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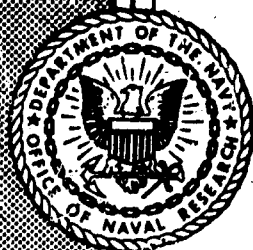
# **THE SILVER OXIDE - ZINC ALKALINE PRIMARY CELL**

## **PART III. CELL DESIGN**

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**NAVAL RESEARCH LABORATORY**

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## **CONTENTS**

Abstract	ii
Problem Status	ii
Authorization	ii
<b>BACKGROUND</b>	<b>1</b>
<b>CELL DESIGN</b>	<b>1</b>
Cell Case	2
Grid Weights	2
Weight of Active Materials	3
Weight of Connectors	4
Weight of Separators	4
Electrolyte	5
Spacers	10
Minimization of Cell Weight	11
Minimization of Volume	13
Maximization of Output	28
<b>SAMPLE CALCULATIONS</b>	<b>28</b>
Minimization of Volume	28
Minimization of Cell Weight	29
<b>LIMITATIONS AND SOURCES OF ERROR</b>	<b>33</b>
Accuracy of Data	34
Extrapolation	35
Assumptions in Calculations	35
Assigning Values to Variables	35
Adaptation of Results to Working Conditions	36
New Variables	36
Design and Manufacture	39
<b>CONCLUSIONS</b>	<b>41</b>
<b>REFERENCES</b>	<b>41</b>
<b>GLOSSARY</b>	<b>42</b>

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## THE SILVER OXIDE - ALKALINE PRIMARY CELL

### PART III. CELL DESIGN

#### BACKGROUND

Because of its many desirable characteristics a considerable demand has arisen for the silver oxide - zinc - potassium hydroxide primary cell. At high current densities, it will deliver more power per unit weight of active material than any other known type of primary battery. Wherever the demand for the cell is based on minimization of weight or volume, a separate design will be needed for each set of conditions. Such a design will require more information than is necessary for the construction of ordinary batteries. The information needed for the design of a cell using sheet-zinc negative electrodes has already been published (1). It has been shown that this information is applicable to other types of negative electrodes (2). In designing a cell of minimum weight or volume, it will be necessary to make certain assumptions and approximations in adapting the available information to the construction and operation of this particular cell. As a rule the errors introduced in so doing will be small, and it will be possible to predict the characteristics of a particular cell with a fair degree of accuracy. However, it is possible to introduce appreciable errors under certain conditions which will be discussed later. As a consequence, the information given in this report should be looked upon by the designer and manufacturer as a guide rather than as a guarantee of specific results.

#### CELL DESIGN

The design contains a negative electrode of zinc, a positive electrode of silver oxide, and an alkaline electrolyte consisting of KOH solution. The metallic zinc is oxidized during discharge and the silver oxide is reduced to silver. Either of the silver oxides,  $\text{Ag}_2\text{O}$ , or the peroxide,  $\text{Ag}_2\text{O}_2$ , can be utilized. All the data were obtained with  $\text{Ag}_2\text{O}$  positive electrodes, the  $\text{Ag}_2\text{O}$  being preferable because of its lower equivalent weight, but the discussion that follows will also be applicable in its major points to cells utilizing  $\text{Ag}_2\text{O}_2$  positive electrodes.

The cell should be assembled in a manner that leaves very little electrolyte between the electrode assembly and the cell case; virtually all of the electrolyte should lie between the electrode faces or else be absorbed in the electrodes. Such an assembly can be attained by using a close-fitting cell case and adjusting the electrolyte level to make it even with the top of the electrodes.

The specifications for a battery of minimum weight will include the emf, discharge current, discharge time, and range of temperature over which the cell must be capable of operating. The desired emf will be obtained by connecting identical cells in series. Since the emf of a single cell is nearly constant under most conditions, the desired emf can be obtained by connecting some number,  $r$ , of identical cells in series. The weight of one of these cells is  $1/r$  times the total weight of the battery. Minimization of this cell's weight

will be equivalent to minimization of the total battery weight. Therefore the emf does not enter into the calculation of the minimum weight even though it does affect the total weight by the factor  $r$ .

To insure the desired results under all conditions, the temperature which has the poorest discharge characteristics is chosen as a basis for the calculations. This temperature will generally be the lowest at which the cell will have to operate. Therefore, the weight at a given temperature will be calculated from the total discharge current,  $I$ , and the discharge time,  $T$ .

The total weight of a cell,  $W_T$ , at a given temperature is equal to the sum of its component parts.

$$W_T = \text{weight of cell case} + \text{weight of negative grids} + \text{weight of positive grids} + \text{weight of negative active material} + \text{weight of positive active material} + \text{weight of internal connectors} + \text{weight of separators} + \text{weight of electrolyte} + \text{weight of spacers.} \quad (1)$$

It is necessary in the ensuing calculations to divide the cell weight into several parts: a part whose weight is minimized when the remainder of the cell weight is minimized, a part whose weight is constant, a part whose weight is directly proportional to the electrode area, a part whose weight is a function of the electrolyte volume, and a part whose weight is the weight of the electrolyte. These are natural divisions, but in some cases certain assumptions must be made.

#### Cell Case

If the weight of the cell case is assumed to be a minimum when the remainder of the cell weight is minimized, then it may be dropped from Equation (1) as far as further calculations are concerned.

#### Grid Weights

The construction of the silver oxide cell involves the use of  $m$  negative plates and  $m \pm 1$  positive plates where  $m$  is an integer. For the purposes of this discussion, the number of positive and negative plates are taken as equal. The error introduced by this assumption generally is small and can be corrected for later if necessary.

Assume a construction such that the electrodes lie in parallel planes. A unit cell is defined as a section of this larger cell taken perpendicular to the electrodes, extending from the center of one positive plate to the center of the adjacent positive plate, and having a cross-sectional area of one square inch. Such a cell contains one complete positive and one negative plate. Let  $N$  equal the number of unit cells necessary to construct the desired cell in a specified problem. If  $W_g$  equals the total grid weight in ounces of a unit cell (one square inch of positive grid plus one square inch of negative grid), then the total grid weight for the desired cell is  $NW_g$ .

The actual area,  $n$ , of a unit cell is defined as the total surface area of the unit negative electrode at the end of the discharge. A unit cell using a sheet-zinc electrode would have an initial total surface area of two square inches. The actual area,  $n$ , at the end of the discharge would also be two square inches, if the electrode were not corroded through in any spots. The term,  $n$  is numerically equal to the ratio of the actual area to the apparent cross-sectional area. If a zinc wire screen were used, the initial surface area would be the

total surface area of all the wires involved in making up the screen. As the zinc dissolves during discharge, the wire diameter and the total surface area becomes smaller. Therefore,  $n$  decreases as the discharge time increases. Methods of making these calculations have been discussed in a previous report (2).

If  $i$  is the current density in amperes per square inch of actual electrode area, then the current flowing in the unit cell is  $ni$ . If the total current needed is  $I$ , then the number of unit cells,  $N$ , required in the desired cell is  $I/ni$ .

The total grid weight may be stated in the form

$$NW_g = W_g (I/ni). \quad (2)$$

In minimizing cell weight, it is desirable to make the unit grid weight,  $W_g$ , as small as possible and still maintain the necessary grid strength and electrical conductance. Thus, the minimum value of  $W_g$  will be determined by the construction of the cell and by the physical and electrical demands made upon it. Actually the minimum value of  $W_g$  can be shown to vary slightly with varying values of  $N$ ,  $n$ , and  $i$ . The effects of such variations are small and can be safely neglected in this discussion.

#### Weight of Active Materials

If the required cell has a specified current,  $I$  in amperes and discharge time,  $T$ , in minutes, then the cell capacity in ampere minutes is a constant,  $TI$ . Since the electrode efficiencies of zinc and silver oxide are very high, it is possible to use Faraday's law in calculating the amount of each consumed during cell discharge. The theoretical amount of zinc needed in ounces is  $K_Z = TI/1395$ . It has been shown that the rate of solution of zinc during discharge may be several times as rapid at the top of the electrode as it is at the bottom.\* Consequently the theoretical amount of zinc cannot be distributed over the electrodes in a manner such that it can be completely utilized. A correction factor,  $b$ , is introduced to take care of the excess zinc needed. As a result, the actual amount of zinc needed is  $W_Z$  where

$$W_Z = bTI/1395 = W_b TI. \quad (3)$$

$W_b$  will vary with the type of electrode used and the skill used in constructing it. For a particular cell,  $W_b$  is substantially a constant, and even though it may vary slightly with change in current density, this variation will be so small that it will have a negligible effect and can be completely neglected.

A special problem arises whenever zinc-sheet or zinc-wire screen is used, because there is no definite line of demarcation between the active material and the grid. Assume the grid weight to be the weight of that portion of the electrode necessary to maintain the desired conductivity and physical strength throughout the discharge. The remainder of the electrode will be the active material to be dissolved during discharge plus the excess of active material necessary because of the uneven dissolution of the zinc during discharge. As before, this may be expressed approximately by the equations

$$W_Z = b_1 TI/1395 = W_{b1} TI \quad (3)$$

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\* This problem will be discussed in a future NRL Report.

The theoretical amount of AgO needed in ounces is  $K_c$ , and

$$K_c = TI/736.$$

Given sufficient quantities of active materials at both electrodes, cell failure will always occur at the zinc electrode. The amount of silver oxide necessary,  $W_c$ , is slightly greater than  $K_c$ , the theoretical quantity. The necessary excess of silver oxide depends upon the method of preparing the electrode and is a function of  $ni$  the unit cell current density. The actual weight of silver oxide may be expressed by the equation

$$W_c = G_w(ni)TI. \quad (4)$$

$G_w(ni)$  is a function of unit cell current,  $ni$ , and is also dependent upon the method of preparing the electrode.  $G_w(ni)$  does not vary appreciably with current density,  $i$ , and consequently its variation can be neglected since it is generally small when compared with the effect of the other factors involved. Therefore  $G_w(ni)$  may be replaced by a constant  $W_d$  and Equation 4 then becomes

$$W_c = W_d TI. \quad (5)$$

#### Weight of Connectors

If the number of plates is increased in a particular battery, the number of wire connectors leading from the grids to the poles is increased. However, the cross-sectional area of each of the wires may be decreased proportionately since each one will be carrying less current. Consequently, the weight of the wire connectors per ampere,  $W_y$ , remains approximately constant. The total weight of connectors will be  $IW_y$ .

From Equations (2), (3), and (5), the total weight of the electrodes and connectors in the cell is approximately equal to

$$(I/ni)W_g + (W_b + W_d)TI + IW_y \quad (6)$$

where  $W_g$  is approximately the minimum grid weight in the unit cell,  $(W_b + W_d)TI$  is the necessary weight of active materials, and  $IW_y$  is the approximate weight of connectors. The term  $i$ , the only variable in this equation, will be determined in the ensuing calculations.

#### Weight of Separators

Separators and spacers are porous nonconducting materials inserted between the plates of the cell for the purpose of holding them apart and preventing electrical contact. For the purpose of this discussion, a separator is defined as a material of constant thickness, inserted between each two plates. Let  $W_f$  equal the weight of two square inches of separator materials, the amount found in a unit cell.  $W_f$  does not include the weight of absorbed electrolyte. Then the total weight of separator material,  $W_p$ , may be stated in the form

$$W_p = (I/ni)W_f. \quad (7)$$



## Electrolyte

The following symbols are established and defined to calculate weight and volume of electrolyte used in this cell.

K, a function of current density  $i$ , equals cell capacity in minutes per gram of KOH per square inch of actual negative electrode area;

$f(i)$ , a function of current density  $i$ , equals cell capacity in minutes per ounce of KOH per square inch of actual negative electrode area;

$V_e$  equals total volume in cubic inches of electrolyte used in cell;

$v_e$  equals volume of electrolyte in cubic inches per square inch of actual negative electrode area;

$F(i)$  equals the most effective concentration in ounces of solid 100 percent KOH per cubic inch of solution at the given temperature;

$M(i)$  equals  $100 \div$  percent concentration of the most effective KOH solution at the given temperature;

$D$  equals density of most effective concentration of electrolyte in ounces per cubic inch; and

$W_e$  equals total weight of electrolyte.

K has been determined and plotted in previous reports (1, 2). The relationship between K and  $f(i)$  is given by the equation

$$f(i) = 28.35K. \quad (8)$$

$f(i)$  is plotted in Figures 1 and 2.

Values of  $M(i)$  and  $F(i)$  were calculated at a given temperature from the concentration of electrolyte that was found to maximize cell capacity for the particular current density question. The results are plotted in Figures 3 and 4. At higher concentrations of the total than these, cell capacities diminish rapidly and the function  $f(i)$  is not valid. The total discharge time,  $T$ , equals  $f(i)$  times the ounces of KOH per square inch of negative electrode area. Consequently,

$$T = f(i) F(i) v_e \quad (9)$$

$$v_e = \frac{T}{f(i) F(i)} \quad (10)$$

The volume of electrolyte per unit cell is

$$nv_e = \frac{T}{f(i) F(i)} \quad (11)$$

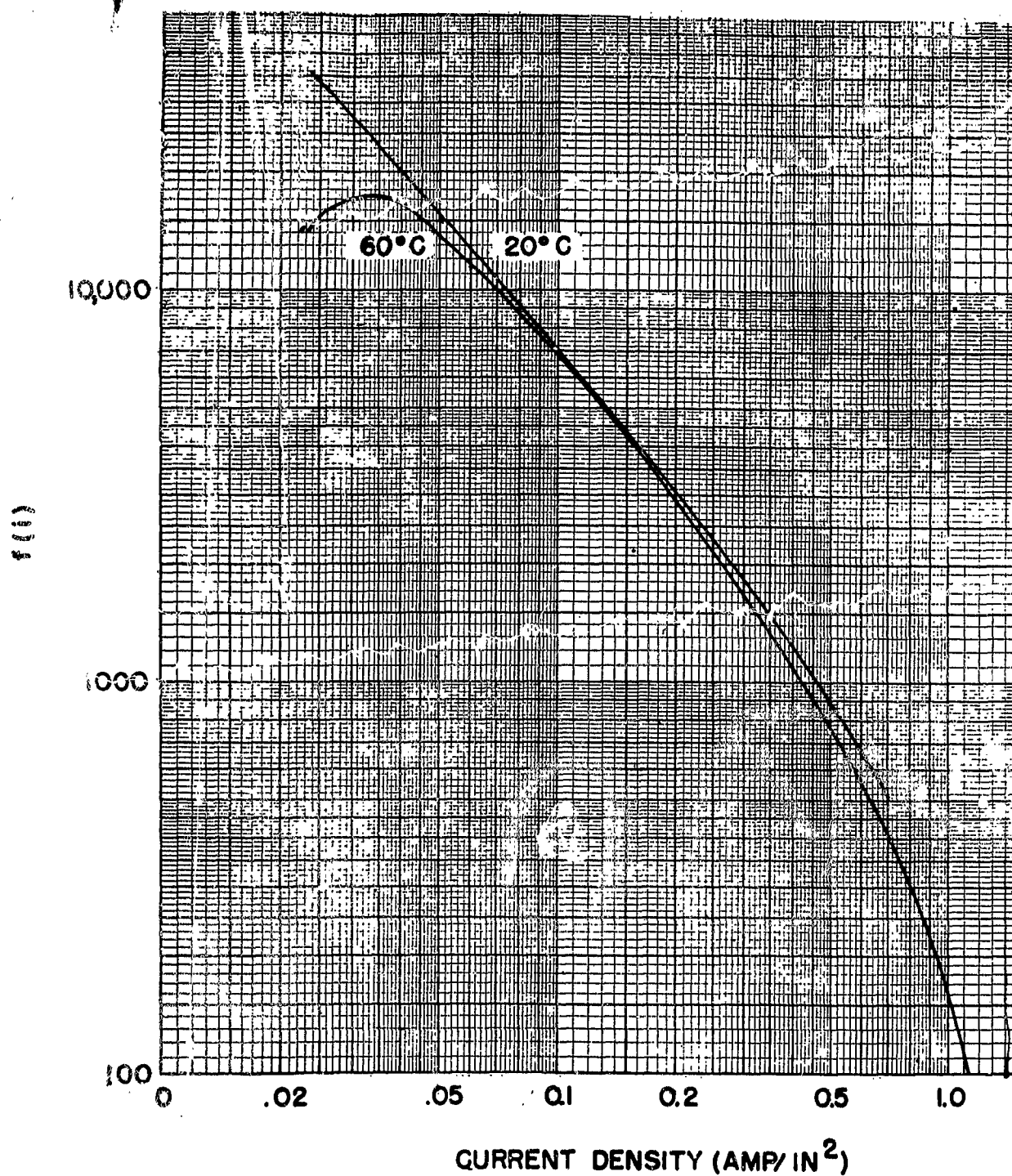


Figure 1 - Effect of current density on cell capacity per ounce of KOH per square inch of actual negative electrode area

