A SURVEY OF MASS TRANSFER STUDIES AT ELECTRODES

AND

DESIGN OF A ROTATING ELECTROCHEMICAL MASS TRANSFER STUDY SYSTEM

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ABSTRACT

The theoretical aspects of the phenomenon of Electro Chemical Mass Transfer have been explained after the introduction of the principles of Mass Transfer and concept of Nernst's diffusion layer. The relation between the layer and mass transfer co-efficient is analysed along with that of between the latter and the current passing during the electrode reaction. It is then shown that application of dimensionless analysis makes it possible to predict mass transfer behaviour from analogues data from other transport processes.

A review of experimental work so far done by other workers in the field of the effect of electrode reactions is presented.

Some practical work done with a view to study the electrchemical mass transfer at cylindrical rotating electrodes in natural and forced convection process have been presented.

The limitations of the experimental set up used are analysed and suggestions for future work using an improved technique has been discussed.

CHAPTER - I

INTRODUCTION

Study of mass transfer at working electrodes is of fundamental importance. (1,2) in analysis of electode phenomena and in consideration of concentration polarization, limiting currents, and rates of electrode reactions. Several typical cases have been analysed by the methods of hydrodynamics and boundary layer theory, and for a few models, experimenteal results were sucdessfully correlated (1,2). The effect of natural convection in electrolysis was quantitatively evaluated by Wagner (3) and Wilke and coworkers (4) among others. Rotating Disc electodes were treated mathematically by Levich (5). This theory applies if the diffusion boundary layer at the disc is laminar. Along the lines suggested by Agar (6), Lin and coworkers (7) correleated limiting current densities for the inner electrode of an annual cell with streamline and turbulent longitudinal flow. An extension of this study for laminar and turbulent flow along flat plate electrodes was reported (8).

When a metal is deposited on a cathode, the concentration of cations in the solution adjacent to the electrode decreases. Because of the deficit of cations at the cathode, cations diffuse towards this electrode. Thus there results or superposition of migration of cations due to the applied electric field and diffusion due to the concentration gradient. The solution being at rest, the current density being given, and the anode being sufficiently remote, H.F. Weber (9), S.R. Milner (10), and others have shown both theoretically and experimentally that the cations concentration at the cathode decreases as a linear function of the square root of the time. When the concentration of the cations at the cathode approaches Zero, a new

cathodic process starts, which in some instances is the evolution of hydrogen. The drop of the cation concentration to zero is to be expected at rather moderate current densities several minutes after the beginning of electrolysis. Actually much greater current densities than calculated can be applied in the case of vertical electrodes because convection takes place and thus decreases the 'diffusion path' which has been calculated from saturation currents by various authors i.e. R.E. Wilson and M.A. Youtz(11) and S. Glasstone (12).

The present investigation is concerned with cylindrical central electrodes rotating in concentric cylindrical cell.

Recently, rotated electrode surfaces have been used in chemical analysis and in corrosion studies in parallel with polarographic methods (13,14). Industrical applications of this forced convection are known and further important uses are anticipated.

The effect of speed of rotation upon rate of mass transfer was first studied by Brunner, (15,16). He found that the diffusion layer thickness, δ decreases with the 2/3 power of the speed. However, he considered neither the effect of rotor diameter nor the dependence of physical properties of the electrolyte. Therefore, only qualitative conclusions can be drawn from these experimental data.

Eucken (17) analysed the effect of laminar flow forced convection upon rate of mass transfer at an electrode. In his experiments the external vessel containing the solution was rotated, and laminar flow pass the fixed inner flat plate electrode resulted. Eucken's mathematical analysis is valid only for this particular condition. Kambara and coworkers(18) adapted Eucken's

treatment to a 0.5 mm diameter platinum wire electrode projecting perpendicularly 6 mm from the axix of a rotating glass rod. In the derivation, it is assumed that the velocity gradient at the electrode surface is proportional to rpm. This is valid for Eucken's model where laminar flow exists in the entire region of flow, but is inadmissible for the turbulent flow case, where laminar flow is restricted to the boundary layer adjacent to the electrode surface.

For the sake of clarity, the term "rotating electrode" is used henceforth only in reference to cylindrical electrodes. Recently, Roald and Beck (19) used such rotating electrodes in a study of dissolution rates of magnesium and its alloys in hydrochloric acid solutions. They found that the rates of dissolution increase in low acid concentrations with the 0.71 power of the speed of rotation. At higher acid concentrations (1.4 M and higher), the reaction rates become entirely independent of rotational speeds, as the stirring effect produced by hydrogen bubbles evolving at the metal interface becomes predominent. This stirring effect, however, should not be ignored even at low acid concentration because of turbulence caused by hydrogen bubbles moving in the boundary layer adjacent to the dissolving magnesium rod. For this reason the work of Roald and Beck represents a rather special case of forced convection mass transfer.

