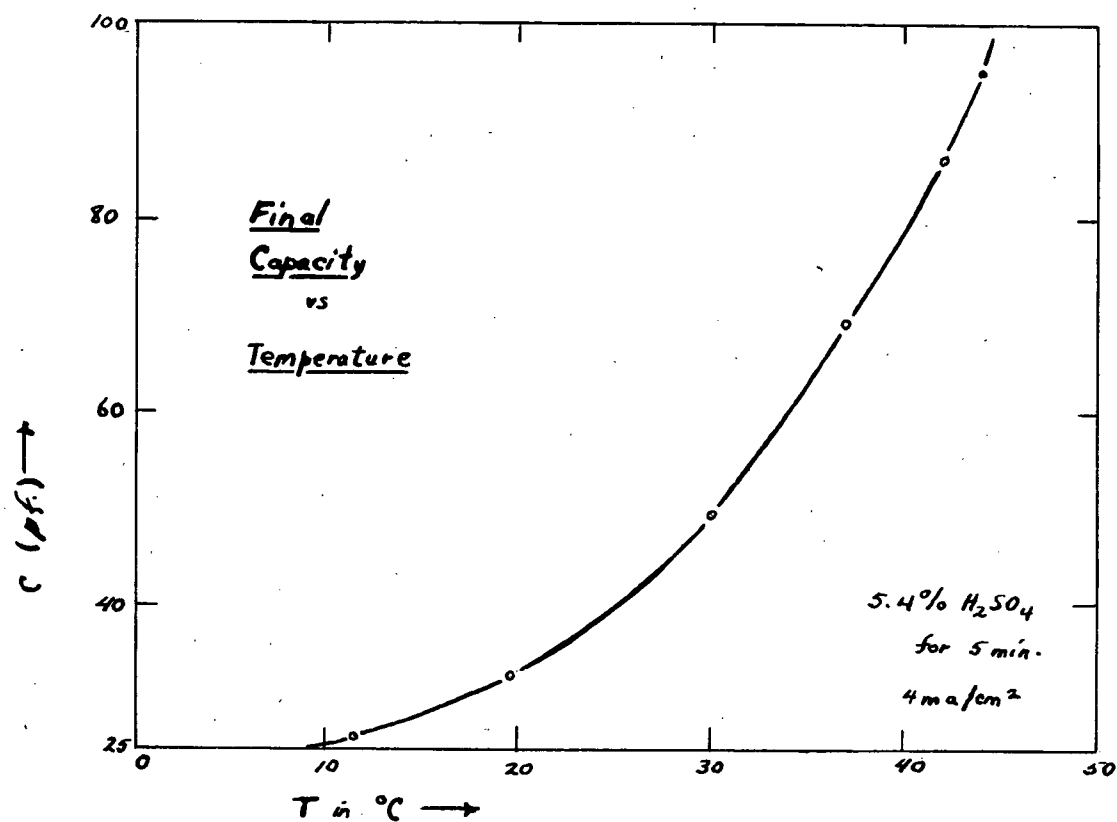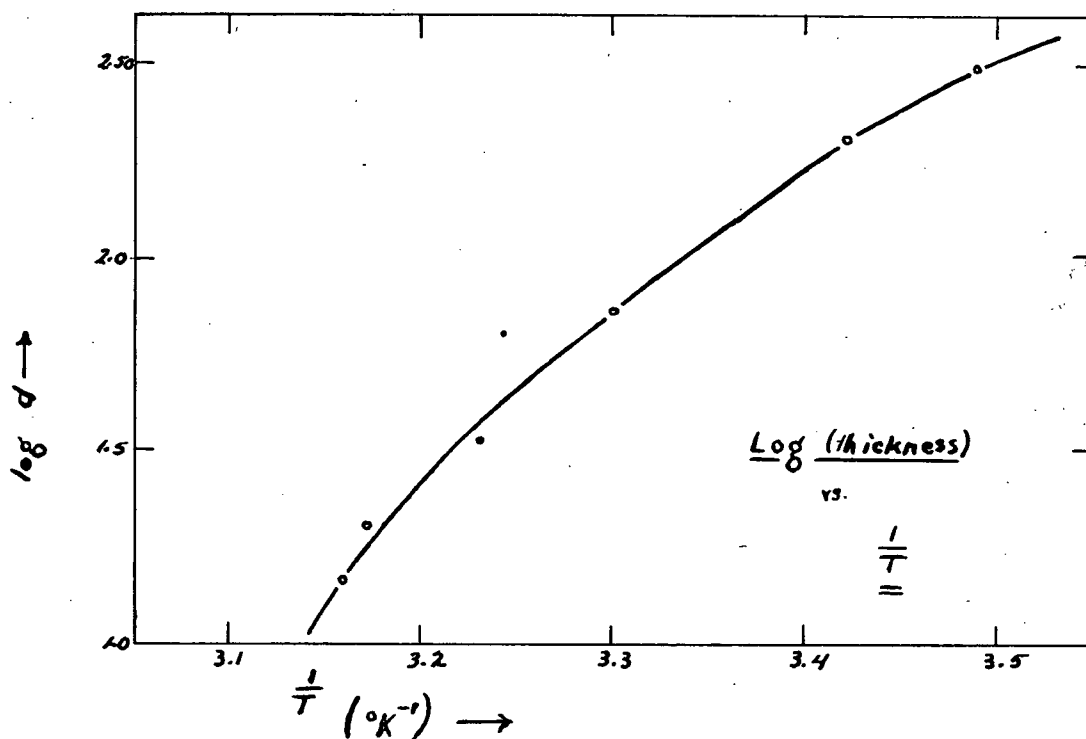