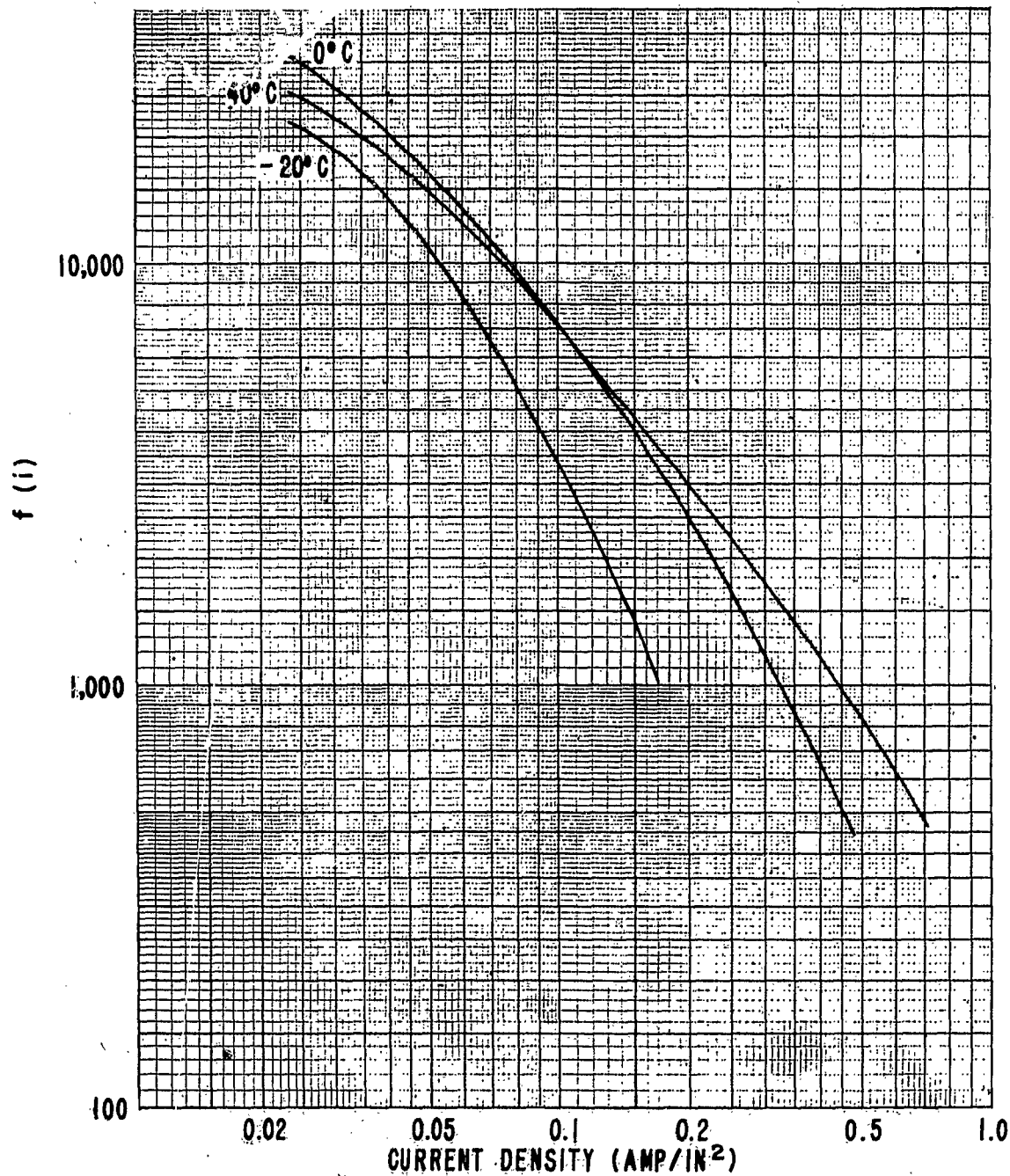
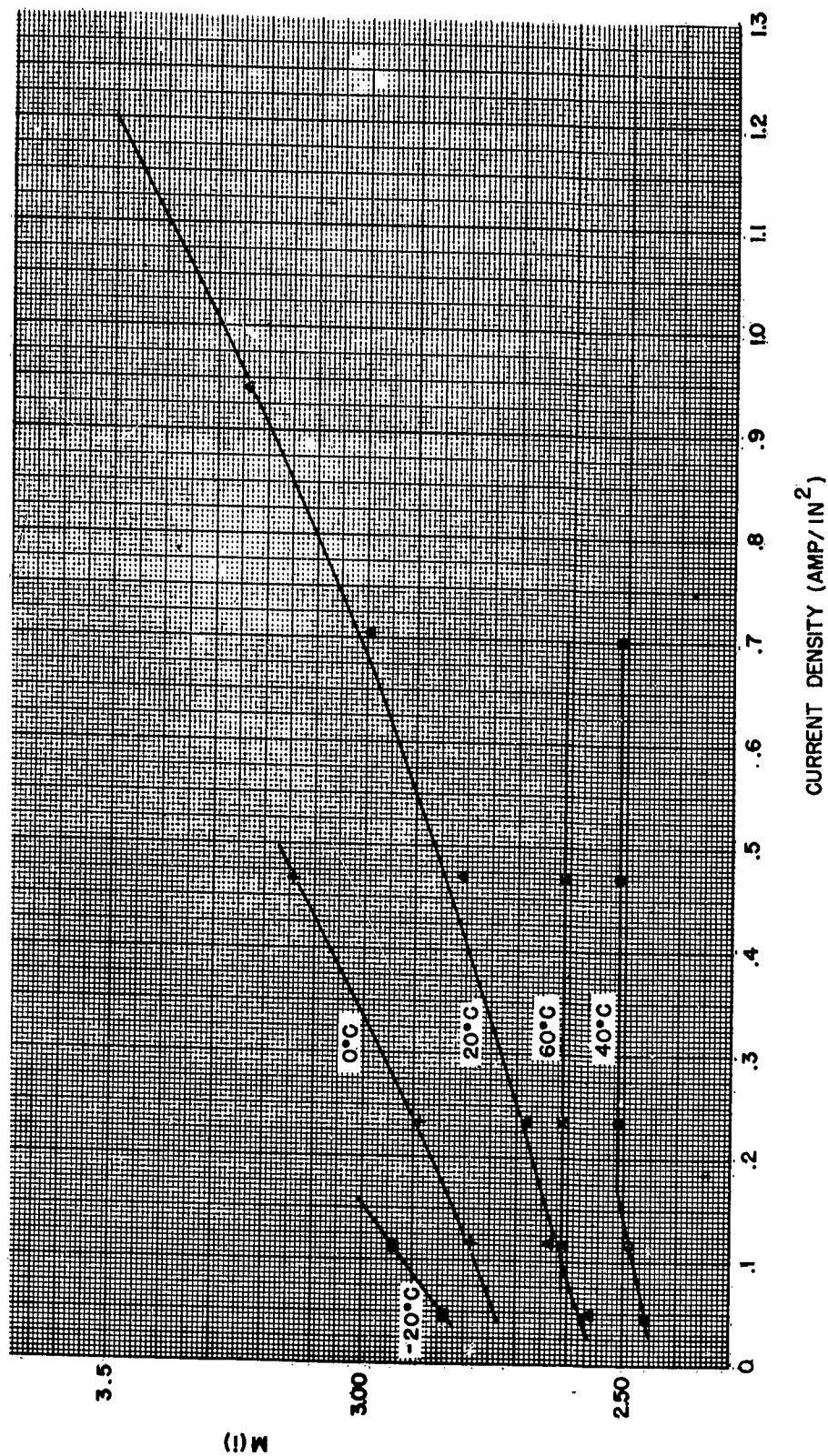


Figure 2 - Effect of current density on cell capacity per ounce of KOH per square inch of actual negative electrode area

Figure 3 - Variation of  $M(i)$  with current density,  $i$

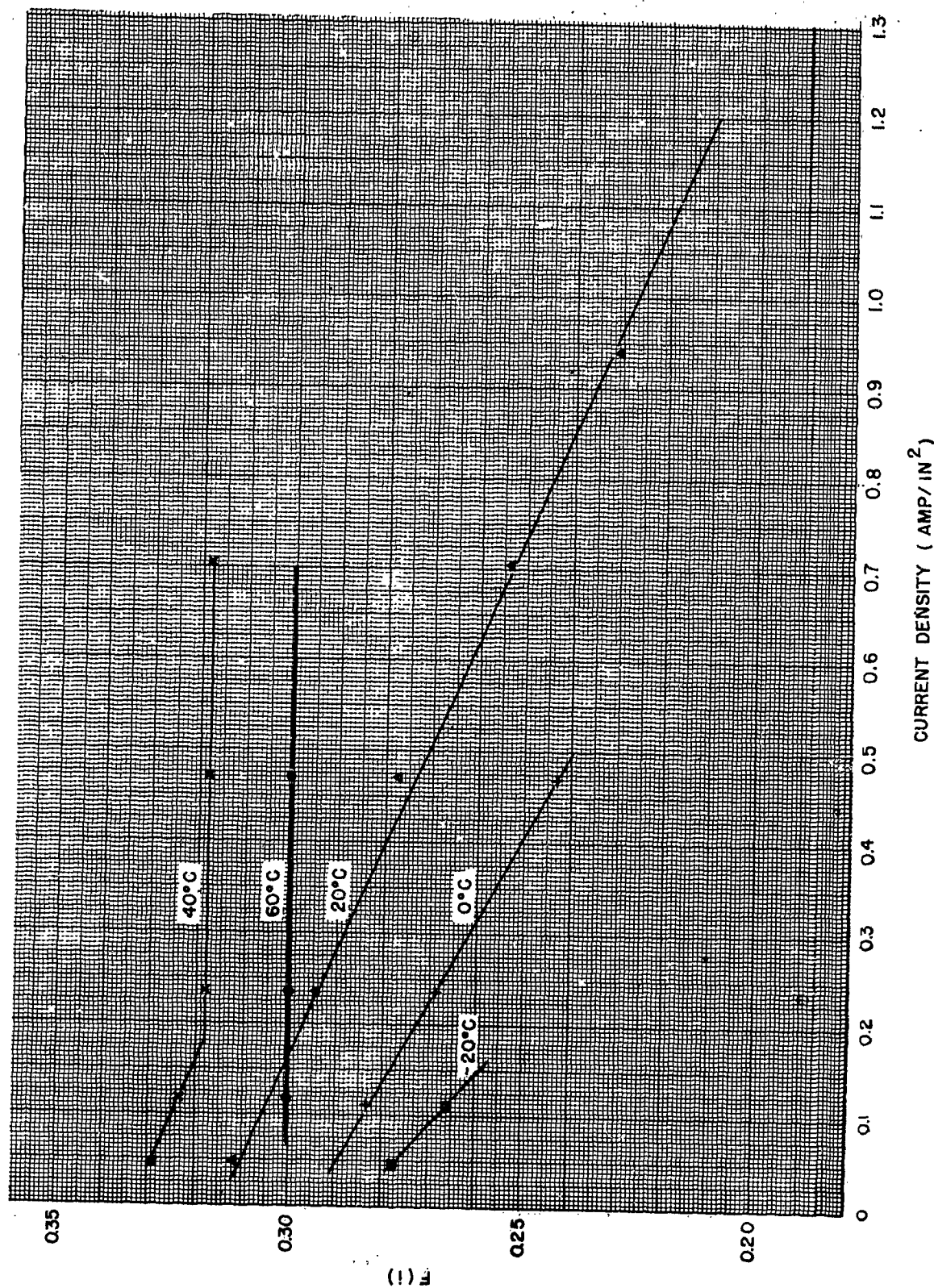


Figure 4 - Variation of  $F(i)$  with current density,  $i$

Multiplying by  $N = I/ni$ , the total volume of electrolyte becomes

$$V_e = \frac{TI}{i f(i) F(i)} \quad (12)$$

By definition

$$\frac{D}{M(i)} = F(i) \quad (13)$$

and

$$D = M(i) F(i). \quad (14)$$

Multiplying by Equation (12) the total weight of electrolyte becomes

$$V_e(D) = \frac{TIM(i)}{i f(i)} \quad (15)$$

### Spacers

The space in an assembled cell may be divided into two parts, that which is occupied by the electrodes and the electrolyte absorbed in the electrodes, and that which lies between the electrode faces. This latter space may be divided into the volume occupied by the separators, the volume occupied by the electrolyte absorbed in the separators, and the remainder of the cell electrolyte plus the volume occupied by the spacers. The weight of spacers of a given material and pattern is directly proportional to the volume of electrolyte not absorbed in the separators and electrodes, and consequently may be expressed by the relationship

$$W_{sp} = W_a(V_e - V_m - V_n) \quad (16)$$

where  $W_{sp}$  is the total weight of spacers,  $V_m$  is the volume of electrolyte absorbed in the separators,  $V_n$  is the volume of electrolyte absorbed in the electrodes at the beginning of the discharge, and  $W_a$  is a constant for a given type of spacer. The amount of electrolyte absorbed in the separators is proportional to the area of the separators, and may be expressed by the equation

$$V_m = j \frac{I}{ni} \quad (17)$$

where  $j$  is the volume of electrolyte absorbed in the separators in a unit cell (normally, two square inches of separator material).

Since the amount of active material and its porosity is constant for a given cell, the volume of electrolyte,  $V_n$ , which the active material will absorb is also a constant.  $V_n$  includes the electrolyte which is absorbed in the silver oxide at the positive electrodes as well as the electrolyte which fills any open space between the two faces of a zinc electrode at the beginning of a discharge. If the negative electrode were made of sheet zinc with holes punched through it,  $V_n$  would include the volume of all these holes.

By substituting Equations (12) and (17), Equation (16) may now be written

$$W_{sp} = W_a \left( \frac{TI}{i f(i) F(i)} - j \frac{I}{ni} - V_n \right) \quad (18)$$



Assume a paired parallel positive and negative electrodes one inch square and a distance  $q$  apart between adjacent electrode faces. If  $s$  equals the thickness of separators used let

$$L = q - s.$$

This gives a volume of  $L$  cubic inches occupied solely by spacers and electrolyte. If  $f$  is the fraction of this space occupied by the electrolyte, then  $fL$  is the volume of electrolyte. If  $w_{sp}$  is the weight in ounces of spacers per cubic inch of volume occupied by spacers and electrolyte, then  $Lw_{sp}$  equals the weight of spacer in the above case. The ratio of spacer weight to electrolyte volume in a given cell is

$$W_a = \frac{Lw_{sp}}{fL} = \frac{w_{sp}}{f} \quad (19)$$

This value of  $W_a$  may be substituted in Equations (16) and (18).

#### Minimization of Cell Weight

It is assumed that the weight of the cell case will be minimized when the weight,  $W$ , of the remainder of the cell is minimized.

When Equations (6), (7), (15), and (18) are substituted in Equation (1), the following equation is obtained

$$W = \frac{I}{ni} W_g + (W_b + W_d)TI + IW_y + W_f \frac{I}{ni} + TI \frac{M(i)}{i f(i)} + W_a \left( \frac{TI}{i f(i) F(i)} - j \frac{I}{ni} - V_n \right) \quad (20)$$

$$= W_G \frac{I}{ni} + k + W_a TI \frac{1}{i f(i) F(i)} + TI \frac{M(i)}{i f(i)} \quad (21)$$

where

$$\bar{W}_G = W_g + W_f - W_a j \quad (22)$$

and

$$k = (W_b + W_d)TI + IW_y - W_a V_n \quad (23)$$

$W_G$  is very closely approximated by the unit cell grid weight,  $W_g$ . The values of  $T$ ,  $I$ ,  $W_a$ ,  $k$ ,  $n$ , and  $W_G$  are all constant or nearly constant for a given problem. All weights are expressed in ounces, volumes in cubic inches, areas in square inches, time in minutes, and current in amperes.