In studies of dissolution and corrosion rates of rotated metal rods King and coworkers (20,21,22, 25) estimated the mass transfer coefficients employing King and Shack's earlier experimental finding (24) according to which "normal diffusion" (or transport) control requires that rates be linear with peripherial speed about 5000 cm/min (25). King

and Cathcart (25) indicated that the mass transfer coefficient is directly proportional to the 0.70 power of the diffusion coefficient of the reacting ionic species.

The effect of cylinder diameter, speed of rotation, diffusion coefficient and viscosity on mass transfer rates has not been successfully incorporated into a single correlation, although Chilton-Colburn analogy for correlating the pertinent variables was realized by Kind and coworkers in 1937 (26).

The present work was undertaken with the following aims in mind:
(a) to establish correlations between physical properties of a system, geometrical and hydrodynamic conditions, and rates at which a solute (ion) is transferred to or from a electrode, both stationary and rotating,
(b) to determine whether such general mass transfer correlations enable prediction of concentration polarization and limiting currents in steady state electrolysis.

CHAPTER - II

MASS TRANSFER IN CONCENTRATION POLARIZATION

Any electrode reactions proceeding at a finite rate involves movement of the solution between the bulk of the liquid phase and the electrode solution interface. Dissolved reactants must be supplied to the interface or products must be removed. In the absence of fluid turbulence ions are transferred from solution to an electrode by three principle mechanisms.

i) By Diffusion.

ii) By Convection (i.e. movement of liquid containing the ions)

and iii) By ionic migration.

Migration and convection cannot account for the whole of material required or produced by the reaction and the cooperation of diffusion is always necessary; the concentration at interface must therefore differ from those in the bulk of the solution. Such differences in ionic concentrations are the cause of concentration overpotential or polarization and limiting currents and play an important role in the kinetics of electrode reactions (27).

For a given species the rate of transfer in the y direction per unit area of the electrode (metal) surface perpendicular to y at any point in the environment (fluid) may be expressed by the equation :

$$N_t = cU\frac{\partial \phi}{\partial y} - D\frac{\partial c}{\partial y} + Vc \qquad \text{--- ---(1)}$$

Where N_t = total rate of transfer in gram ions/cm^2-Sec, C = Concentration of given species gm ions/cm^3, U = mobility, cm^2/Sec volt, ϕ = potential

in volts, y = distance in direction of transfer, cm, D = diffusion coefficient, cm^2/sec, V = velicity of bulk fluid motion in direction of transfer, cm/sec. The three term on the right of the equation (1) represent respectively the contribution of migration, diffusion and convection.

For steady state process it is possible to define the migration term in terms of current per unit area perpendicular to the direction of transfer (28) as

$$N_M = cU\frac{\partial \phi}{\partial y} = \frac{T_a I}{nF} \qquad \text{--- ---} \qquad (2)$$

Where N_M = rate of migration in gm-ions/cm^2-sec; T_a = transport number for the particular species; n = number of electrons transported during the ionic reaction; and F= the Faraday's constant. In the presence of sufficient amount of inert electrolyte the transference or transport number of the species concerned may be taken as negligible, making the migration term unnecessary(2).

By excluding the effects of migration one is left with the combined effects of diffusion, eddy diffusion and convection . Transport of ions or molecules by these means are termed as "Mass Transfer". The mass transfer process is known as "forced convection" when the system ie externally agitated by mechanical means such ae stirring or pumping. It is termed "free or natural convection" when mixing takes place due to density differences accompanying concentration differences from point to point within the fluid. A steady state process referred to earlier, implies that the transfer rates, current density, concentration, temperature and other variables associated with operation of the electrolytic cell are independent of time at any particular point in the system.

The different mass transfer mechanisms take part to a varying degree as ions move from the electrode solution interface to the bulk of the solution, with the nature of the process at any distance from the metal electrode depending on solution motion, shape and position of the cell comprising cathodic and anodic areas on the metal surface, and other potential variables. As a result of the participation of diffusion in transfer process the movement of ions towards or away from the electrode results in a decreasing concentration of the species in the direction of transfer, thereby producing a concentration gradient. It is stated that this concentration gradient provides the driving force for mass transfer to take place.