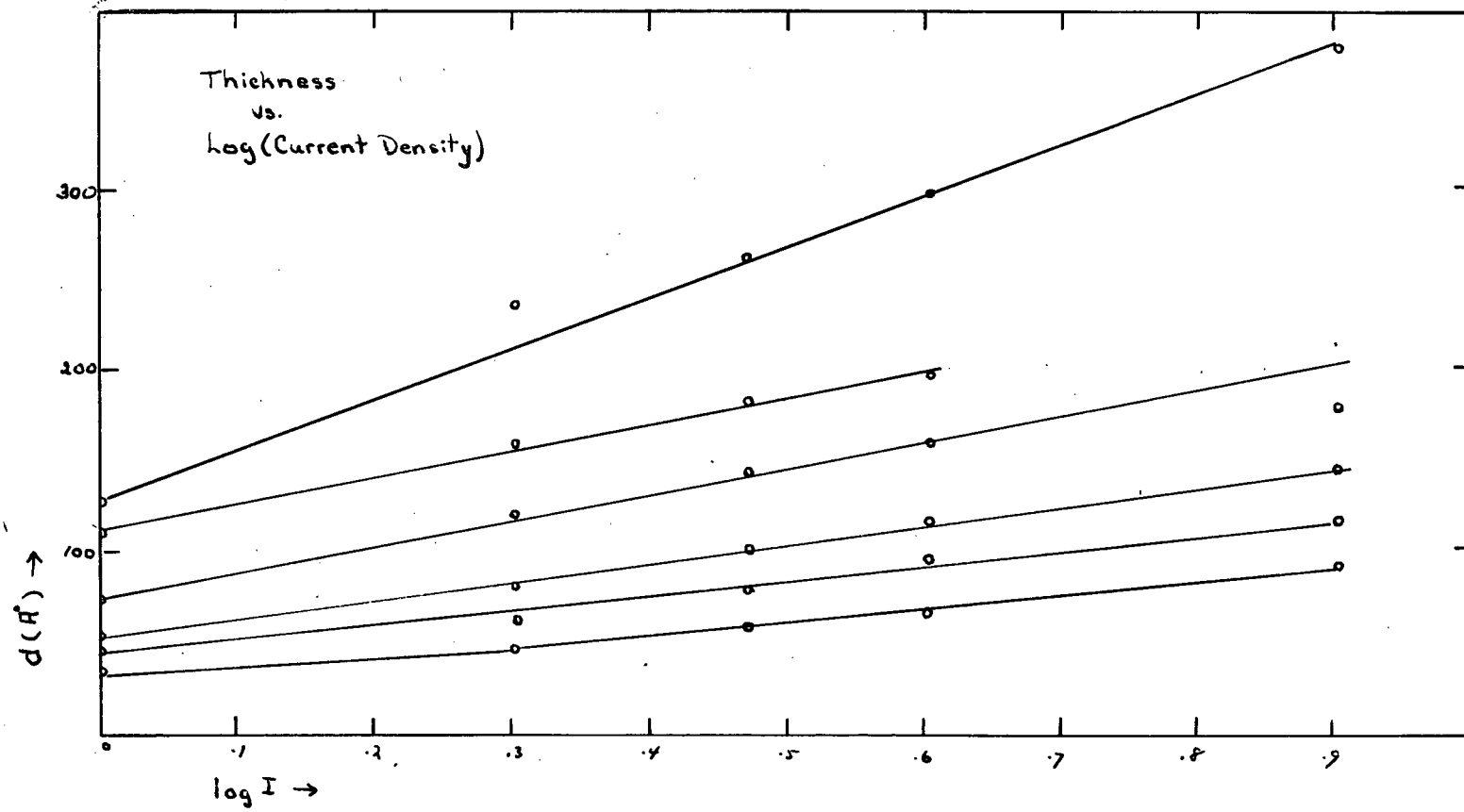
IV - DISCUSSION