Differentiate  $W$  with respect to  $i$  and equate the derivative to zero. Now,

$$\begin{aligned} dW/di = & -\frac{W_G I}{ni^2} + TI \left( \frac{i f(i) M'(i) - M(i) i f'(i) - M(i) f(i)}{i^2 f^2(i)} \right) \\ & - W_a TI \left( \frac{i f(i) F'(i) + i f'(i) F(i) + f(i) F(i)}{i^2 f^2(i) F^2(i)} \right) = 0. \quad (24) \end{aligned}$$

By solving this equation the value of  $i$  is determined which gives a minimum cell weight for the given conditions.

$$\text{Let } P = \frac{M'(i) i f(i) - M(i) i f'(i) - M(i) f(i)}{f^2(i)} \quad (25)$$

and

$$Q = -\frac{i f(i) F'(i) + i f'(i) F(i) + f(i) F(i)}{f^2(i) F^2(i)} \quad (26)$$

Substituting Equations (25) and (26) in (24), and multiplying by  $i^2/TI$

$$\frac{W_G}{nT} = P + W_a Q. \quad (27)$$

$P$  and  $Q$  were calculated from previously determined cell characteristics and plotted in Figures 5 to 9. In Figures 10 to 14 values of  $W_G/nT$  are plotted against  $W_a$  for various values of current density,  $i$ . Once  $i$  is determined, the remainder of the cell information can be calculated readily. The number of unit cells required equals  $I/ni$ . The values of  $M(i)/i f(i)$  and  $1/i f(i) F(i)$  are plotted in Figures 15 to 18. Data from these curves are used to calculate the total electrolyte weight  $TI M(i)/i f(i)$  and the total electrolyte volume  $T I/i f(i) F(i)$ .

Some interesting results are obtained from a study of Equation (27).

Assume  $W_G/nT$  is equal to  $k$ , a constant. Since  $W_a$  is constant for a particular type of spacer the resultant current density,  $i$ , is shown by Equation (27) to be constant also. If the ampere minutes  $TI$  are equal to another constant  $k_2$ , Equation (21) may be rewritten as

$$W = W_G \frac{I}{ni} \text{ plus a constant.}$$

Since  $TI = k_2$ ,  $I/T = I/k_2$ , substituting in  $W_G/nT = k_1$ ,

$$\frac{W_G I}{n k_2} = k_1$$

and

$$\frac{W_G I}{ni} = \frac{k_1 k_2}{i} = \text{a constant,}$$



since  $i$  is constant. Therefore  $W$ , the minimum cell weight is constant whenever  $W_a$ ,  $TI$ , and  $W_G/nT$  are constants. For a given output in ampere minutes, The minimum cell weight is constant whenever  $W_G$ ,  $n$  and  $T$  vary in a manner such that  $W_G/nT$  is constant.  $W_G$  is essentially the same as the unit grid weight  $W_g$ . If  $W_g$  were changed to  $hW_g$  the cell current  $I$  could be changed to  $I/h$  and the discharge time,  $T$ , changed to  $hT$  without any change in cell weight. If  $W_g$  stayed constant and the electrode unit area were multiplied by  $1/h$ , thus changing  $n$  to  $n/h$ , the same result would be obtained.

### Minimization of Volume

The discussions leading up to Equation (20) can also be applied to minimization of volume if certain minor changes are made. The arguments under the subheading "Electrolyte" remain the same. The remainder of the discussions are also true in every instant if the word volume is substituted for weight (volume in cubic inch for weight in ounces) and  $W$  is replaced by  $V$  in each symbol and numbered equation.

It is assumed that the total volume of the cell is minimized when the volume,  $V$ , of everything except the cell case is minimized. Then

$$V = \frac{I}{ni} V_g + (V_c + V_d)TI + IV_y + V_f \frac{I}{ni} + \frac{TI}{i f(i) F(i)} + V_a \left( \frac{TI}{i f(i) F(i)} - j \frac{I}{ni} - V_n \right) \quad (28)$$

$$= V_G \frac{I}{ni} + K_1 + (1 + V_a)TI \left( \frac{1}{i f(i) F(i)} \right) \quad (29)$$

where

$$V_G = V_g + V_f - V_a j \quad (30)$$

and

$$K_1 = (V_c + V_d)TI + IV_y - V_a V_n. \quad (31)$$

$V_G$  is closely approximated by the unit cell grid volume.  $K_1$  is approximately the volume of the active materials. The values of  $TI$ ,  $V_a$ ,  $K_1$ ,  $n$ , and  $V_G$  are all constant or nearly constant for a given problem. Differentiate  $V$  with respect to  $i$  and equate the derivative to zero

$$dV/di = - \frac{V_G I}{ni^2} - (1 + V_a)TI \left( \frac{i f(i) F'(i) + i f'(i) F(i) + f(i) F(i)}{i^2 f^2(i) F^2(i)} \right) = 0. \quad (32)$$

By solving this equation the value of  $i$  is determined which gives a minimum cell volume for the given set of conditions

$$\frac{V_G}{(1 + V_a)nT} = Q. \quad (33)$$

The graphs in Figures 5 to 9 give values of  $i$  for various values of  $Q$ .

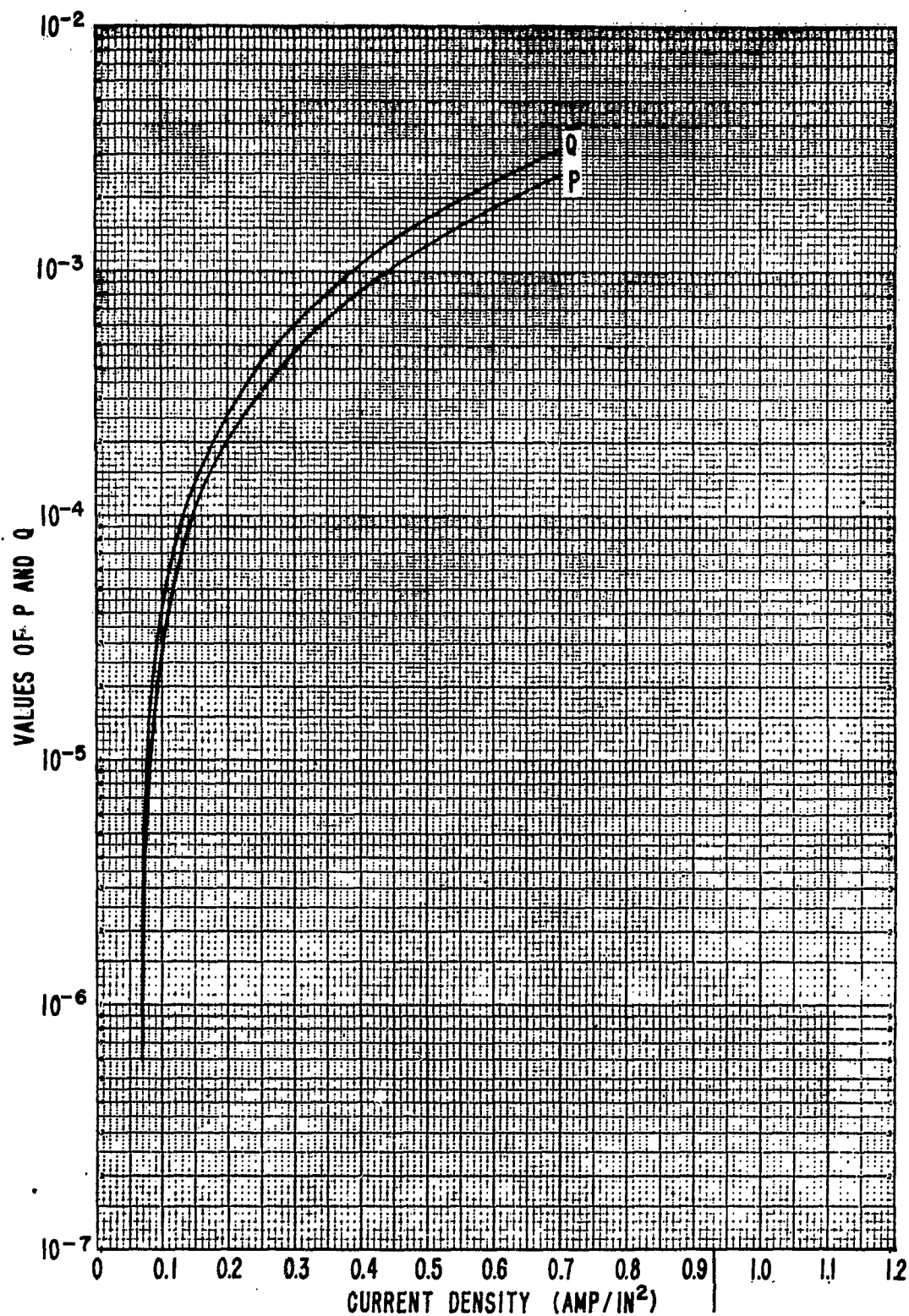


Figure 4 - Variation of  $F(i)$  with current density,  $i$

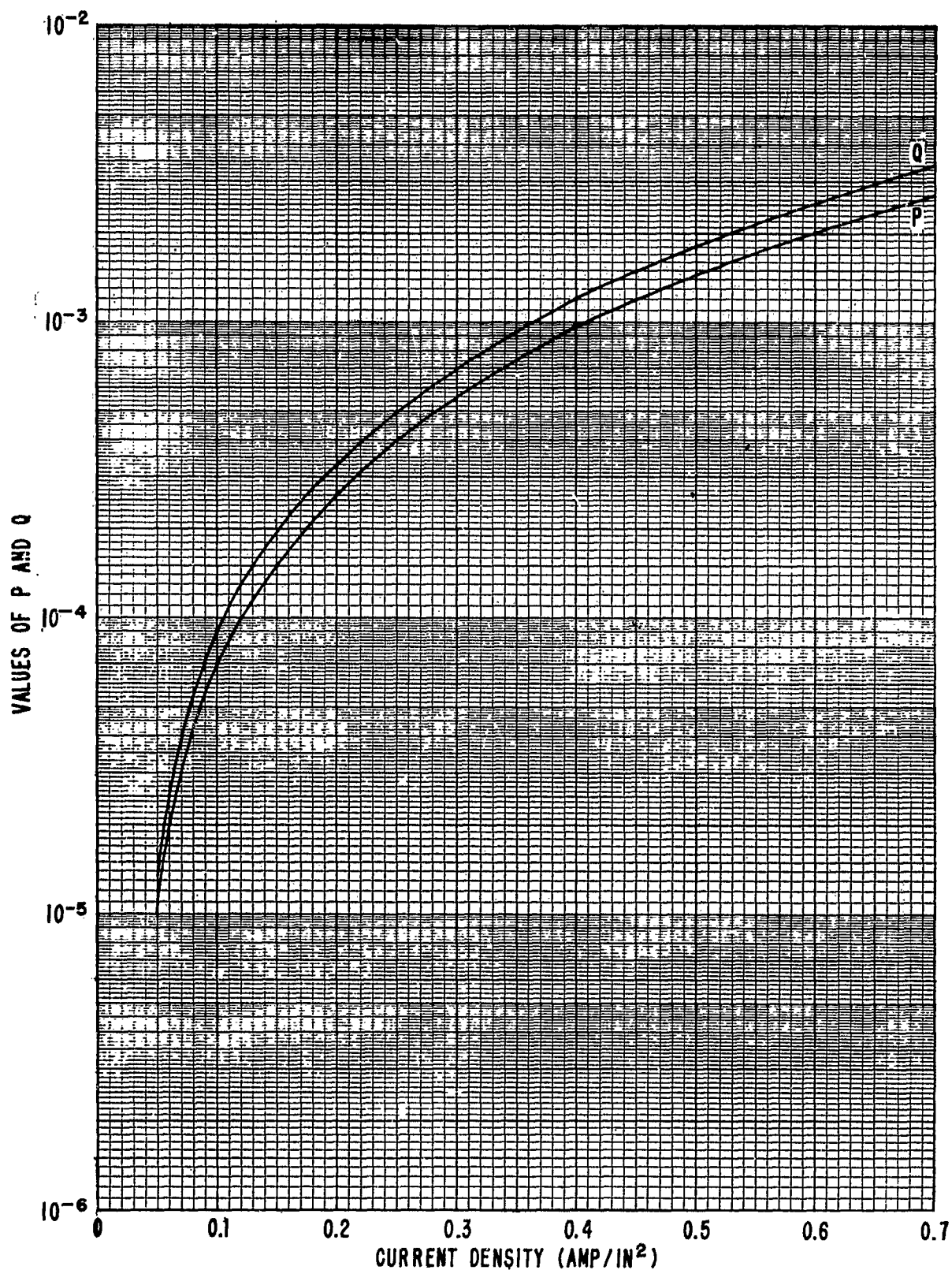


Figure 6 - Variation of P and Q with current density,  $i$ , at  $40^\circ\text{C}$

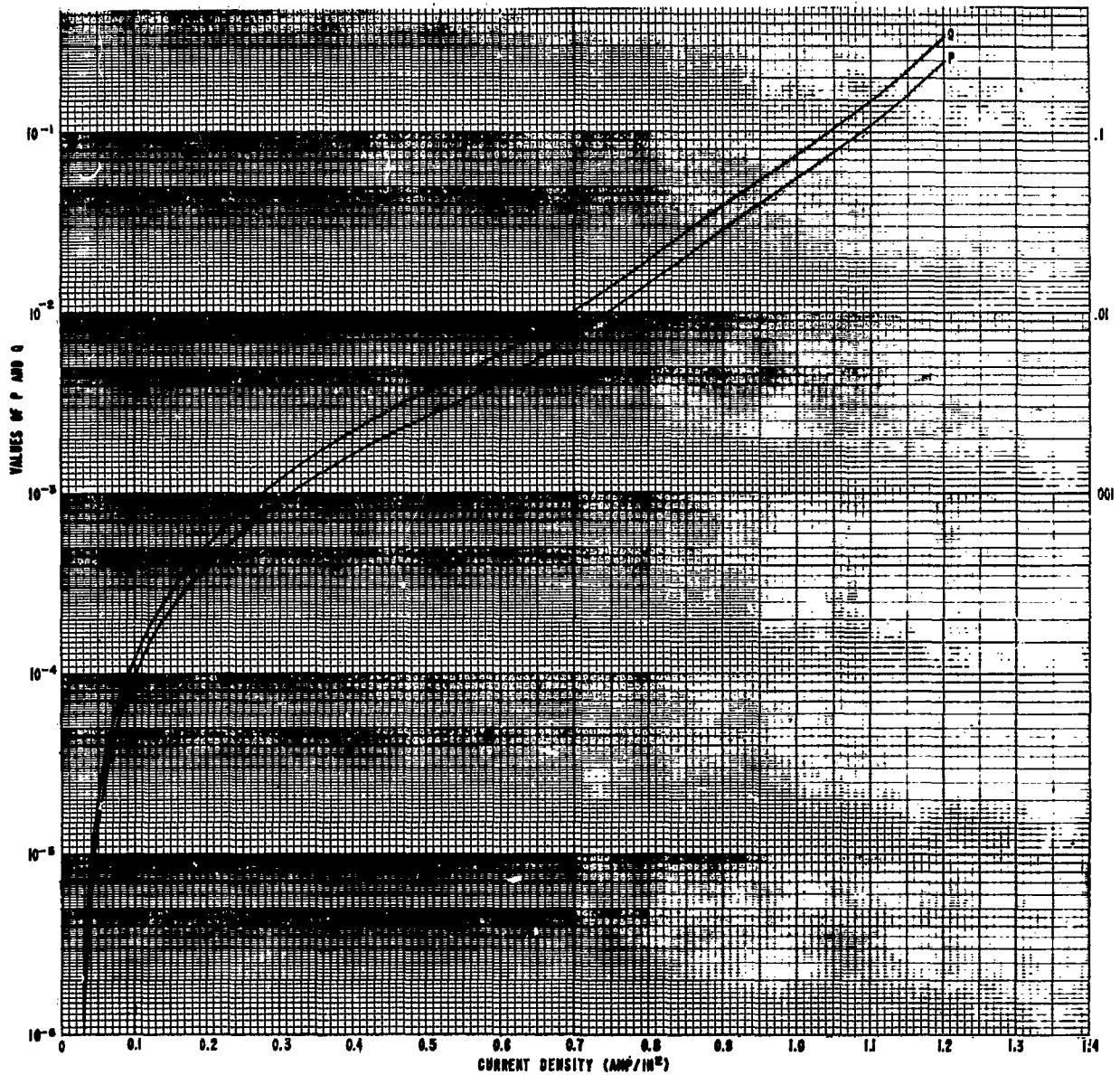


Figure 7 - Variation of P and Q with current density,  $i$ , at  $20^\circ\text{C}$