The overall mass transfer process is sometimes expressed with the help of equations of a simple empirical form which relate the mass transfer rate to the concentration gradient (the difference between the bulk concentration of the ions and the concentration at the electrode solution interface). Thus the rate of transfer is expressed by coefficient K_L defined as:

$$N_d = K_L(C_b - C_i) \qquad \text{--- ---} \quad (3)$$

where Nd = mass transfer rate at any particular point on the electrode, gm-ions/cm^2-sec; K_L = mass transfer coefficient, cm/sec; C_b = bulk concentration gm ions/cm^3 and C_i = interface concentration.

Nernst Layer.

Nernst postulated a stationary layer of liquid in contact with the electrode; within the layer only diffusion is operative, while outside this layer the concentration is maintained at a constant value by convection, diffusion being negligible (30). The implications of the assumption made by him may be stated in modern terms as follows :

(1) That the chemical processes at the surface always proceed very much faster than one of the two transfer processes,

(2) That in a well stirred system the concentration gradient is confined to a thin layer of solution adhering to the solid surface,

(3) That within this layer the concentration varies linearly with distance, measured normal to the surface, and

(4) That the thickness of this layer, whilst being a function of the rate of stirring and of the geometry of the system is independent of the coefficient of diffusion of the ions or solute, of the viscosity of the electrolyte, and of the temperature. None of these assumptions are entirely correct (29).

It has been stated by several authors (30,31,32) that there are certain chemical reactions where kinetics are controlled by factors other than that of transport. The assumption that the diffusion layer is stationary with respect to the surface is not true. The suggested values of δ , the diffusion are of the order of 0.03 mm which corresponds to layers of 50,000 molecules thick - rather an improbably high figure. It has also been experimentally observed that fluid motion does exist even down to very short distances. Under such circumstances, the assumption that the ion

concentration is a linear function of the distance y (measured normal to the surface) over the range $0 \leq y \leq \delta$ is only an approximation. And, finally experiments have shown that δ does depend upon D which means viscosity and temperature are also determining factors.

According to the Nernst theory (33), the rate at which a solution passes through the diffusion layer is

$$N_d = \frac{D (C_b - C_i)}{\delta} \qquad \ldots\ldots\ldots \quad (4)$$

Where,

D = Diffusion coefficient,

C_b, C_i = Bulk and electrode concentrations,

δ = Thickness of the diffusion layer.

Provided the transference number Ta is independent of concentration, Nd is given by :

$$Nd = \frac{I (1-Ta)}{AnF} \qquad \ldots\ldots\ldots \quad (5)$$

Where I = The total current,

A = the electrode area,

F = the Faraday's constant,

n = the no. of Faradays required per mole reacting.

and Ta = the transport number of the reacting ion.

The diffusion layer δ in equation (4) has also been termed the equivalent film thickness. This concept expresses the mass transfer process by the rate equation for steady state diffusion from C_b to Ci over a

hypothetical layer of stagnant fluid thickness δ . The diffusional term of equation (1) i.e. Fick's first law is integrated to provide equation (4). Although the hypothesis of a stagnent layer put forward by Nernst has been proved to be wrong, the true concentration profile in the vicinity of the electrode can be represented by an equivalent concentration profile as represented in Fg. 1(2).

In presence of sufficient amount of inert electrlyte Ta in equation may be neglected. In such a case :

$$\frac{I}{nF} = \frac{D(C_b - C_i)}{\delta} \qquad \ldots\ldots\ldots\ldots \quad (6)$$

under limiting current conditione when $C_i = 0$,

$$I_2 = \frac{nFD}{\delta} C_b \qquad \ldots\ldots\ldots \quad (7)$$

It should, however, be mentioned here that the theoretical maximum current density cannot be reached in practice because of the development of electrode polarization associated with depletion of the reacting ions in the region of the electrode. This polarization is approximately equal to the emf of a concentration cell formed between two solutions contsining the reacting ions as concentrations C_b and C_i.

From equation (7) it is apparent that I_2 may be increased by decreasing δ and this will subsequently increase the overall mass transfer rate. This can be done, as will be seen in the next chapter by agitating the electrolyte. When the electrolyte is agitated, mass transfer is said to take place by forced convection laws of hydrodynamics come into play and