1. EXISTING THEORIES:

A discussion of the experimental results involves a consideration of the present theories of formation of aluminum oxide in electrolytic solutions: the original theory (Verwey - 8) requires aluminum migration only; and the other, recently proposed by Anderson (1) and based on measurements by Edwards and Keller (4,5), suggests that both aluminum and oxygen migration occur.
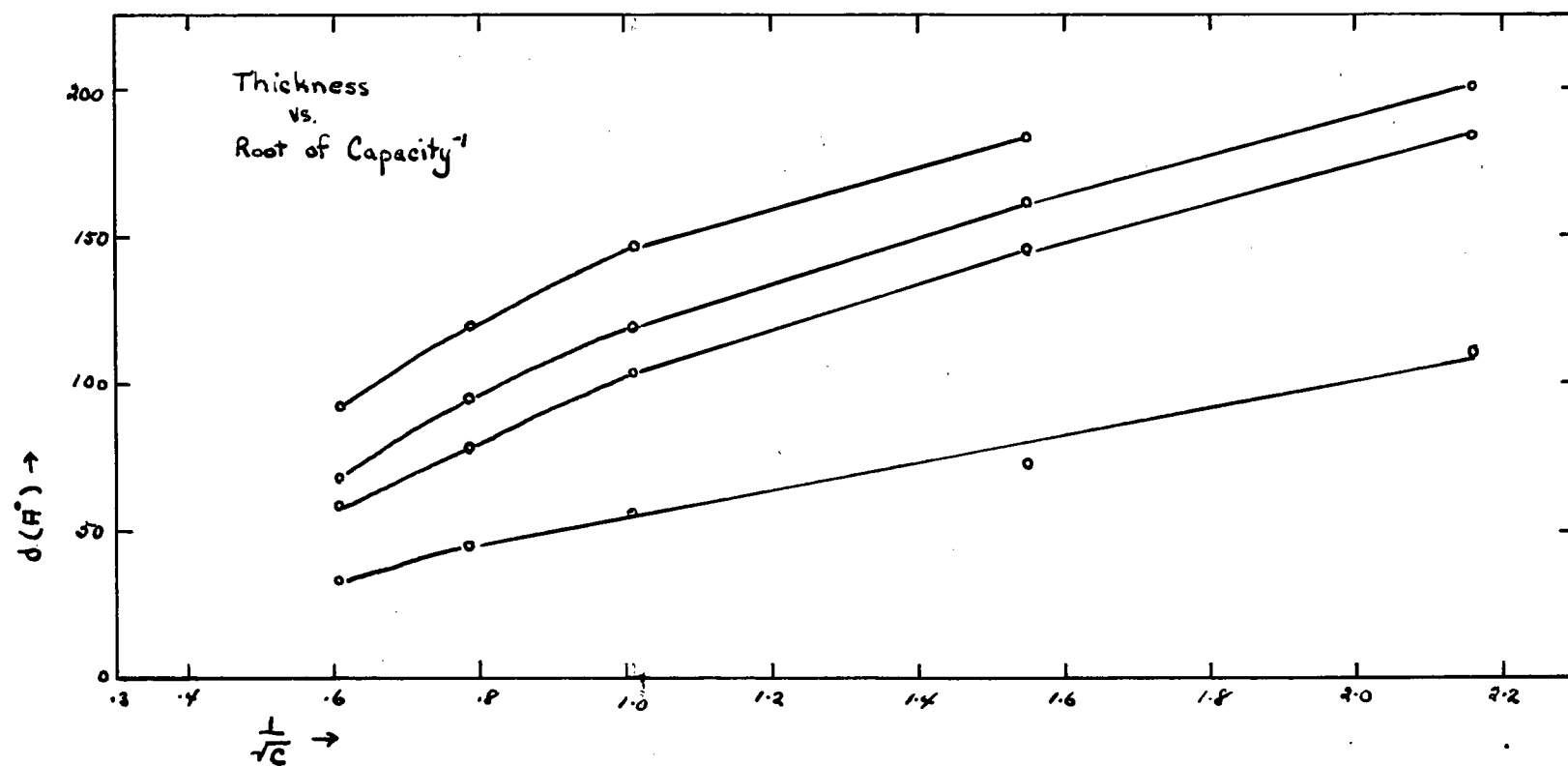
Now it is undisputedly shown by X-ray analyses that aluminum has a face-centred cubic structure with a $\simeq$ 4.04; and that Al_2O_3 formed in electrolytic solution has the structure of $\gamma'-Al_2O_3$, a close-packed face-centred oxygen lattice (a = 3.95) with the cations distributed statistically over the interstices, the only restriction being that 70% of the cations occupy an octahedron hole and 30% a tetrahedron hole (ref. 8).

By the first theory, when aluminum is made the anode in an electrolytic solution, oxygen ions collect over the surface of the anode in this orderly f.c.c. arrangement. Then under the influence of the high field (10^7v./cm.), Al ions diffuse from lattice positions on the surface of the metal to interstitial positions in the oxygen ion lattice. Electrons in the metal, 'abandoned' by the migrating Al ions flow through the external circuit and preserve the current

continuity; which process can be contrasted with the case of O_2 being liberated from the anode surface of a metal which does not form an oxide, since then it is the 2 electrons from each of the oxygen ions that flow into the metal. Continued growth of the oxide layer depends on the ability of the Al ions to diffuse through the oxygen lattice.

It appears to me that this process presents one major problem: the problem of the space vacated by migrating Al ions. Possibly more Al ions move up from the metal so that there is a gradual shifting through the whole aluminum lattice. However, there is no appreciable field in the aluminum lattice, the applied potential difference being chiefly over the oxide layer and only a very small fraction over the electrolytic solution (conductivity 500 ohm-cm.$^{-1}$); and since lattice positions are positions of minimum potential for the ions, the ions are not likely to assume the looser structure of the shifting arrangement without a strong external field. The only other possibility seems to be that when a row of Al ions have moved into the oxygen lattice, the whole oxide lattice moves closer to the metal, which would be an erratic movement. Both these explanations seem to imply a less dense region on the whole metal surface, which is contradictory to the observed tenacity of the oxide to the metal.

Anderson's theory, on the other hand, leads to a very convincing explanation for this tenacity. According to his theory, one out of every three Al ions, having a small radius of 0.5 Å, diffuses easily through the oxide lattice;

if the other two rearrange slightly, there is sufficient room
in the metal for adjacent oxygen ions to jump in under the
influence of the strong electric field. The positions vacated
by these oxygen ions are then filled by others from further
out in the film and the process is repeated until vacant oxy-
gen spaces are filled by ions from the electrolyte. The cur-
rent then is carried by outward diffusion of aluminum ions and
inward shift of oxygen ions in the ratio 1:2 ; or if inward
shifting of oxygen ions is the same as outward movement of
positive holes, then the current is carried 1/3 by positive
ions and 2/3 by positive holes. So growth takes place both at
the oxide-solution interface and at the oxide-metal interface,
one molecule of Al_2O_3 at the former for every 2 molecules at
the latter.