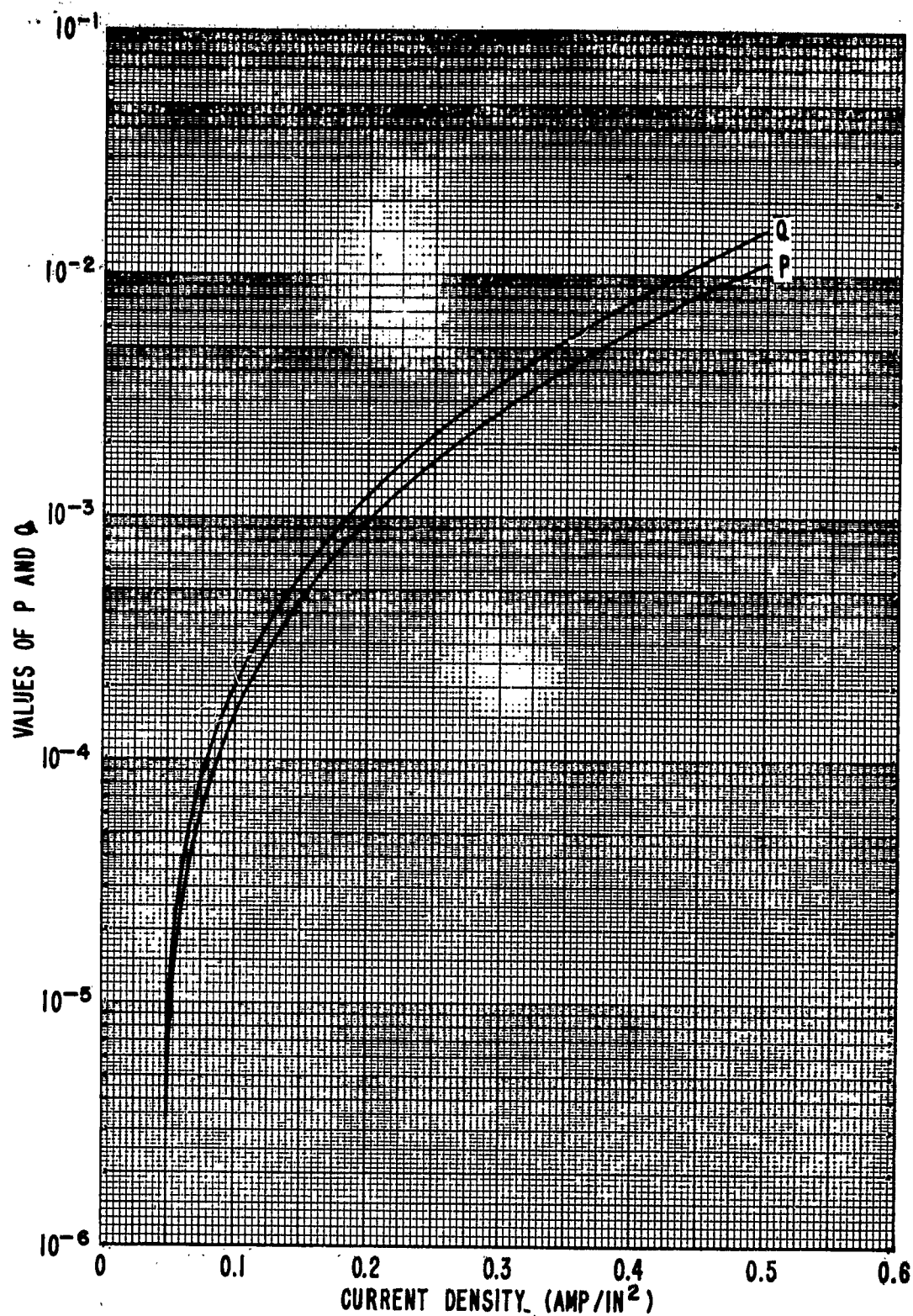


Figure 8 - Variation of P and Q with current density at 0°C

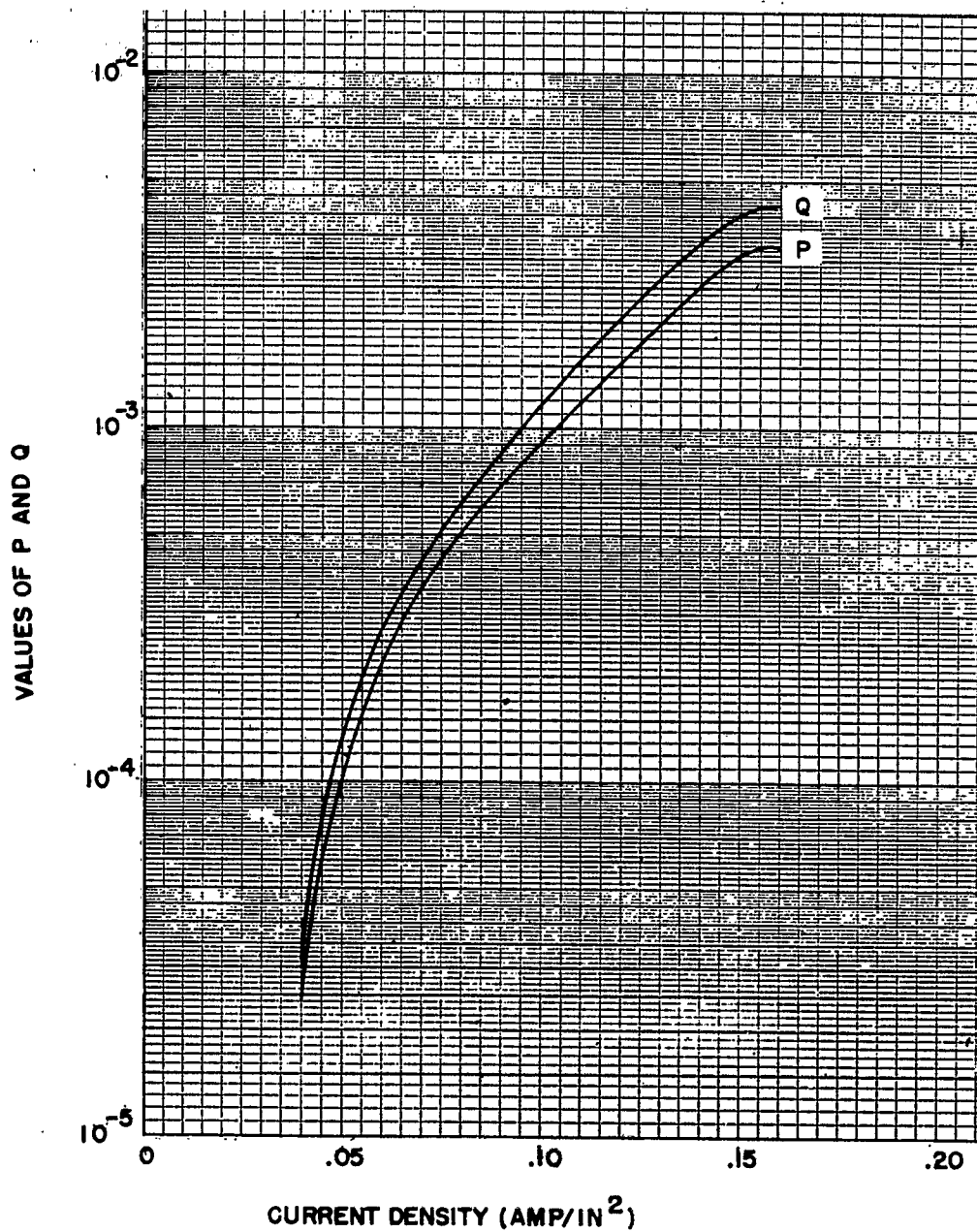


Figure 9 - Variation of P and Q with current density at -20°C



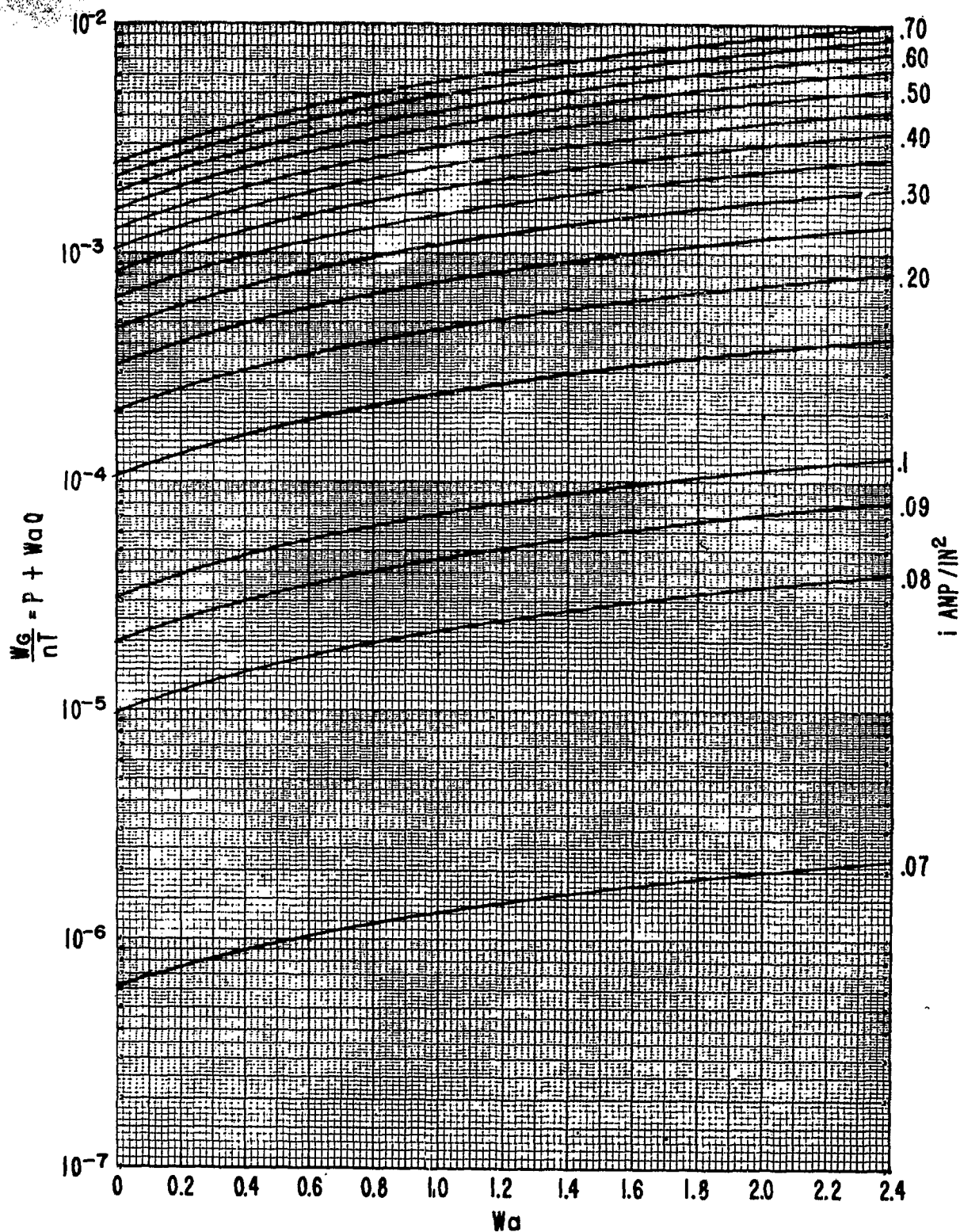
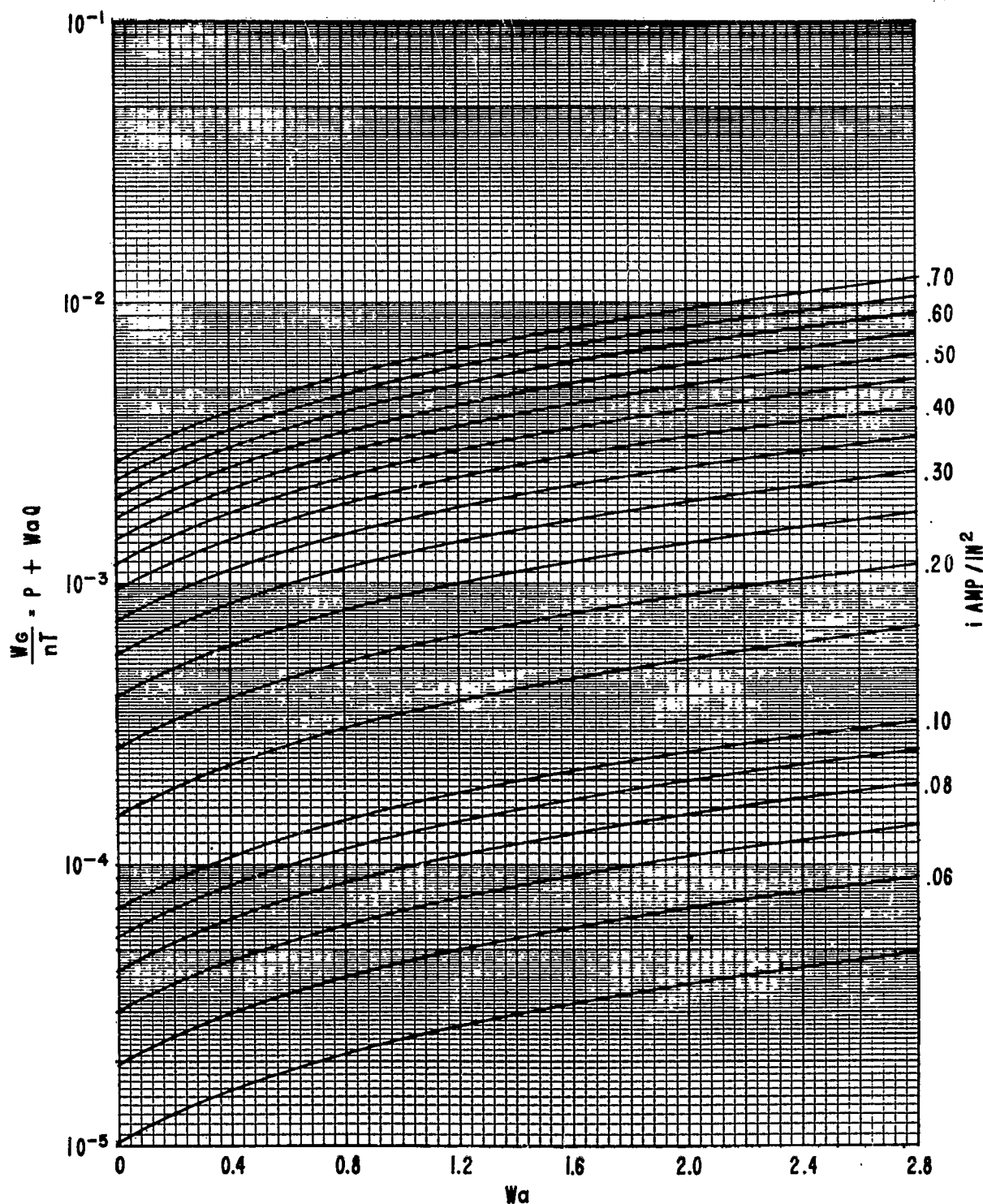