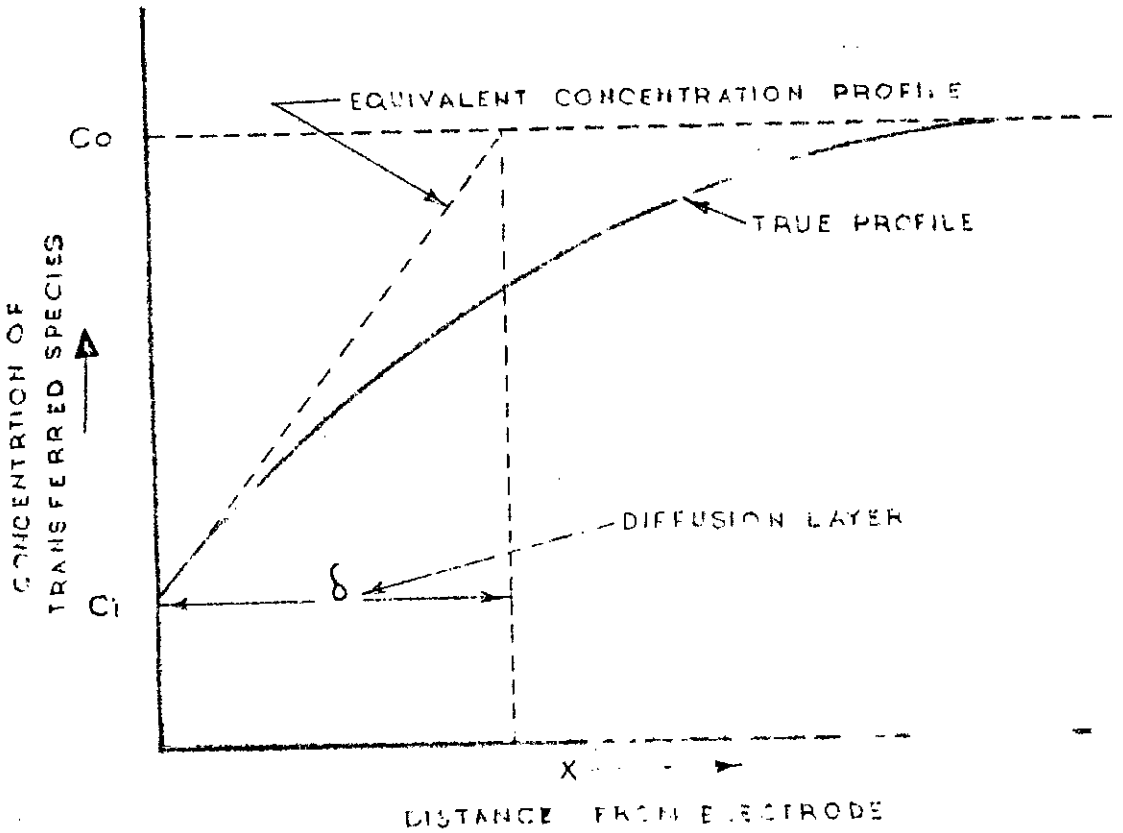

EQUIVALENT CONCENTRATION PROFILE
Co
TRUE PROFILE
CONCENTRATION OF TRANSFERRED SPECIES
DIFFUSION LAYER
δ
Ci
X
DISTANCE FROM ELECTRODE

FIG. 1

effects the kinetics of the electrode reaction. By combining equations (5) and (5), assuming the presence of sufficient amount of inert electrlyte and for unit electrode area, it can be show that :

$$I = nF\,(C_b - C_i)\,K_L \qquad \ldots\ldots\ldots \quad (8)$$

This equation clearly indicates the dependence of the current in an electrolyte reaction on the mass transfer coefficient.

CHAPTER - III

ANALYSIS OF MASS TRANSFER

Since mass transfer involves concentration changes, a more detailed analysis of such changes taking place in a solution seems desirable. The rate of change ~~solution~~ of concentration is given by the differential equation:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) - \left(u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} + \omega\frac{\partial c}{\partial z}\right) \quad ---(9)$$

Where t is time, D is the diffusion coefficient, and u,v,w, are the x,y,z components of the velocity 'V' at the point x,y,z. The first term on the right represents the effect of diffusion, which is assumed to obey Fick's Law as in a stationary fluid, the second term gives the change in concentration due to convection. The velocity components are determined by the Navier Stokes equations and by the equation of continuity, togather with appropriate boundary conditions. A brief discussion is given in order to show the factors on which motion depends.

The components of velocity u,v and w in a liquid are determined by the equation of continuity :

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial \omega}{\partial z} = 0 \quad --- \quad ---(10)$$

together with Navier - Stokes equations:

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} + \omega\frac{\partial \omega}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial x} + X + \nu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right) \quad --- \quad ---(11)$$

and two analogues equations in v and w. ρ, P, ν are respectively the density total pressure and knematic viscocity and X is the x component of the extraneous forces acting on unit mass of the liquid. The terms on the left, taken together, are the acceleration of a particle of the liquid and after multiplying by ρ the equation (11) has the form:

density X acceleration = Pressure gradient + extraneous forces + viscous forces.