So far it has been assumed that all the aluminum is
used to form oxide; but in truth this is only so in certain
electrolytic solutions, such as boric acid, in which aluminum
oxide is not soluble. In these solutions the crystalline
layer of the oxide forms uniformly over the whole surface of
the metal. In other solutions, such as H_2SO_4, oxalic acid, and
chromic acid, all the aluminum is not used to form aluminum
oxide; and in such cases the layer has been observed to have a
porous structure. The pores have a diameter of about 10^{-5}cm.,
and are oriented mainly at right angles to the surface. (See
electon-microscope micrograph, ref. 3.) These pores do not
go right through to the aluminum as has been shown by many in-
vestigators,but end in a very solid layer that seems to be the

base of the porous section. This solid layer has insulating properties as can be found from capacity measurements. The important fact is that aluminum oxide is soluble in these acids. Anderson states that in this case the aluminum ions which migrate to the surface of the oxide layer do not combine with oxygen to form more oxide, but form a soluble sulphate, for example, and go into solution. Concerning the fact that a porous structure is formed in this latter type of solution, Anderson says:

"Once the acid attack is initiated at a point, there is established the electrical field distribution of a charged point near a plane. The aluminum ions and positive holes will diffuse toward that point which forms the base of a pore. Thus we have the growth processes taking place in a spherical cap around the base of the pore as centre. Pores are formed with sufficient density that their spheres of action just overlap those of adjacent pores. The diffusing ions move along radius vectors drawn from the base of the pore to the aluminum sheet."

The pro and con evidence for these two theories, one of aluminum migration only and the other of both aluminum and oxygen migration, seems to be the following:

1. As already mentioned, the observed tenacity of the oxide layer to the parent metal is better explained by Anderson's theory since the constant migration of oxygen ions into vacant metal positions as they occur keeps the two layers in close contact.

2. A short calculation of volumes involved in the Anderson theory shows the proposition is feasible:

A unit cell of Al has a volume = $(4.04)^3$ $Å^3$, and contains 4 Al atoms.

∴ Each Al atom is associated with a volume

$$\frac{(4.04)^3 \; Å^3}{4} = 16.5 \; Å^3.$$

3 Al atoms are associated with volume of 49.5 $Å^3$. A unit cell of Al_2O_3 has a volume $(3.95)^3$ $Å^3$ and contain 4/3 Al_2O_3 molecules. ∴ Each oxide molecule is associated with a volume of 46 $Å^3$.

Then if three Al ions are removed, the space they leave (49.5 $Å^3$) is sufficient room for one molecule of oxide; i.e., one Al ion is simply removed by diffusion to the electrolyte surface, and the other two remain to form an oxide molecule with oxygen which is able to jump into the space provided due to the high field. Notice, however, that the space provided is larger than necessary. So at this point it is necessary to point out the following discrepancy:

Volume of unit cell of Al, $(4.04)^3$ $Å^3$, contains 4 Al atoms.

Weight of unit cell = 4 x at. wt. Al. x 1H

Weight of 1 c.c. Al $= \dfrac{4 \times 27 \times 1.67 \times 10^{-24}}{(4.04)^3 \times 10^{-24}}$

$= 2.74$ gms.

This is in agreement with the accepted density of aluminum.

Similarly:

Volume of unit cell of oxide is $(3.95)^3$ $Å^3$, and contains 4/3 oxide molecules.

Weight of unit cell = 4/3 x 102 x 1.67 x 10^{-24} gms.

Wt. of 1 c.c. oxide $= \dfrac{4/3 \times 102 \times 1.67 \times 10^{-24}}{(3.95)^3 \times 10^{-24}}$

$= 3.7$ gms.

But, Burgers (2) experimentally determined the

density as 3.1 . Now the oxide may contain adsorbed water and acid molecules, which would explain a density value being too low; as will be seen later, porosity will affect measurements of the densities of layers formed in certain solutions; and of course it is very difficult to take very reliable thickness measurements of layers which are only microns in thickness, especially when the aluminum must first be dissolved off the layer.

3. Another piece of experimental evidence for this theory of Anderson's is the fact that no value of the efficiency ratio in excess of 1.59 has yet been observed with electrolytes in which the oxide is slowly soluble (Edwards and Keller - 4). This efficiency ratio is the ratio of the oxide formed to the weight of aluminum reacting and being lost to the sheet. If all the aluminum reacting appeared as oxide, the ratio would be 1.89. When Anderson calculates the ratio in the light of his theory, he finds a maximum possible value of 1.59; Edwards and Kellar (4) experimentally have obtained no values above 1.46.

4. It is certainly true at least that growth processes do not take place at the top of the oxide separating the pores. Rummel (7) painted this part and then continued oxidation to find that the new oxide was growing underneath the painted layer. This is surely to be expected, since the oxide between the pores is so much thicker than the thin layer at the base of each pore that the migration due to the field strength must be directed toward the bases of the pores.

5. Finally there is some evidence for the first theory of aluminum migration alone; evidence which depends on the accuracy of the determinations of density of the porous and solid crystalline layers:

Dekker and Van Geel (3) measured the rate of change of voltage during oxidation at constant current in boric acid; i.e., for the solid crystalline layer. Then they formed a porous layer on another plate in oxalic acid, again measuring the rate of change of voltage for the oxidation in boric. In this second case, assuming only aluminum migrates and that therefore the only formation proceeds on the surface, they considered that the boric oxidation was filling the pores. Then the ratio of the two rates of change of voltage in boric acid is the ratio of the pore area to the total area of the plate. For a particular current density they found the pores were about 30% of the total area, which is in keeping with the density ratio of porous to crystalline layers of 2.5/3.1 .

Now if Anderson (1) is right, then the second oxidation is not only filling the pores, but is also forming oxide at the metal-oxide interface, one molecule of oxide on the surface to every two below. So a slightly longer calculation than that used above is needed to convert the dv/dt ratio to the area ratio:

For oxidation of the porous layer in boric acid:

When x cm.^{3} of oxide are formed below, $x/2$ cm.^{3} are formed in the pores on the surface.

Let the area of the pores be $1/f$ of the total area A

of the plate; i.e., outside area = $\frac{1}{f}$(inside area).