Figure 10 - Variation of  $P + W_a Q$  with  $W_a$  and  $i$  at 60°C

Figure 11 - Variation of  $P + W_a Q$  with  $W_a$  and  $i$  at 40°C



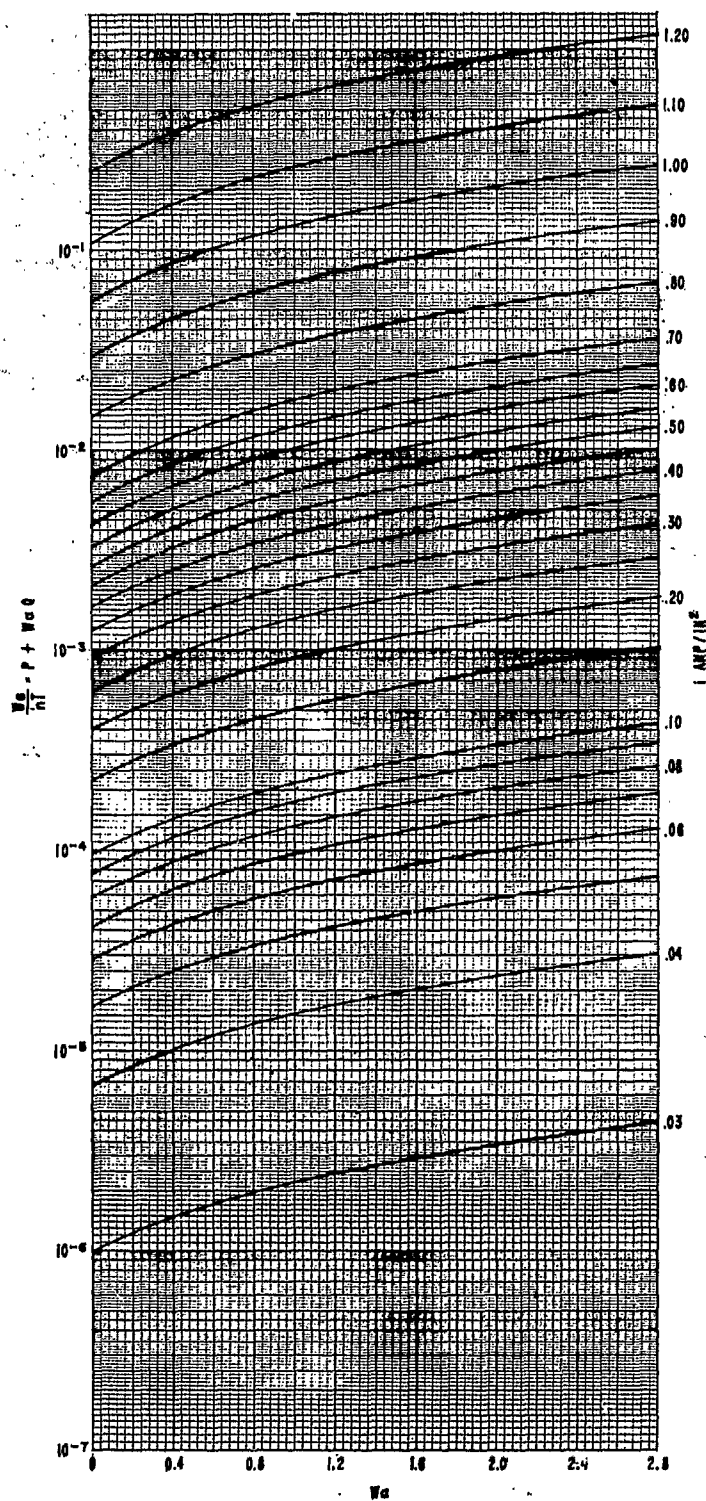


Figure 12 - Variation of  $P + W_a Q$  with  $W_a$  and  $i$  at  $20^\circ\text{C}$

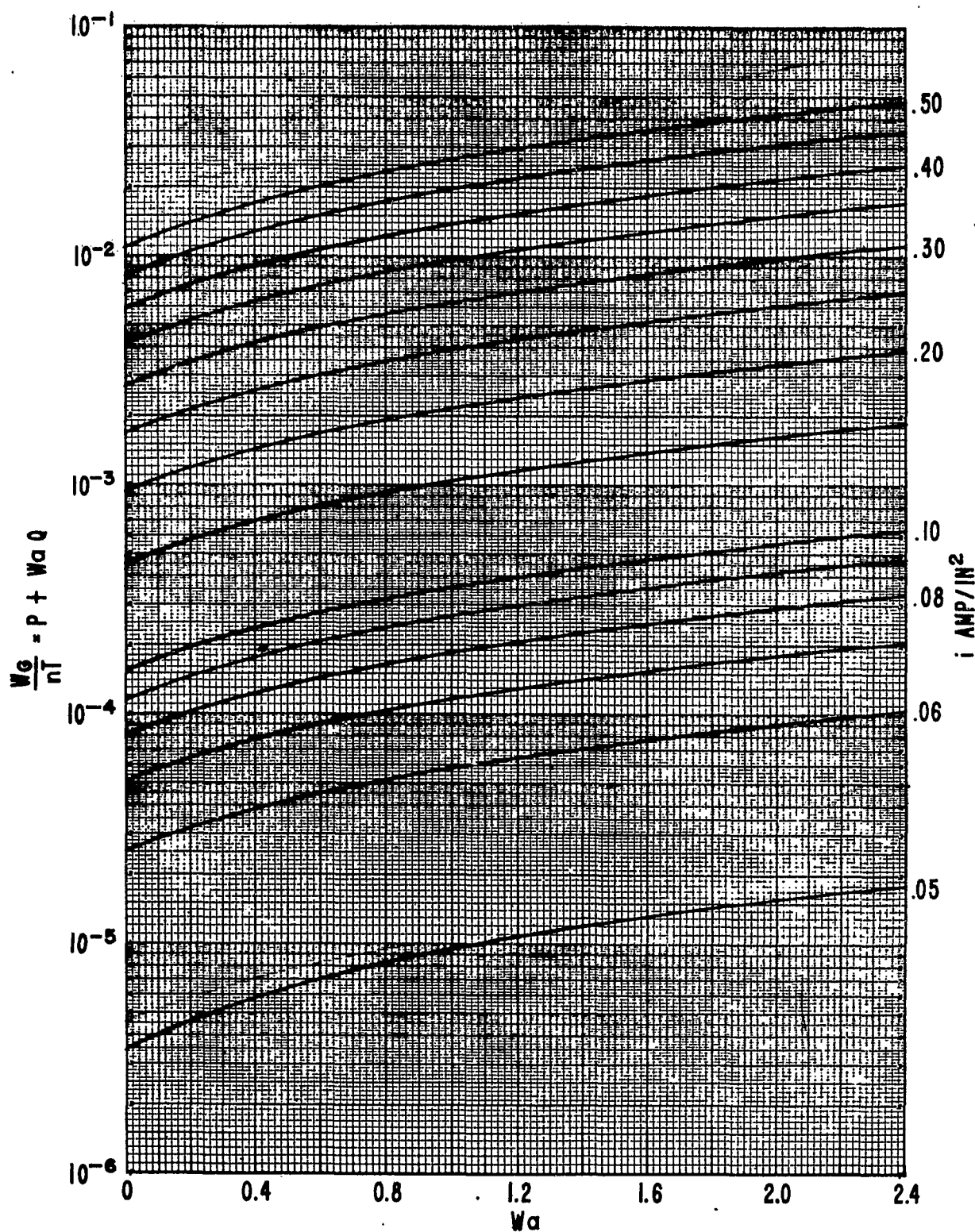


Figure 13 - Variation of  $P + W_a Q$  with  $W_a$  and  $i$  at  $0^\circ\text{C}$

RESTRICTED  
SECURITY INFORMATION

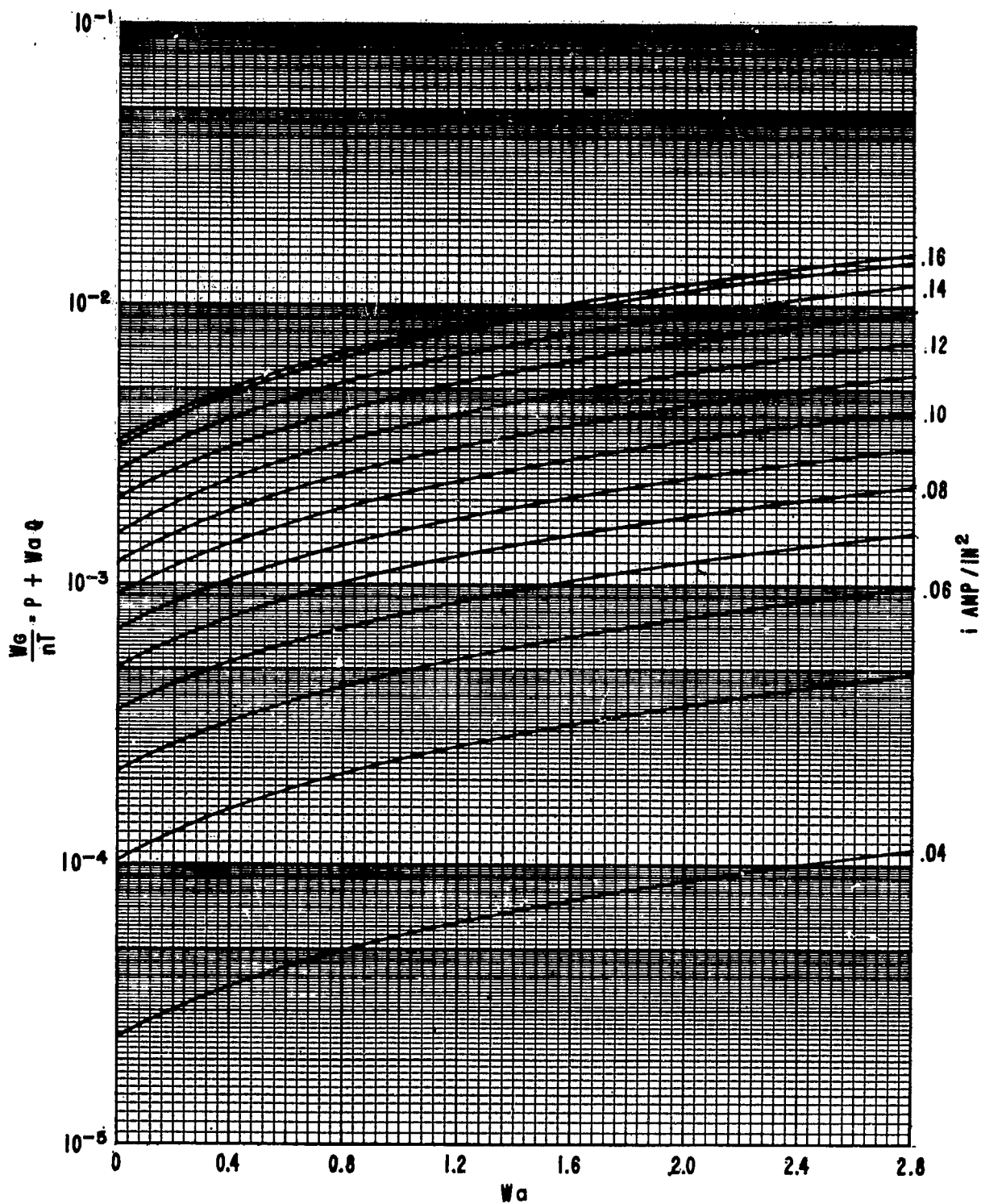


Figure 14 - Variation of  $P + W_a Q$  with  $W_a$  and  $i$  at  $-20^{\circ}\text{C}$

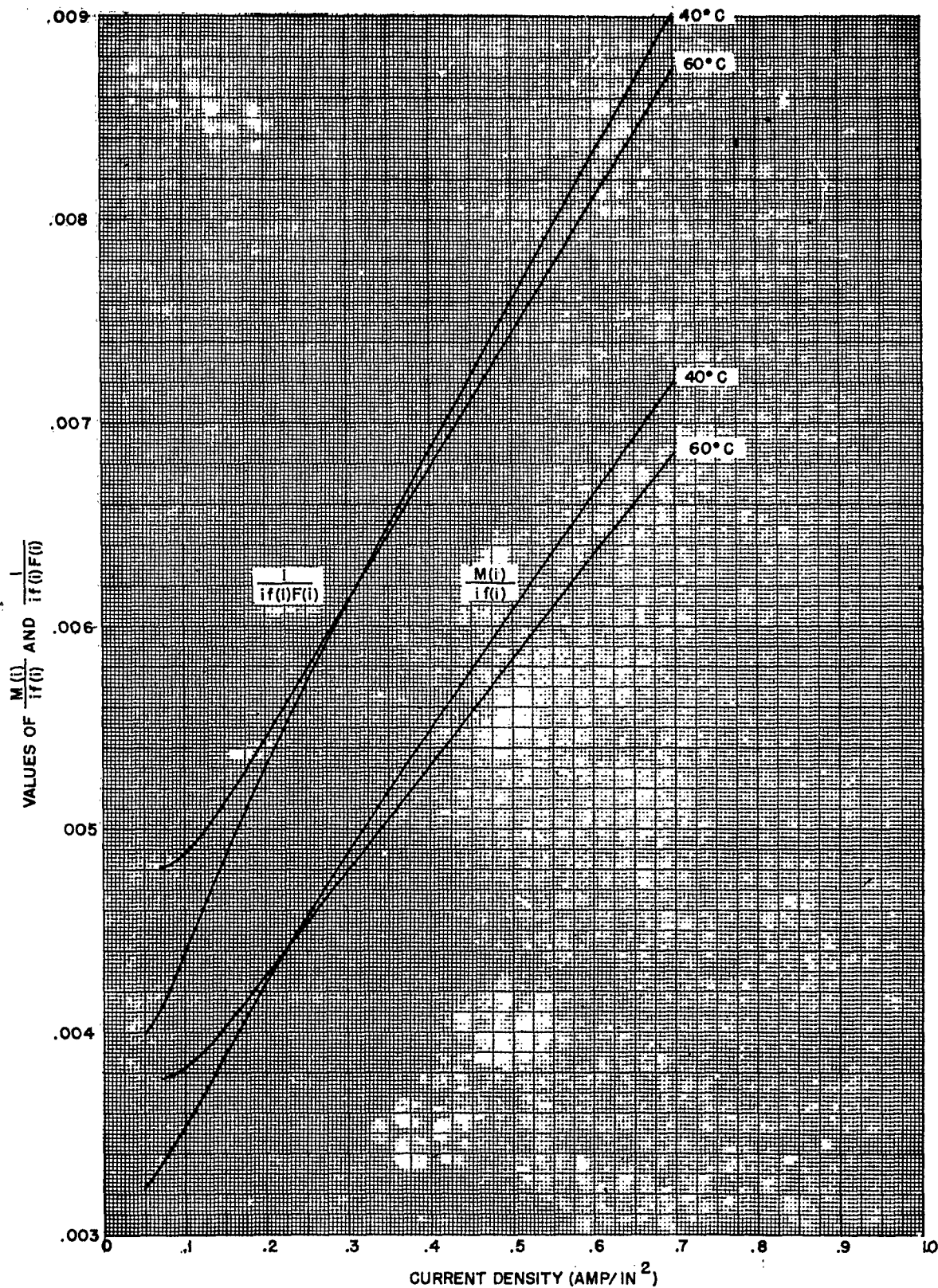


Figure 15 - Variation of  $M(i)/if(i)$  and  $1/if(i)F(i)$  with current density,  $i$

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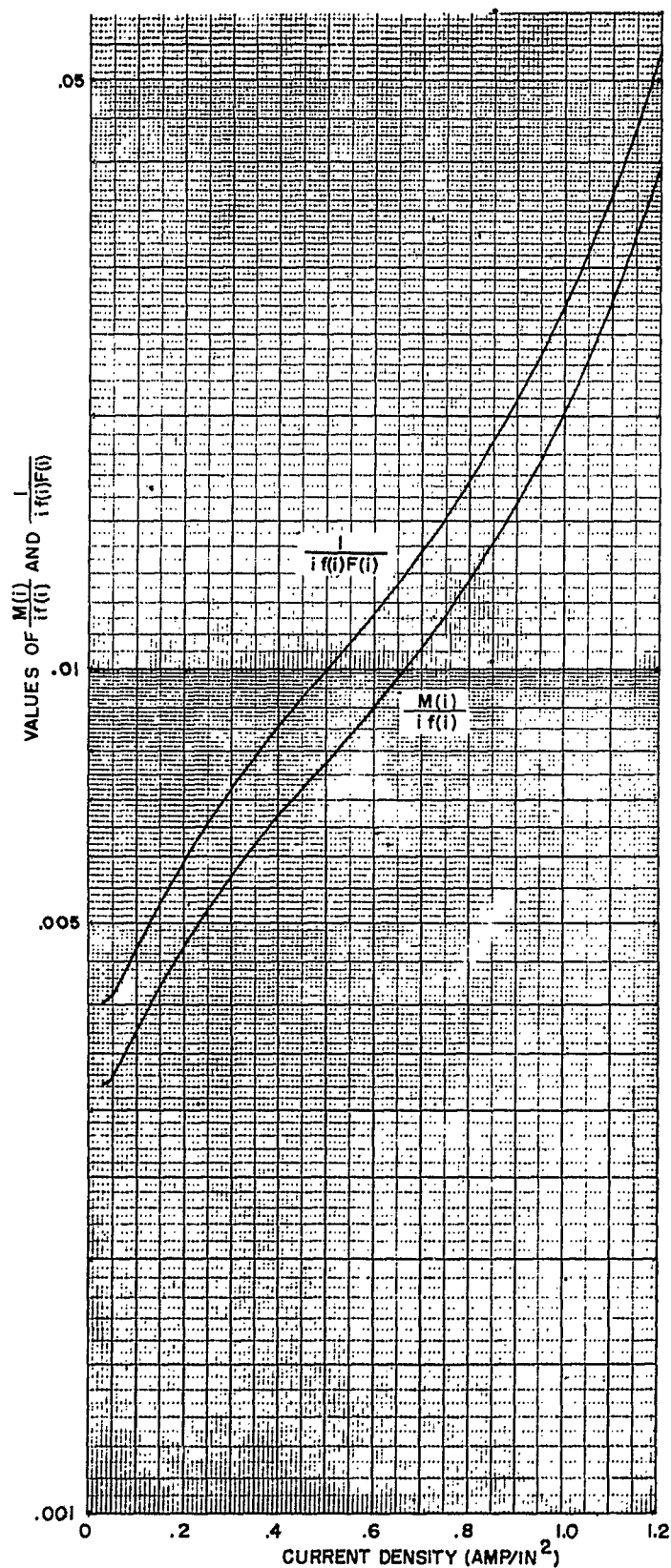


Figure 16 - Variation of  $M(i)/i f(i)$  and  $1/i f(i) F(i)$  with current density,  $i$ , at 20°C



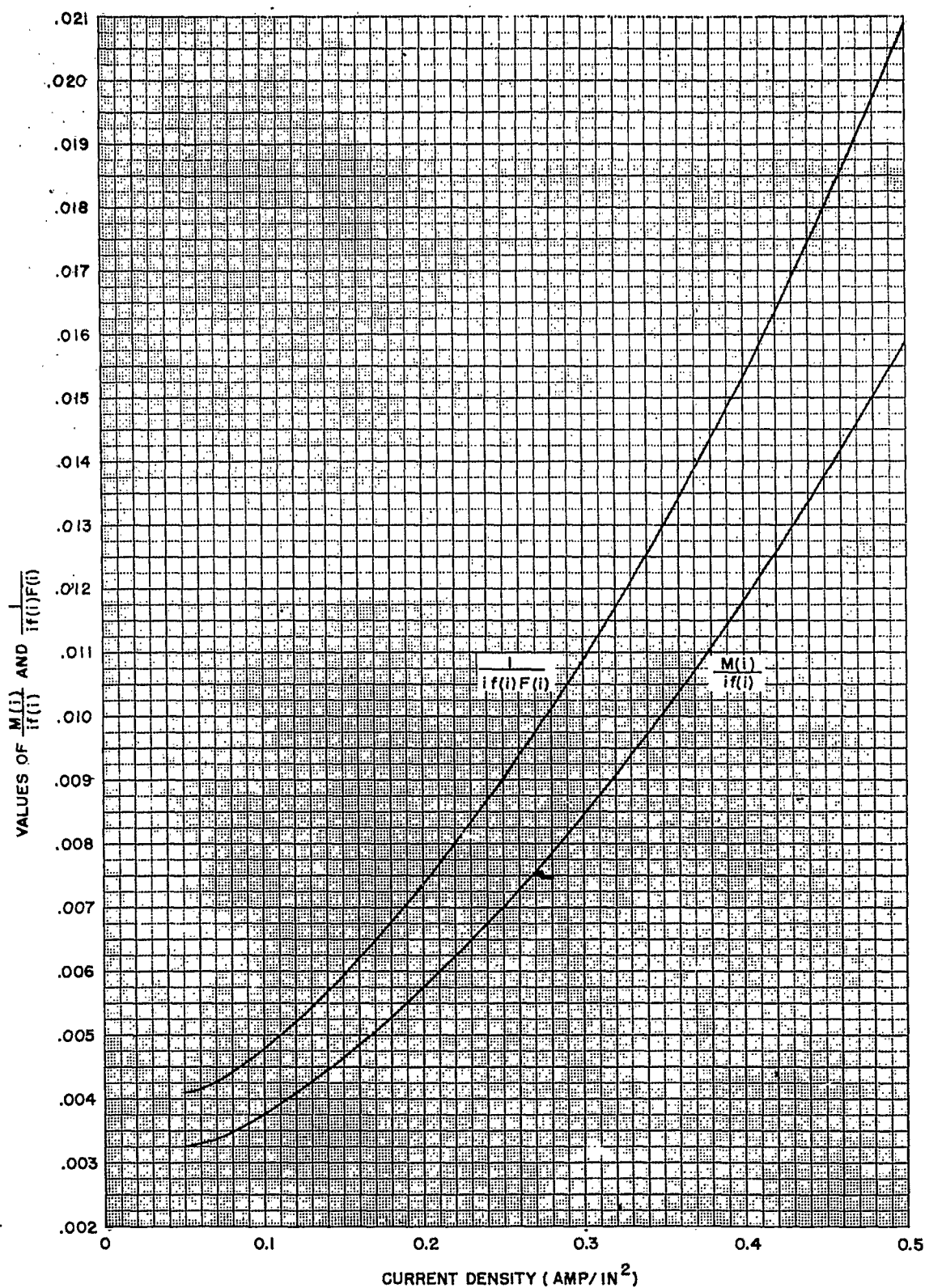


Figure 17 - Variation of  $M(i)/if(i)$  and  $1/if(i)F(i)$  with current density,  $i$ , at 0°C

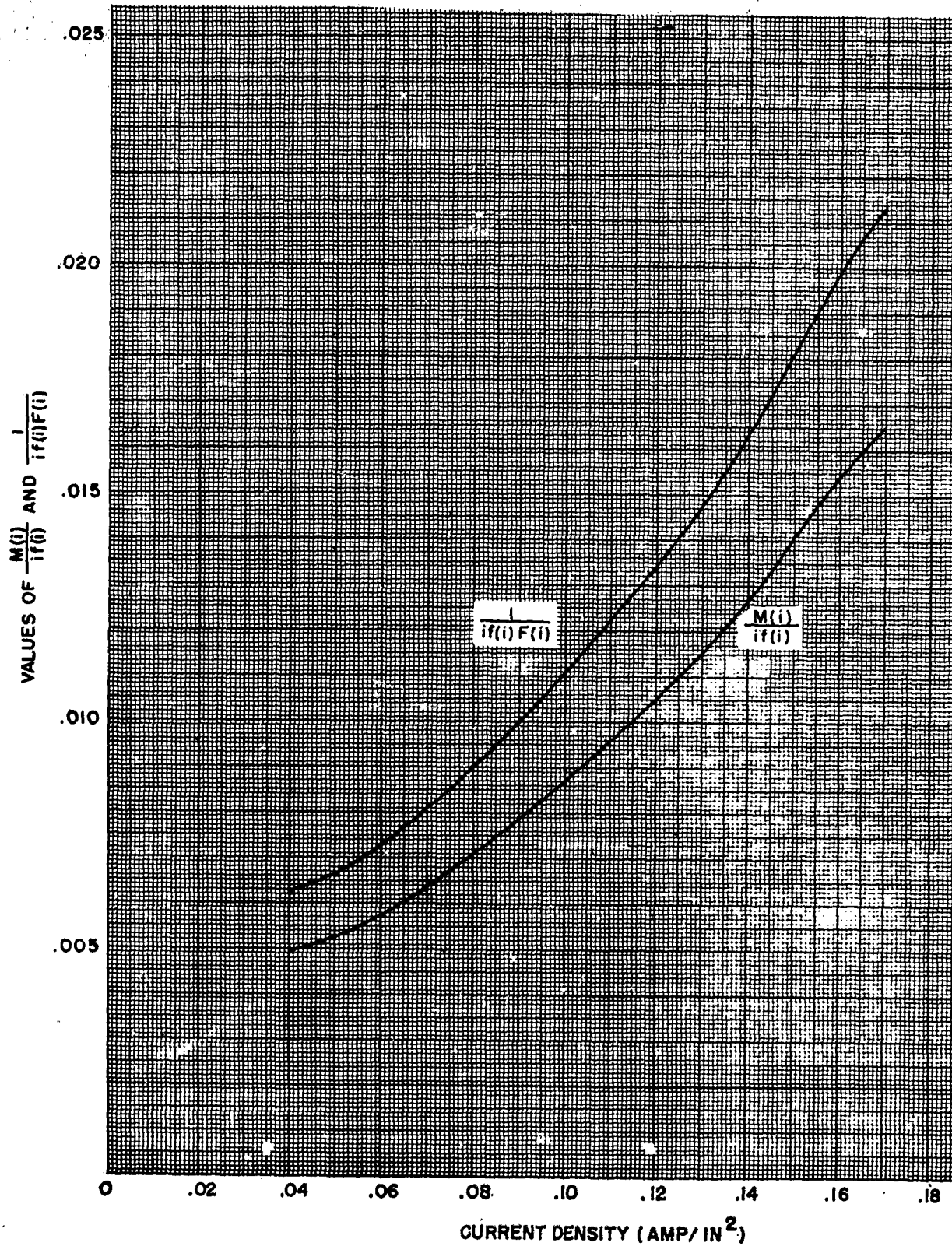


Figure 18 - Variation of  $M(i)/if(i)$  and  $1/if(i)F(i)$  with current density,  $i$ , at  $-20^{\circ}\text{C}$

A closely packed cell will be required in most cases where cell volume is minimized by use of Equation (33). The wide variation of design that is possible in the minimization of cell weight will not be obtained in such cases.

#### Maximization of Output

In many cases it is desirable to design a cell of given weight in which the discharge time for a given current is maximized or else the current for a given discharge time is maximized. In these cases it will be necessary to design a cell case and calculate its weight. When the weight of the cell case is added to the minimized cell weight obtained from Equations (20) and (27), there is obtained the minimum total weight of the cell having a given current,  $I$ , and discharge time,  $T$ . This minimum total cell weight can be calculated for a given current,  $I$ , and several values of discharge time,  $T$ . If these values are plotted, a curve is obtained showing minimum cell weight for varying values of discharge time,  $T$ , at a constant current,  $I$ . This may be restated by saying that the curve shows the maximum discharge time, obtainable for various cell weights at a given current,  $I$ . If a particular cell current and weight is given, the maximum discharge time can be obtained from this cell-weight curve.

Similarly, if the discharge time,  $T$ , is held at a constant value, and minimum weights are calculated for several values of current, a new curve will be obtained which shows the maximum discharge current obtainable for various cell weights at a particular time. If a particular time and cell weight is given, the maximum current can be obtained from the cell-weight curve.

Similar procedure is followed in designing a cell of given volume in which the discharge time for a given current is maximized or else the current for a given discharge time is maximized.

#### SAMPLE CALCULATIONS

##### Minimization of Volume

The volume is to be minimized for a cell producing 200 amperes for 5 minutes at 20°C and having a 60-mesh, 0.008-inch wire diameter, copper-screen positive grid. The negative plate is sheet zinc, 0.003-inch of which is taken as grid and must be remaining at the end of the discharge. The term  $n$  equals 2, since the area of both sides of a one-inch square sheet is 2 square inches. The effect of separators is neglected. The porosity of the spacers is 80 percent. Therefore  $V_a = (100 - 0.80)/0.80 = 0.25$ .

$F = \sqrt{1 + M^2 D^2}$  where  $M$  is mesh (2) and  $D$  is wire diameter. The volume of a one-inch square of the positive grid is

$$(\pi/2)D^2MF = (\pi/2)(.008)^2(60)1.11 = 0.006705 \text{ cubic inch.}$$

Then

$$V_G = 0.006705 + 0.003 = 0.009705.$$

$$Q = \frac{V_G}{(1 + V_a)nT} \quad (33)$$

$$= \frac{0.009705}{(1 + 0.25)(2)5} = 0.000776.$$



From Figure 7, when  $Q = 0.000776$ ,

$$i = 0.244 \text{ amp/sq in.},$$

and  $ni = 0.488 \text{ amp};$

therefore

$$N = \frac{I}{ni} = \frac{200}{0.488} = 410 \text{ unit cells in the desired construction.}$$

From Figure 16, at  $0.244 \text{ amp/sq in.},$

$$\frac{1}{i f(i) F(i)} = 0.00653$$

and

$$\frac{M(i)}{i f(i)} = 0.00515.$$

Then

$$\frac{T I}{i f(i) F(i)} = 6.53 \text{ cubic inches of electrolyte required for the cell, and}$$

$$T I \frac{M(i)}{i f(i)} = 5.15 \text{ oz of electrolyte.}$$

From Figure 3, at  $0.244 \text{ amp/sq in.},$  at  $20^\circ\text{C},$   $M(i) = 2.696.$  Therefore,  $100/M(i) = 100/2.696 = 37.1 \%$  KOH, the desired concentration of electrolyte. The emf at a current density of  $0.244 \text{ amp/sq in.}$  is found to be approximately  $1.45 \text{ volts}$  (Figure 19).

#### Minimization of Cell Weight

The weight is to be minimized for a battery operating at  $20^\circ\text{C}$  and producing  $100 \text{ amperes}$  at  $30 \text{ volts}$  for  $10 \text{ minutes.}$  The grids are  $60\text{-mesh } 0.008\text{-inch-diameter}$  copper wire screen. The negative grid is plated with zinc, two-thirds of which is utilized during the discharge. The silver oxide on the positive plate has a  $40 \text{ percent}$  porosity and is  $80 \text{ percent}$  utilized during discharge. The separator is one layer of  $0.005\text{-inch thick}$  paper,  $60 \text{ percent}$  porous and weighing  $0.0014 \text{ ounce per square inch.}$  The spacer has a value of  $f$  equal to  $0.8$  and  $W_{sp}$  equal to  $0.12.$  The weight of connectors,  $IW_y,$  is  $0.298 \text{ ounce.}$

$j = 0.6 (2) 0.005 = 0.006 \text{ cubic inch,}$  the volume of electrolyte absorbed in the separators in a unit cell.

$$W_a = \frac{W_{sp}}{f} = \frac{0.12}{0.8} = 0.15.$$

$$W_{aj} = 0.006 (0.15) = 0.0009 \text{ oz.}$$

$W_f = 2 (0.0014) = 0.0028 \text{ oz,}$  the weight of separator material in a unit cell.