So $x/2$ cm.^{3} are formed on an area A/f.

Then thickness of outside layer is l_s = vol./area
$$= xf/2A$$

whereas inside, x cm.^{3} are formed on area A.

Then thickness of inside layer is $l_i = x/A$

So $l_s = \frac{f}{2} l_i$, $\frac{d}{dt}(l_s) = \frac{f}{2}\frac{d}{dt}(l_i)$

Now the change in voltage is proportional to change in thickness.

$$\text{Total rate of change} = \frac{d}{dt}(l_T) = \frac{d}{dt}(l_i + l_s)$$
$$= \frac{d}{dt}(l_i + \frac{f}{2}l_i)$$
$$= (1 + \frac{f}{2})\frac{d}{dt}(l_i)$$

So $\frac{d}{dt}(V_A) \propto (1 + \frac{f}{2})\frac{d}{dt}(l_i)$ for the porous layer (1).

For the simple boric layer with no pores, $d_s = d_i/2$ since oxidation takes place over the whole surface in this case.

$$\frac{d}{dt}(l_T) = \frac{d}{dt}(l_s + l_i) = \frac{3}{2}\frac{d}{dt}(l_i)$$

So $\frac{d}{dt}(V_B) \propto \frac{3}{2}\frac{d}{dt}(l_i)$ for the boric crystalline layer.
(2).

Experimentally, Dekker and Van Geel found $\frac{d}{dt}(V_B) = 12$ and $\frac{d}{dt}(V_A) = 52$.

So $\frac{d}{dt}(V_B) = \frac{12}{52}\frac{d}{dt}(V_A)$, or approximately,
$$\frac{d}{dt}(V_B) = \frac{1}{4}\frac{d}{dt}(V_A).$$

Comparing formulae (1) and (2) above:

$$(1 + \frac{f}{2})\frac{d}{dt}(l_i) = 4\cdot\frac{3}{2}\frac{d}{dt}(l_i)$$
$$(1 + \frac{f}{2}) = 6, \text{ and } f = 10.$$

So the pores are $\frac{1}{10}$th of the total area in contrast with Dekker and Van Geel's value of $\frac{1}{4}$th which, however, was more in keeping with the density ratio of $\frac{2.5}{3.1}$. The density ratio has already been discussed.

2. DISCUSSION OF EXPERIMENTAL RESULTS:

1. Regarding oxidation in boric acid:

During oxidation in boric acid at constant current density, the rate of formation should be constant, as has been observed for high purity aluminum, and with 100% current efficiency (ref. 3).

The commercial aluminum used in this investigation was of 99.5% purity, whereas that mentioned above was 99.99%. This seems to be sufficient difference to lower the efficiency of formation as evidenced by the deviation of graph 1 from a straight line. Note that the deviation becomes greater as the layer becomes thicker. An explanation may be as follows:

Assuming that the oxygen lattice is made up of close-packed hard spheres in a face-centered cubic arrangement, the space through which the diffusing aluminum ions must pass can be calculated from the dimensions of the triangle formed by three oxygen ion positions in the centers of three adjacent cube faces. Every migrating aluminum ion must pass through a succession of tetrahedral and octrahedral positions, and in order to do so must pass through this triangle which is then the highest potential barrier that must be passed; otherwise the aluminum ions are relatively unhindered since even in a complete Al_2O_3 lattice there are many vacant lattice positions.

The cube side is $a = 3.95$ Å.
Then $b = \frac{1}{2} a\sqrt{2} = 2.8$ Å.

So the maximum radius for undeformed oxygen spheres

is $\quad \dfrac{b}{2} = 1.4$ Å.

$$\frac{b}{2 \sin 60°} = r = \frac{b}{\sqrt{3}} = 1.6 \text{ Å}$$

Then $\quad c = r - \dfrac{b}{2} = 0.2$ Å, the radius of the largest sphere which can pass between the oxygen ions.

If it takes a field of 10^7 volts/ cm. before aluminum ions of radius 0.5 Å can migrate through this space, then it seems likely that impurity atoms such as a copper atom, having radius $= 0.8$ Å, could not pass at all. As the layer becomes thicker, more of these ions which are incapable of diffusing are incorporated in the oxide lattice as it grows from the bottom; and thus it becomes increasingly more diffi-cult for the migrations to occur. Under these circumstances an appreciable electronic current flows liberating oxygen from the anode.
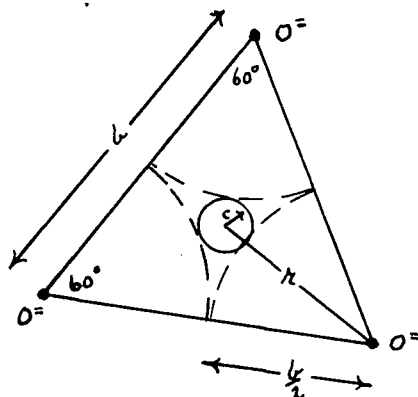

fig. 4.