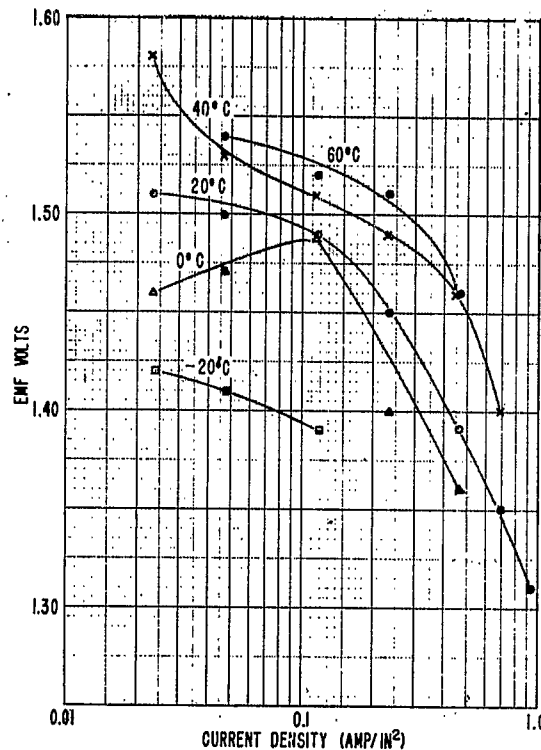


Figure 19 - Variation of emf with current density

$W_g = 2(\pi/2) D^2(MF) d$ , where  $d$  is the density of copper in ounce per cubic inch.

$$W_g = \pi (.008)^2 (60)(1.11) 16.4/28.35 (8.92)$$

= 0.06916 oz, the weight of grids in a unit cell.

$$W_G = W_g + W_f - W_{aj} = 0.0692 + 0.0028 - 0.0009 = 0.0711 \text{ ounce.}$$

Values have now been obtained for all the necessary factors in Equation (27) except  $n$ . Since  $n$  varies slightly with current density, it may be determined by the method of successive approximations. The term  $n$  is the number of square inches of negative electrode area in the unit cell at the end of a discharge. This area has been plotted in Figure 20 against quantity of current expressed as ampere minutes. The values on this curve were obtained by making the approximate assumption that two-thirds of the zinc plated on the grid is converted to current and that the remaining one-third was left evenly distributed over the grid at the end of the discharge.

Assume a value of  $n$  equal to 4. Then

$$P + W_a Q = \frac{W_G}{nT} = \frac{0.0711}{4(10)} = 0.00178.$$

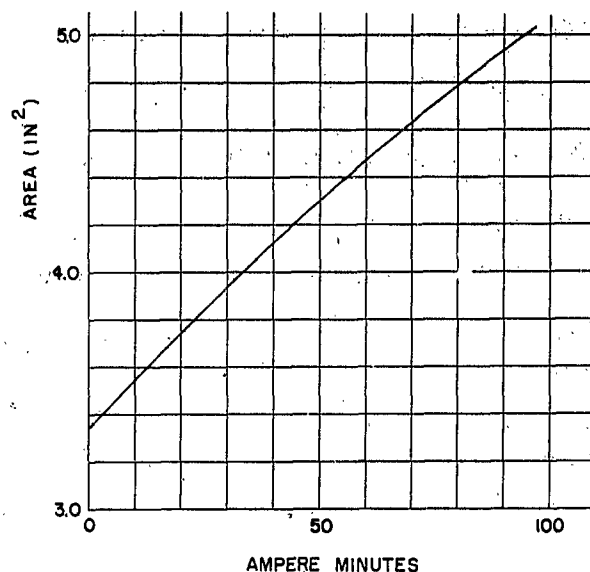


Figure 20 - Variation of final electrode area with capacity

From Figure 12,  $i = 0.37$  ampere per square inch for  $P + W_a Q = 0.00178$  when  $W_a = 0.15$ .

$ni = 1.48$  amperes current in a unit cell.

$1.48$  amperes (10 minutes) =  $14.8$  ampere minutes per unit cell.

From Figure 20 the value of  $n$  corresponding to  $14.8$  ampere minutes is  $3.65$  sq in. Since this value is considerably lower than the assumed value of  $n$ , the above calculations are repeated below on the basis of a new assumed value of  $3.65$  for  $n$ .

$$P + W_a Q = \frac{W_G}{nT} = \frac{0.0711}{10 (3.65)} = 0.001947.$$

$i = 0.40$  amperes per square inch from Figure 12.

$ni = 1.46$  amperes per unit cell.

$$N = \frac{I}{ni} = \frac{100}{1.46} = 68.5, \text{ the number of unit cells which are necessary.}$$

$1.46 (10) = 14.6$  ampere minutes per cell.

From Figure 20,  $n = 3.65$  square inch which is the same as the assumed value and is therefore correct. A check may be made from Figure 7 where  $P = 0.00162$  and  $Q = 0.0022$  for a value of  $i$  equal to  $0.40$  and  $P + W_a Q = 0.00162 + 0.15 (0.0022) = 0.00195$ , which corresponds to the above value of  $0.001947$ .

From Figure 18,  $1/i f(i) F(i) = 0.00856$  and  $M(i)/i F(i) = 0.0067$ .

$V_e = TI/i f(i) F(i) = 8.56$  cubic inch of electrolyte needed in the cell.

$W_e = TI M(i)/i f(i) = 6.70$  ounces, the weight of the electrolyte.

From Figure 4,  $F(i) = 0.2796$ .

$F(i)V_e = 2.39$  ounces of solid, 100 percent KOH needed to make up the electrolyte.

From Figure 3,  $M(i) = 2.796$ .

$100/M(i) = 35.8$  percent KOH the concentration of the electrolyte.

From Figure 1 the value of  $f(i)$  for a current density of 0.4 amp/in<sup>2</sup> is 1070. The amount of KOH present is 2.39 ounces, and the total negative electrode area ( $N_n$ ) is 68.5(3.65). The cell capacity should be  $1070 (2.39) / [(68.5)(3.65)] = 10.23$  minutes. The difference between this value and the original value of 10.0 minutes is due to errors made in adjusting curves to the data and in taking readings from these curves.

$W_Z = b TI/1396 = 3/2 \quad 100 (10)/1395 = 1.075$  ounces of zinc needed in the cell.

$W_c = 1.0/0.8 (TI/736) = 1.698$  ounces of AgO needed in the cell.

$(W_b + W_d)TI = 1.075 + 1.698 = 2.773$  ounces of active materials.

$\frac{1.698 (28.35)}{16.4 (7.44)} = 0.3945$  cubic inch of silver oxide in cell.

At 40 percent porosity,  $0.4/0.6 (0.3945) = 0.263$  cubic inch electrolyte absorbed in AgO.

The ampere minutes per unit cell is 14.6. Since only two-thirds is utilized, zinc equivalent to 21.9 ampere minutes is plated on each square inch of negative electrode. This amount of zinc gives an average wire diameter of 0.010 inch or an electrode thickness of 0.020 inch. The volume of 68.5 square inches, 0.02 inch thick is 1.37 cubic inches. The volume of wire present is  $68.5 (\pi/4) (0.001)^2 (2) (60) (1.11) = 0.717$  cubic inch.

$1.37 - 0.717 = 0.653$  cubic inch of electrolyte present in the interstices of the screen.

$V_n = 0.653 + 0.263 = 0.916$  cubic inch of electrolyte held in the electrodes.

$W_a V_n = 0.15 (0.916) = 0.137$ .

$K = (W_b + W_d)TI + IW_y - W_a V_n = 2.773 + 0.3 - 0.137 = 2.936$ .

$\widetilde{W} = W_G N + K + W_a TI/i f(i) F(i) + TI M(i)/i f(i)$

$= 68.5 (.0711) + 2.936 + (.15) 8.56 + 6.7$

$= 4.87 + 2.936 + 1.284 + 6.7 = 15.79$  ounces, the total weight of cell minus the weight of the cell case.

$V_m = N_j = 68.5 (0.006) = 0.411$  cubic inch of electrolyte absorbed in separators.

$V_e - V_m - V_n = 8.56 - 0.411 - 0.916 = 7.23$  cubic inches.

$7.23/68.5 = 0.105$  inch. This is equivalent to a distance of 0.052 between adjacent electrodes, not counting the separator. Adding in the separator, the distance between adjacent electrode faces is 0.057 inch.

The volume of the AgO plates equal the volume of the grids + volume of AgO + volume of absorbed electrolyte =  $68.5(0.006705) + 0.3945 + 0.263 = 1.116$  cubic inches.

$1.116/68.5 = 0.0163$  inch, the thickness of the AgO plate.

The thickness of the unit cell is obtained by adding the thicknesses of the individual components.

0.0163	thickness of AgO plate
0.020	thickness of zinc plate
0.01	thickness of separators
<u>0.105</u>	thickness of spacers
0.151	thickness of unit cell

In all, 68.5 of these unit cells are needed. If a space 3 inches wide and 4 inches high is available for the cell assembly, then 6 negative plates will have an area of 72 square inches, which will be slightly more than is necessary. In the actual construction, seven negative plates would be assembled with six positive plates, whereas the above calculations call for an equal number of positive and negative plates. This error could have been corrected for by increasing the value of  $W_g$  by one-twelfth and basing the above calculation on this new value of  $W_g$ . The effect of such a small change on the calculated results would not be large. The omission of minor factors in such a calculation will not materially affect the final result. On this basis, the data on separators could have been omitted from this example, thereby simplifying the calculations, without affecting appreciably the final cell design.

The emf obtained at 20°C and a current density of 0.40 is shown in Figure 19 to be approximately 1.40. If 30 volts were desired 22 of these cells would have to be connected in series.

It must be emphasized that the above calculation does not give the minimum weight for any cell that fulfills the stipulated specifications. It gives only the minimum weight of a cell using the above types of materials and construction. It will be necessary for the designer to make a new calculation for each choice of grids, electrodes, spacers, and separators, since variations in their characteristics cause variations in values of  $W_g$ ,  $W_a$ ,  $K$ ,  $n$ , and  $i$ . On the basis of these calculations, the designer can select the most effective combination of materials that will fulfill the stipulated requirements. Factors which decrease grid weight or increase electrode area, thereby decreasing  $W_g$  or increasing  $n$ , will be found to have the greatest effect in decreasing the cell weight.

If a curve of cell weight,  $W$ , versus actual current density,  $i$ , is calculated and plotted, for a given specification the variation of  $W$  with  $i$  is generally found to be very small in the region of minimum cell weight. Consequently, a crude approximation of  $i$  will give a very close approximation of the conditions necessary for minimizing cell weight.

#### LIMITATIONS AND SOURCES OF ERROR

This method of battery design will give fairly accurate results over a wide range of working conditions. Since it is not practical to evaluate all the factors that could enter into the construction of a cell, it is possible for errors to be introduced when the described

technique of cell design is used. Results obtained by such calculations must not be accepted as absolute until they have been verified by construction and physical evaluation of the particular cell.

The main sources of variation will be found in the following factors:

1. Accuracy of data
2. Extrapolation
3. Assumption in calculations
4. Assigning values to variables
5. Adaptation of results to working conditions.
6. New variables
7. Manufacture and design.

#### Accuracy of Data

An appreciable variation in results is obtained whenever an attempt is made to duplicate a particular discharge by constructing an equivalent cell and discharging it under the same working conditions. The standard deviation of the discharge time was found to be approximately five percent, which indicates a variation of more than ten percent from the average in about every tenth trial (Reference 1). A larger standard deviation could be expected under adverse conditions such as low temperature or very high current density. In actual cell construction the presence of other factors can cause a variation in the above values of the standard deviation.

At low temperatures and current densities a large variation in cell capacity is obtained for repeated runs at a particular set of conditions (Reference 1). The low limits of these results were used in making all further calculations. If such conditions are encountered in actual practice, a large percentage of the capacities obtained will be considerably higher than the predicted values.

If high current-densities are used at low temperatures, a marked reduction in the cell voltage is sometimes encountered for a short time at the beginning of the discharge. The emf rapidly climbs up to its normal value, generally in less than a minute. In general, the emf is practically constant over the major portion of the discharge (Reference 1). If a recharged positive electrode is used, the cell may have a considerably higher voltage for a short period at the beginning of the discharge (Reference 1). The emf at the time the cell is two-thirds discharged was found to be essentially equivalent to the average discharge voltage, and was considered to be the representative voltage of the cell.

Approximate values of this average cell voltage for various temperatures and current densities have been plotted in Figure 19. Because of the IR drop due to internal resistance, cell voltage will vary with change in electrode spacing. Cells utilizing closely spaced electrodes will generally have higher emf's than shown in Figure 19, particularly at high current densities.

### Extrapolation

Any extension of calculated relationships beyond the area in which the data was observed can be subject to considerable error. Most of the data for the silver cell were taken with electrolyte volumes of 0.2 to 0.05 cubic inch per square inch of actual electrode area, which correspond to electrode spacings of about 0.1 inch down to as low as 0.015 inch. Within these limits the cell capacity was found to be directly proportional to the electrolyte volume. Therefore, a straight line drawn through the data for a particular set of conditions, will pass through the origin, which is the point of zero electrolyte volume and zero capacity. Although very little data is available in the small region between zero and 0.05 cubic inch of electrolyte per square inch of electrode area, it is fairly safe to assume that this relationship would still be true. Theoretically a closely packed cell, using this small volume of electrolyte and having a porous negative electrode such as an electropolated wire screen, might have a slightly higher capacity than would be calculated from this relationship.

The top curves in Figures 10 to 14 represent the highest current densities for which data were available. The bottom curves represent approximately the lowest current densities at which it is feasible to operate.

A small amount of extrapolation was necessary in obtaining all the values of  $M(i)$  and  $F(i)$  needed in calculating values of  $P$  and  $Q$ . A theoretical relationship exists between  $M(i)$  and  $F(i)$  since they are both calculated from the concentration of electrolyte that gives maximum capacity at a particular temperature and current density. Because the curves in Figures 1 and 2 are approximations, a small variation may exist at a particular point between the observed values on the two curves and their theoretical relationships. This difference is negligible within the limits shown on the graphs. If extrapolation is necessary, it would probably be advisable to extrapolate  $F(i)$  and use the information obtained to calculate the necessary values of  $M(i)$ . In general very little extrapolation was used in the analysis and presentation of the enclosed data. However, in utilizing this information, it is possible for the calculations to enter a region not covered by the original data. Considerable caution should be taken in using the results of such calculations.

### Assumptions in Calculations

Some variation was introduced by fitting algebraic equations and curves to the original data. In no case is this error appreciable. The largest variation of this type will be found in the curves for  $M(i)$  and  $F(i)$  given in Figures 3 and 4.

The assumptions involved in deriving Equations (27) and (33) have already been discussed. The derivation of these equations was based on the assumption that certain factors such as  $W_g$ ,  $n$ , and  $G_w(ni)$  were constant, when actually under certain conditions they vary slightly with change in  $i$ . The error introduced by these assumptions will be fairly small and can be minimized by assigning values to the factors and making the calculations — if necessary, assigning new values to the factors and repeating the calculations until the final results are in accord with the assigned values. If this method is used, the error will be negligible since the variation of the various factors with change in  $i$  is small.

### Assigning Values to Variables

Values of  $W_b$  and  $W_d$  have not been thoroughly evaluated over an adequate range of working conditions. Until this evaluation is made it will be necessary to assign them arbitrary values. Fortunately, variation in their values has no effect on the calculated values of  $i$  and  $N$  although they do affect the final weight of the cell.

Values assigned to such factors as grid weight, type of grid, and factors involving separators and spacers, will depend upon the choice of available materials and the judgement of the designer. Each new set of factors will give a new cell design when substituted in Equations (27) or (33).

Values of these factors must be measured directly or else calculated from other measurements. As a rule these determinations will be simple and fairly accurate but occasionally they will require ingenious techniques to keep out errors. The biggest difficulty may be encountered in determining the area of the zinc electrode at the end of the discharge. Fortunately, small variations in the values of these factors will not cause any appreciable variation in the final cell design. In most cases the effect of separators can be neglected, thus making  $W_G$  equal to  $W_g$ , the weight of grids in an unit cell.

#### Adaptation of Results to Working Conditions

The results obtained from calculations based on Equations (27) and (33) must be adapted to available materials and to the working conditions. The calculated electrode area may have to be varied so that the available cell space may be most effectively utilized. Electrode spacing may be changed so that available thickness of spacers can be used. If the calculated electrolyte volume should be insufficient to cover the electrodes, or if the calculated electrode spacing should be too small, practical adjustments should be made. The necessary adjustments of this type are, as a rule, fairly small and their effect on cell characteristics can be readily calculated.

#### New Variables

The factors we have discussed so far introduce a variation that is generally small and in these cases can be evaluated by further calculations. The major source of deviation from the calculated results will be caused by the introduction of new variables in the design and construction of the cell. It is not feasible nor is it necessary to evaluate all of these factors. Incomplete information is available on some of the factors, some will be investigated further, and some will be neglected completely until they are encountered in a particular cell design.