2. Regarding oxidation in sulphuric acid, which produces porous layers.

Now Anderson (1) has stated that when oxidation is carried on at constant voltage in sulphuric acid, the field strength decreases as the film thickness increases, and the rate of growth of the barrier layer then diminishes until

equilibrium is reached between the rate of acid attack and the rate of growth. Following this reasoning, one would expect that if oxidation were continued in sulphuric acid solution with constant current, that the rate of growth would be constant, and that therefore the unbroken basic layer below the pores would continuously increase in thickness. That is not the case, however,

I have found that for a given acid concentration, temperature, and constant current density, only one final capacity is obtainable (table 2); i.e., the thin basic layer will not increase beyond a certain thickness, no matter how long the oxidation process is continued. Heavier current density results in a thicker basic layer; higher temperature or higher acid concentration result in a thinner layer (graphs 3 and 4). Since the thickness of the oxide separating the pores does increase with time, the conclusion naturally follows that growth is certainly taking place at the metal-oxide interface as Anderson suggests. In order that the unbroken layer remain the same thickness the acid must be attacking the base of the pores at the same rate as the layer increases in thickness at the metal side.
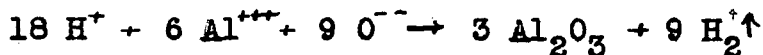
The reaction equation in the solution could be written:

$$H_2SO_4 \rightarrow 2 H^+ + SO_4^{--}$$
$$SO_4^{--} + H_2O \rightarrow H_2SO_4 + O^{--}$$
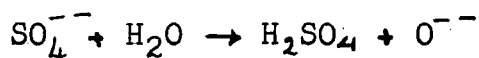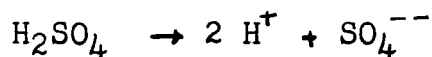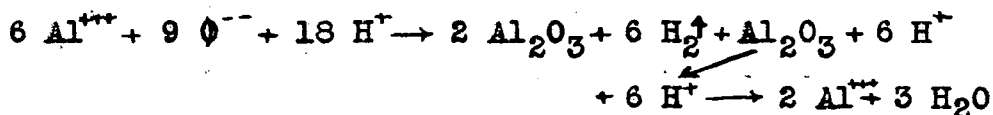
so the net result is simply: $H_2O \rightarrow 2H^+ + O^{--}$

There appear to be three possible reactions for oxide formation:

a. The reaction equation for oxide formation in boric acid must be:

$$18 \ H^+ + 6 \ Al^{+++} + 9 \ O^{--} \longrightarrow 3 \ Al_2O_3 + 9 \ H_2^+\uparrow$$

1 molecule is produced on the surface for every 2 molecules next to the metal.

b. The equation for oxide formation in sulphuric acid, using Anderson's picture would be:

$$6 \ Al^{+++} + 9 \ O^{--} + 18 \ H^+ \longrightarrow 2 \ Al_2O_3 + 6 \ H_2^+ + Al_2O_3 + 6 \ H^+$$
$$+ \ 6 \ H^+ \longrightarrow 2 \ Al^{+++} \ 3 \ H_2O$$

the oxide produced on the surface going into the solution.

c. Finally there could be this equation which represents the state of constant thickness of the thin layer beneath the pores; i.e., acid attack faster than in the last equations given; as fast, in fact, as the oxide is being formed:

$$6 \ Al^{+++} + 9 \ O^{--} + 18 \ H^+ \longrightarrow 3 \ Al_2O_3 + 18 \ H^+ \longrightarrow 6 \ Al^{+++} + 9 \ H_2O$$
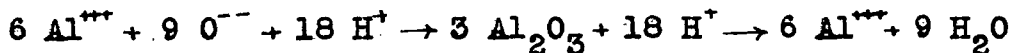
The problem is why at any time during oxidation equation (c) should be prefered over equation (b); i.e., why the layer should dissolve as rapidly as it is formed after it has attained a certain thickness.

Now I have noticed when forming these porous layers at constant current, that the voltage over the layer rises rapidly for about the first half minute, then drops as rapidly a volt or two before levelling off to become constant; this

could be interpreted as growth over the whole surface until a critical thickness is reached at which this rapid acid attack begins to form pores. The concentration of aluminum ions will be greater at the metal-oxide interface than at the solution-oxide interface, as will the concentration of oxygen ions be greater at the latter interface than at the former. This variation of concentration of ions will affect the way the field varies through the oxide; possibly under given current, concentration, and temperature conditions there is a critical thickness beyond which the oxide is not stable under such field conditions.

In order to find the way in which the thickness of the basic layer depends on current density, concentration and temperature, data from tables 3 and 5 are used as follows to plot graphs 5, 6 and 7.

From Table 3:

H_2SO_4 conc:	15%	9%	5.4%	2.3%	1.19%;	Oxalic
log I (ma)	d (Å)	d(Å)	d (Å)	d (Å)	d (Å)	d (Å)
log 1 = 0	33.8	45.5	55.8	72.6	111	128
log 2 = .301	48.3	62.6	81.4	122	160	238
log 3 = .477	59.7	79.6	104	146	184	264
log 4 = .602	67.7	96.5	119	162	200	299
log 8 = .903	92.9	120.5	147	182	---	380

Table 6.

These figures are plotted on Graph 6, d vs. Log I, where d is the final thickness of the basic layer expressed in Ångstroms, and where I is the current density. Note then that the values of d for constant concentration vary directly as the log of the current density.

$$\log I = \propto d \; ; \quad \propto = \text{constant for given concentration and temperature.}$$

From Table 5:

d (Å)	$\log \frac{d}{100}$	$\frac{1000}{T}$ °K^{-1}
31.8	1.16	3.16
37.0	1.31	3.17
45.8	1.52	3.23
64.5	1.86	3.30
99.7	2.30	3.42
119.0	2.48	3.49

Table 7.

Graph 5 shows $\log d$ vs. $\frac{1}{T}$, which is a straight line except for the last 2 points. So

$$\log d = \frac{B}{T} \; ; \quad B = \text{constant for given concentration and temperature.}$$

Here it may be useful to point out the difficulty encountered when oxidizing with currents over 4 m.a./cm. in 1.2% H_2SO_4 at 13° C., which may have some bearing on the deviation from a straight line in the above case for the lower temperatures. Under the mentioned conditions the plates corroded visibly, but an oxide layer still covered the whole plate, since a capacity measurement was obtained, although the value did not lie on the graph for lower current densities at the same concentration and temperature. This may be attributable to solubility product effects, since in some cases dilute solutions have been observed to give rise to much more serious electrolytic corrosion than more concentrated solutions.