The choice and assembly of spacers and separators can cause cell capacity to vary from 0 to 100 percent of the calculated value. The data, used as a basis for determining the general cell characteristics, were taken from a cell using open spacers which would not affect capacity. The available information indicates that a careful selection of spacers and separators will give a capacity very close to the calculated value.

A limited amount of data is available on the preparation and the efficiencies of the silver oxide electrode. There is a wide range of conditions that are satisfactory for the preparation of this plate. Within these limits, the method of preparation does not affect cell capacity although it does affect appreciably the efficiency of utilization of the silver oxide (Reference 1).

More data should be obtained on the various types of zinc electrodes. If the area of the negative electrode can be visibly observed and calculated, then the data for a sheet zinc electrode can be utilized according to the methods outlined in this report to predict the approximate cell characteristics. Since variable factors which have not been evaluated are present in the various types of this electrode, deviations will be obtained from the calculated characteristics (Reference 2). Although these deviations are appreciable in a few cases, they are not large enough to invalidate the results obtained by the outlined methods. If the surface area of the zinc electrode is not readily measurable, and if this area is not readily available to an



appreciable amount of electrolyte, the capacity can not be calculated at present by the enclosed methods. An electrode of this type has been prepared by pasting powdered zinc on a grid (Reference 2). The available data on this electrode is not sufficient to make possible a prediction of cell capacity. The heavy shedding of the pasted zinc electrode is a serious drawback to its general use.

More information is needed on the stand life of the silver oxide cell. After the electrolyte is added, the capacity of the cell decreases slowly. The type of separator used can greatly affect this rate of self-discharge. A separator that is satisfactory if the cell is to be discharged immediately may be unsatisfactory if the cell must stand for a period of time after the electrolyte has been added.

The silver oxide electrode loses much of its capacity if it stands for a long period of time in the open air. A preliminary test indicates that the deterioration is due to the formation of silver carbonate and can be overcome by having an airtight cell case or by sealing the cell in an airtight container.

If potassium hydroxide solution is exposed to the air it will absorb carbon dioxide and form potassium carbonate solution, which is not effective as an electrolyte. Therefore, the electrolyte must also be stored in an airtight container. The calculations in this report are based on an electrolyte consisting of pure potassium hydroxide solution. In actual practice there was a small amount of potassium carbonate present even though C. P. potassium hydroxide was used in preparing the solution. The electrolyte was analyzed for potassium hydroxide content and the small quantity of potassium carbonate present was ignored in all further calculations.

The metals from which the grids are prepared can affect cell characteristics. If a non-conducting oxide is formed on the grid, the resultant IR drop may be appreciable and it is possible that the contact with the active material will be so poor that the cell capacity will be diminished. This effect will be more pronounced at high current-densities particularly when the oxide film has a low porosity. If the grid material is soluble, it may act as a poison and decrease cell capacity. The grid materials used in obtaining the laboratory data were zinc and zinc-plated copper for the negative, and silver and silver-plated copper for the positive. If a plated copper grid is used, care must be taken to be sure that all the copper is completely covered.

If the cell case is too large or if the electrolyte level is too high, a portion of the electrolyte will not fall between the electrode faces. Limited data shows that an appreciable portion of the electrolyte may lie between the electrode assembly and the cell case or above the top of the electrodes without changing the predicted cell capacity under ordinary conditions. However, under extreme conditions, cell capacity would probably be materially reduced. Careful construction and assembly will minimize this factor, and make it have no significant effect.

The use of addition agents in the positive active material, the negative active material, and the electrolyte is another promising field in which little work has been done.

The data on which this report is based was taken from cells which were discharged at a constant current. The emf of the cell is virtually constant throughout nearly all of the discharge. As a consequence, the current will be nearly constant, whenever the cell is discharged through a constant resistance. Most of the demands for the cell will be of this nature. Whenever the discharge is intermittent, or, whenever the cell current varies appreciably, it becomes difficult to predict the cell capacity with accuracy. If the current is not varying too rapidly at the end of this type of discharge, the cell capacity can be estimated roughly from the final current at the time of cell failure by assuming the total ampere

minutes actually obtained would be equal to the total ampere minutes that would have been obtained if the cell had been discharged at a constant current equal to the final current. This method can also be used whenever the cell construction is such that the emf, and consequently the current, decline appreciably throughout the discharge. It is not likely that this condition will appear very often in practical cell design.

The value of the current density at a particular point on the zinc electrode is determined mainly by the position of that point on the electrode, the length of time the battery has been discharging, and the total current that is flowing through a given area. The value of the current density,  $i$ , used in this report is the average current density taken over the entire face of the electrode. The basic data were taken from cells having open spacing and using sheet zinc negative electrodes 1.5 inches high. In this type of construction, zinc dissolves during discharge, forming a heavy layer of electrolyte which flows down the face of the electrode resulting in a heavy concentration of zinc in the electrolyte at the bottom of the cell.\* In a closely packed cell, separators placed against the negative electrode face would interfere with this type of electrolyte circulation.

Factors such as these indicate that there can be considerable variation in the distribution of the current density over the face of the electrode for a particular average current density. Although variations of this type might be expected to affect cell capacity, the limited data available indicates that this effect is negligible. However, such variation in current density on the electrode face is undesirable because it causes uneven dissolution of zinc. Since the current density is much higher at the top of the zinc electrode during discharge than it is at the bottom, cell capacity might be affected by variation in electrode height. Actual measurements made under various conditions of temperature, current density, and electrolyte volume and concentration showed that no significant change in cell characteristics was obtained when the electrode height was varied from 0.75 to 4.5 inches (Reference 1). It is possible, however, that a significant change might be obtained with a much deeper electrode.

Another factor, whose importance is emphasized by deep electrodes, particularly at high current densities, is the resistance of the plate. A high plate resistance may cause an excessive drop in the cell emf and may also generate internal heat, which is often undesirable. The controllable part of the plate resistance lies in the grid. Since the current density is higher at the top of the plate and since all of the current as a rule flows through the top of the plate, a uniform grid that would be large enough to handle this current without excessive IR drop, would be much larger than is needed at the bottom of the plate. This factor could be remedied by tapering the grid in some suitable manner.

The IR drop from the bottom to the top of the grid is one of several factors that cause the potential between adjacent positive and negative plates at the top of the cell to be larger than it is at the bottom of the cell. If this IR drop is sufficiently large, the resultant variation in potential will cause an increase in the current density at the top of the electrode and a decrease at the bottom of the electrode. Although the resistance of the grid can contribute in this manner to the variation in current density over the face of the electrode, it is not believed to be the major cause of such variation.

There are a number of these factors that have not been thoroughly evaluated. In general, their effect on cell capacity should not be large, but there can be no certainty of this in many cases until they are tested either in the laboratory or by actual construction. Since the manufacture of a practical cell is apt to introduce some of these factors, the possibility is present

\* This problem will be discussed in a future NRL report.

of obtaining an appreciable deviation from the calculated cell characteristics. In many of these cases it should not be difficult to determine the factor that is causing the deviation and to make any corrections that might be necessary.

### Design and Manufacture

For various reasons which have been and will be discussed, a cell constructed on the basis of the foregoing calculations may have characteristics which vary considerably from the calculated values. The major variation obtained will be in cell capacity. For this reason, the manufacturer and designer are faced with the problem of maximizing the output from any particular cell by making further changes. This procedure will be outlined briefly.

The resultant cell should have characteristics which show a moderate agreement with the previously calculated values. If the variation between the predicted and the measured results is appreciable, then a new design may be necessary, or else it may be feasible to change the size of the cell. This change may be accomplished by varying  $N$ , the number of unit cells present, by some definite percentage, which is equivalent to varying the electrode areas and the weight of each cell component by that same percentage. For example an increase of ten percent in the size of a cell having a capacity of ninety minutes will increase the capacity to slightly over ninety-nine minutes under the same operating conditions. In any case, the final result will be a cell in which numerous changes in design were introduced after the calculations had been made for the minimization of weight or volume. Such a cell will not be the cell of minimum weight or volume for the given operating conditions. However, no change will have been made in the unit grid weight or volume ( $W_g$  or  $V_g$ ), which is the main factor in the minimization calculations. The only factor that would be apt to cause an appreciable deviation from the conditions of minimization is the current density,  $i$ . Under most operating conditions the variation of cell weight or volume with current density is fairly small in the region of minimization. As a consequence, appreciable changes can be made in the cell design after the final minimization calculations without causing much departure from minimization conditions. If the changes are small the resultant cell is essentially the cell of minimum weight or volume.

Many of the problems facing the designer have already been discussed. The information given in this report should be considered as an aid, not as a substitute for the judgment and abilities of the designer and manufacturer. There are many possible cell designs based on various types of materials and construction of cell components. It will be up to the judgment of the designer, based on his knowledge and on such calculations as are given here, to decide which is the best. It will then be necessary to construct a cell based on this design and to determine its characteristics.

Because of the cost, it is not feasible at this point to construct the complete cell. An open container of the same size and shape as the cell case can be used for assembling the cell components and testing the design. The components are assembled and the electrolyte volume is adjusted, if necessary, to bring the level of the liquid just above the top of the electrodes. The capacity is determined by discharging at the desired working conditions. If a reference electrode is inserted in the setup, it will be possible to tell which electrode fails first and thus to determine whether sufficient active material is present.

It already has been shown that the presence of a new factor may cause the capacity of a cell to vary appreciably from the calculated value. It is possible that an increase in capacity may be obtained but it is more probable that a decrease will be observed. If this decrease is appreciable, the separators and spacers should be studied since they are the most likely cause of a drop in cell capacity from the calculated value. They will also have considerable effect on the shelf life of the cell after the electrolyte has been added.

Cell capacity is proportional to electrolyte concentration, and there is reason to suspect that the most effective concentration may vary somewhat from the predicted value under certain conditions, such as close packing of the cell components. Therefore, it is advisable to test the cell at several concentrations of electrolyte in the neighborhood of the predicted value to determine which is the most effective.

It is assumed that these tests have been made in the presence of a sufficient amount of active material. The available information is not sufficient to predict accurately the minimum amounts of zinc and silver oxide needed for a given cell. A few tests at this point will enable the manufacturer to minimize the amounts of active materials. In all observed cases, the negative electrode fails first if there is sufficient silver oxide present. A reference electrode measurement will indicate whether this is occurring. Actual tests along with examination of the discharged negative electrode will indicate whether further reduction in the amount of zinc can be made. The amount of silver oxide may be minimized by varying the quantity present until the electrode fails at approximately the same time as the zinc electrode fails. The three factors, zinc, silver oxide, and potassium hydroxide solution, are now balanced in such a manner that they all fail at approximately the same time.

Some variation in results may be experienced at first because of faulty techniques in constructing and assembling cell components. This difficulty is easily overcome with a little practice. However, in all of this work duplicate runs should be made, and more if necessary, to insure the validity of a particular result.

At this point it will be known if the particular cell design will give the desired results. It will now be possible to design the cell case and to calculate the total cell weight and size. If the cell does not now meet all the desired specifications, it will be necessary to try new designs. In the end, it may be necessary to sacrifice on certain factors and it may even become necessary to adapt the specifications to fit the limitations of the cell.

The complete cell is then constructed and thoroughly tested, if possible, under all working conditions. The cell case should remain airtight and leakproof when subjected to normal use and abuse. Since the stand life is poor once the electrolyte has been added, it will be necessary to add the electrolyte shortly before the beginning of the discharge. In many cases this problem will be handled by storing the electrolyte in a separate portion of the cell case and using a breaker mechanism to drop the electrolyte into the cell. Such a mechanism should be very thoroughly tested. In a closely packed cell it may be necessary to use a wetting agent to speed up the addition of the electrolyte.

If the cell is being manufactured in quantity, it may be advisable to institute a system of quality control. The techniques of quality control are well-known, are easily applied, and generally result in a decreased number of rejects, an increased quality of product, and a decrease in the cost of manufacture. If the cell can be brought under statistical control a number of discharges should be made to determine the standard deviation since these will tell how much variation to expect and thus make possible a computation of the necessary safety factors.

It has been pointed out that some of the data on which Equations (20) and (28) are based is incomplete. Further information, particularly on factors  $W_b$  and  $W_d$ , would be of value. The resulting data could make possible a considerable saving in the work necessary to construct a particular cell but would give very little increase in the accuracy of the design.

The development of this technique of cell design was made much easier by the simple relationship existing between cell capacity and the volume and concentration of electrolyte. Obviously, this method of cell design can be applied to other types of cells. The amount of

data required, the analysis of the data, and the methods of presentation will depend on the number of variables involved and on the complexity of their relationship. In some cases it might be desirable to maximize or minimize more than one characteristic. For example, it might be desirable in a storage battery to maximize some function of cell capacity and cell life for a given set of working conditions. Theoretically, under certain conditions of mass production, it would be possible to minimize unit costs by a similar analysis. In any case, the labor involved would be large, and the cost of the program could be justified only by the desirability of the results.

## CONCLUSIONS

The demands for the silver oxide - zinc alkaline cell are highly specialized, and in most cases it is desirable to minimize cell weight or cell volume or to maximize output for a given cell weight or volume. The theoretical development presented for making these computations is also applicable in cases where minimization of size or weight is not necessary. Presentation of the data in a graphical manner greatly simplifies all the necessary calculations for a given cell design.

The minimization of cell weight,  $W$ , for a given set of conditions depends upon the determination of that value of the actual current density,  $i$ , for which  $dW/d(i)$  equals zero. The variation of cell weight,  $W$ , with actual current density,  $i$ , in this region is small. As a result, errors introduced by this method in the design of a particular cell will tend more to cause a deviation from the predicted capacity than they will to cause a deviation from the conditions which minimize cell weight.

\* \* \*

## REFERENCES

1. Shepherd, C. M., "The silver oxide - zinc alkaline primary cell, Part I," NRL Report No. C-3478 (Unclassified), July 1, 1949
2. Shepherd, C. M., "The silver oxide - zinc alkaline primary cell, Part II, NRL Report No. 3876 (Restricted), December 20, 1951

\* \* \*

## GLOSSARY

All weights are given in ounces, volumes in cubic inches, time in minutes, current in amperes, current density in amperes per square inch, and area in square inches unless otherwise indicated. In general, only those symbols used regularly are included; symbols used for temporary convenience are not included.

- D Density of the most effective concentration of electrolyte in ounces per cubic inch.
- f(i) Cell capacity in minutes per ounce of KOH per square inch of actual negative electrode area.
- F(i) The most effective concentration in ounces of solid 100 percent KOH per cubic inch of solution at the given temperature.
- i Actual current density on the negative electrode.
- I Total discharge current.
- j Volume of electrolyte absorbed in the separators in a unit cell.
- K Cell capacity in minutes per gram of KOH per square inch of actual negative electrode area.
- M(i) 100 ÷ percent concentration of the most effective KOH solution at the given temperature.
- n Total area of unit negative electrode at the end of the discharge.
- N Number of unit cells necessary.
- P A function of i defined by (25).
- Q A function of i defined by (26).
- T Discharge time.
- $v_e$  Volume of electrolyte per square inch of actual negative electrode area.
- $V_e$  Total volume of electrolyte used in cell in cubic inches.
- $V_m$  Volume of electrolyte absorbed in separators.
- $V_n$  Volume of electrolyte absorbed in electrodes at the beginning of the discharge.
- $W_a$  Constant dependent upon the type of spacer.
- $W_b$  Weight of zinc necessary for each ampere minute of discharge.

- $W_c$  Total weight of silver oxide needed in cell.
- $W_d$  Weight of silver oxide needed for each ampere minute of discharge.
- $W_e$  Total weight of electrolyte.
- $W_f$  Weight of separators in unit cell.
- $W_g$  Weight of grids in the unit cell in ounces.
- $W_G$   $W_g + W_f - W_a J$  and is approximately equal to  $W_g$ .
- $W_{sp}$  Total weight of spacers.
- $W_T$  Total cell weight.
- $W_y$  Weight of wire connectors pere ampere of current.
- $W_z$  Total weight of zinc needed in cell.

\* \* \*



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