Another reason for expecting deviations for thinner layers may be the following. The bases of the pores can be

thought of as a series of small plates set some distance from a single large plate (the metal); when the plates are very close together, the area must be the sum of the areas of the small plates; but when the separation becomes large enough, the area for the capacity measurement approximates the area of the single large plate. This would lead to deviations in the direction observed.

From Table 3, rearranging to keep current density constant, there is the following relation between concentration (in moles/litre) and thickness of the basic layer (expressed in Ångstroms): (See Graph 7)

Table 8.

Conc. H_2SO_4	moles/ litre	$\dfrac{10}{\sqrt{c}}$	d at 1 mil/cm^2	d at 3 ma/cm^2	d at 4 ma/cm^2	d at 8 ma/cm^2
15.0 %	2.71	6.07	33.8	59.7	67.7	92.9
9.0 %	1.63	7.85	45.5	79.6	96.5	120.5
5.4 %	.98	10.1	55.8	104.0	119.0	147.0
2.3 %	.416	15.5	72.6	146.0	162.0	182.0
1.19%	.215	21.6	111.0	184.0	200.0	--

So $d = \dfrac{f}{\sqrt{c}}$ where f = constant, for given temperature and current density.

To summarize the experimental results:

1. For given temperature and current density, d is proportional to $\dfrac{1}{\sqrt{c}}$,

2. For given concentration and current density, log d is inversely proportional to T,

3. For given concentration and temperature, d is proportional to log I,

where d refers to the thickness of the thin basic oxide layer

underneath the porous oxide structure formed in sulphuric acid.

3. SUGGESTED THEORY FOR FORMATION OF BASIC LAYERS OF CONSTANT
THICKNESS:

Experiment has shown that for given concentration
of sulphuric acid, temperature and current density, a basic
layer of constant thickness is formed under the porous structure;
and that this thickness is proportional to the logarithm of the
current density. It is proposed to show by the following
theoretical calculation that this relation is correct.

A. First some numerical values must be calculated.

1. Concentration of Al^{+++} ions per c.c. without field:

Structure of Al_2O_3 formed in boric acid is of the
γ'-type (ref. 9), a face-centered cubic lattice of
oxygen ions with a statistical distribution of the
Al^{+++} ions over octahedron and tetrahedron holes. The
lattice parameter is a $= 3.95$ Å. Then, since there
are on the average 8/3 Al^{+++} ions inside a cube of side
a (equivalent to 4 $O^=$ ions), the concentration of
Al^{+++} ions per c.c. without a field is $n_0 \approx 4.3 \times 10^{22}$.

2. Coefficient β in electrolytic current formula
$I = \alpha e^{\beta F}$, where F is the field strength:

A study of the f.c.c. oxygen lattice shows that
one Al^{+++} ion must make 4 jumps through alternate
octahedron and tetrahedron positions to cover a dis-
tance a=3.95 Å in one specific direction.
A projection of this path leads to fig. 5 for the

potential curve inside the oxide where

$b = \frac{a}{4} \simeq 1$ Å. The activation energy U
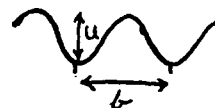
for an octahedron-tetrahedron jump will   fig. 5.

for simplicity be assumed equal to that

for a tetrahedron-octahedron jump. If the vibration

frequency is $\nu \simeq 10^{12}$, the probability for a jump

without an applied field is $\nu e^{-U/kT}$. With a strong

field, assuming diffusion and jumping against the

field are negligible, the probability for an Al^{+++} ion

to jump is

$$\nu e^{-U/kT} \ e^{\frac{3eFb}{2kT}}$$

Assuming that there is an effective number of ions/

cm.^{2} equal to N_0, the current/cm.^{2} inside the oxide,

assuming no space charge, is given by

$$I = N_0 . 3e \nu e^{-U/kT} \ e^{\frac{3eFb}{2kT}}$$

Now a volume of oxide with a cross-section of 1 cm.^{2}

and b cm. in length contains N_0 ions; and therefore

$N_0 = b \ n_0$.

$$N_0 \simeq 10^{-8} \times 4.3 \times 10^{22} \simeq 4.3 \times 10^{14}$$

Comparing with the experimental formula $I = \propto e^{\beta F}$,

we see that $\beta = \dfrac{3}{2} . \dfrac{4.8 \times 10^{-8} \times 10^{-10}}{1.38 \times 10^{-16} \times 300}$

$$\simeq 1.74 \times 10^{-4} \text{ at room temperature,}$$
for F in e.s.u.

giving $\beta \sim 0.6 \times 10^{-6}$ for F in V/cm.

N.B. Verwey finds $\beta = 0.7 \times 10^{-6}$ for F in V/cm. Güntherschulze[1]

finds 6 times as much, but that leads to $b \sim 10^{-7}$ which is the-

oretically impossible. It is too difficult to measure β ;

[1]Güntherschulze, A, & Betz, H., Z. Phys. 91, 70 (1934).

calculation is to be prefered.

    3. Height of the lattice potential barrier, U:

    We have $I = bn_0.3e^\nu e^{-U/kT} e^{\beta F}$

From measurements of Dekker and Van Geel (3), oxidation in boric acid of 440 cm.^{2} with a current of 200 m.a. gives at a voltage of 300 volts (1 e.s.u.) a capacity $\frac{1}{C} = 13 \times 10^{-8}$ cm.$^{-1}$

So thickness $d = \frac{\varepsilon A}{4\pi C} = \frac{8 \times 440 \times 13 \times 10^{-8}}{4\pi}$

$$= 3.64 \times 10^{-5} \text{ cm.}$$

So, in that case, the field strength in e.s.u. is

$$F = \frac{1}{3.64 \times 10^{-5}} = 2.75 \times 10^4 \text{ e.s.u./cm.}$$

    Then $e^{\beta F} = e^{4.78} \approx 120$

Now $I = \frac{200}{440} \frac{\text{m.a.}}{\text{cm.}^2} = 1.36 \times 10^6$ e.s.u./cm.^{2}

So all quantities but U in the current equation are known.

Solving for U: $e^{U/kT} = 5.5 \times 10^{13}$

$$U \simeq 30 \text{ kT} \simeq .75 \text{ eV.}$$

N.B. Verwey calculates from Guntherschulze's $\propto$ a value of 1.8 eV., which seems to agree very roughly with the fusion point.

B. **Now the field strength can be calculated as a function of x:**

    Assume that only the Al^{+++} ions are mobile; then the metal oxide interface can be considered as a source giving off metal ions. (If the motion of O^{--} ions in the opposite direction is taken into account, the metal-oxide interface could be considered a source of metal ions and of positive holes. The O^{--} current depends on the Al^{+++} current because the O^{--} ions

can only move when the Al^{+++} ions jump from the metal into the oxide, leaving holes which then move in the same direction as the Al^{+++}.)

If, during the time current is flowing, the concentration of Al^{+++} ions is $n(x)$, we have

$$I(x) = n(x) \, b \, 3 \, e \, \nu \, e^{-U/kT} \, e^{\beta F(x)} + \text{negligible diffusion term} \quad (1)$$

$$I(x) = n(x) \cdot \gamma \, e^{\beta F} \quad \text{with} \quad \gamma = 3 \, eb\nu e^{-U/kT}$$
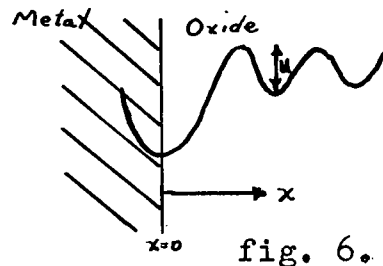$$\simeq 2.6 \times 10^{-19}$$

fig. 6.

On the other hand, because of possible space charge, we have $\dfrac{dF}{dx} = \dfrac{4\pi\rho}{\varepsilon} = \dfrac{4\pi \cdot 3e}{\varepsilon}(n(x) - n_0)$ $\qquad$ (2)

assuming the number of O^{--} ions remains the same as without a field.

From (1) we have $n(x) = \dfrac{I}{\gamma} \, e^{-\beta F(x)}$

Substitute in (2), giving

$$\frac{dF}{dx} = \frac{12\pi e}{\varepsilon}\left(\frac{I}{\gamma} \, e^{-\beta F(x)} - n_0\right)$$

OR $\displaystyle\int_{F_0}^{F} \frac{dF}{\left(\frac{I}{\gamma}e^{-\beta F} - n_0\right)} = \int_{0}^{x} \frac{12\pi e}{\varepsilon} \, dx$

$$\therefore \quad \frac{12\pi e}{\varepsilon} x = -\int_{F_0}^{F} \frac{e^{\beta F} dF}{-\frac{I}{\gamma} + n_0 e^{\beta F}}$$

$$= \frac{1}{n_0 \beta}\left[\log(n_0 e^{\beta F_0} - \frac{I}{\gamma}) - \log(n_0 e^{\beta F} - \frac{I}{\gamma})\right]$$

This gives F as a function of x:

$$\frac{n_0 e^{\beta F_0} - \frac{I}{\gamma}}{n_0 e^{\beta F} - \frac{I}{\gamma}} = e^{\frac{12\pi e n_0 \beta x}{\xi}} \sim e^{1.7 \cdot 10^{10} x} = e^{px}$$

Now suppose at $x = 0$ the effective density of the aluminum ions in the metal is m_0.

Then $I_0 = I = m_0 \gamma e^{\beta F_0}$

or $\frac{I}{\gamma} = m_0 e^{\beta F_0}$

Substituting this for $\frac{I}{\gamma}$, we have

$$\frac{n_0 - m_0}{n_0 e^{\beta(F - F_0)} - m_0} = e^{px}$$

When $n_0 \gg m_0$,

$$1 = (e^{\beta(F - F_0)} - \frac{m_0}{n_0}) e^{px}$$

For those values of x for which px is of the order of 1 or smaller, we see that we should have

$\beta F - \beta F_0 + px = 0$

because we can omit $\frac{m_0}{n_0}$;

and since $\beta F_0 = \log \frac{I}{m_0 \gamma}$, then

$x = \frac{1}{p} \log I - \frac{1}{p} \log m_0 \gamma - \frac{\beta F}{p}$

which means that if we assume solution of the layer begins when F reaches a critical value F_c (being the same value in all cases where the concentration of the solution is the same), then the critical value of $x = x_c$ will be a linear function of $\log I$, as found experimentally, where I is the

oxidizing current.

$$\text{i.e.} \quad x_0 = \frac{1}{p}\log I - \frac{1}{p}\log m_0 \gamma - \frac{\beta}{p}F_c$$

Now p has been calculated to be 1.7×10^{10}, so

$$\frac{1}{p} = .59 \times 10^{-10},$$

whereas the experimental slope (Graph 6) is of the order of 10^{-6}.

Now the space charge of Al^{+++} ions can only be distributed over the vacant lattice positions, not continuously through the oxide as has been assumed in the preceeding theory, and this fact may explain why the right relation but wrong order has been obtained.

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