The extraneous forces to be considered are gravity and in a liquid of constant density this is balanced by the hydrostatic pressure (27).

In general the differential equation for changes in concentration can only be solved for those cases where the equations for fluid motion can be reduced to a simpler form. Solution can be obtained for certain systems and in one case Levich (5) has given a detailed treatment of mass transfer under nonturbulent conditions. His system consisted of a flat disc in an infinite volume of solution. Under these conditions Levich solved the equation (9) for nonturbulent conditions. He obtained :

$$-\frac{\delta c}{\delta t} = \frac{DA}{V} \cdot \frac{(C_b - C_i)}{0.893\delta} \qquad \text{--- ---(12)}$$

Where V is the solution volume and δ the thickness of the region adjacent to the plate over which the concentration differs significantly from the bulk concentration. By integrating equation (12) and compairing with equation (4) the thickness of the fictitous Nernst layer is given by the expression :

$$\delta = 0.893\delta' = 1.612\, D^{1/3} \nu^{1/6} \omega^{-1/6} \qquad \text{--- --(13)}$$

For nonturbulent flow this relationship has been proved to be satisfactory.

Application of Dimensional Analysis to Mass Transfer

The solution of the differential equations is a function of the coefficients which occur in them and the quantities which appear in the boundary conditions. Hence the mass transfer rate N depends on U, ν, D and $(C_b - C_i)$; it also depends on the distance y perpendicular from the electrode surface and on the various coordintes which determine the position and size of the electrode (including the area A), and of the other boundary surfaces. All these latter quantities can be expressed in terms of some characteristic length (1) (i.e. length of the electrode or the corroding surface), together with dimensionless ratios of the type X/I. This provlem thus involves six dimensional quantities, N_d, U, ν I, D, and $(C_b - C_i)$.

It is possible to express the ratios between these six quantities inx a form which is independent of the units employed, u as a relation between dimensionless group. Table - I shows the dimensions and units of quantities listed in the previous paragraph :

Table - I

Symbol	Quantity	Dimensions
N_d	Mass Transfer rate per unit area (mol/cm^2 - sec.)	$ML^{-2}T^{-1}$
C	Concentration difference (mole/cm^3)	ML^{-3}
D	Coefficient of Diffusion (Cm^2/Sec.)	L^2T^{-1}
ν	Kinematic Viscosity (cm^2/sec.)	L^2T^{-1}
I	Characteristic Length	L
U	Characteristic Velocity	LT^{-1}
g	Gravity X density coefficient	$M^{-1}L^4T^{-1}$

Elimination of three fundamental units M, L and T imposes three conditions, hence 6-3 = 3 independent dimensionless quantities can be formed from the six variables. They may be choses in various ways, but the following have been shown to be most convenient :

Reynold's Number : $Re = \frac{UI}{\nu}$

Nusselt's Number : $Nu = \frac{N_d I}{\Delta C D}$

Prandtl's Number : $Pr = \frac{\nu}{D}$

The relation between the six variables can thus be reduced to :

$$Nu = \phi(Re, Pr) \quad --- \quad --- \quad --- \quad (14)$$

The form of function ϕ depends upon the geometry of the apparatus. Equation (15) is a modified version of the equation above equation :

$$Nu = \phi'(Re)^a (Pr)^b \quad --- \quad --- \quad --- \quad (15)$$

Thus, however, is only true for forced convection because in natural convection velocity U does not appear. Instead of quantities g and α have to be taken into account. From the six variables N_d, I, ν, D, ΔC and $(g\alpha)$ three dimension less quantities can be formed; the usual choice is N_u and Pr as in forced convection along with

Grashhof's number : $Gr = \frac{I^3 g' \alpha \Delta C}{\nu^2}$

Hence, Nu = G (Gr, Pr) ..... (16)

It must be mentioned here that analogues relationships are held true for the variables effecting heat and momentum transfer. Data from analogous experimental observations in one form of transport phenomenon

is frequently employed for prediction of behaviour in others (27,29,34).

The physical significance of the dimensionless groups is of interest. For mass transfer, the Nusselt's number, (then sometimes termed the Sherwood number) represents the ratio of the actual rate of mass transfer per unit area Nd, to rate of mass transfer by diffusion in the stationary fluid $\frac{\Delta CD}{1}$. The Prandtl's number (sometimes in the case of mass transfer the Schimidt number) is the ratio of the fluid property governing the transfer of momentum by viscous forces due to a velocity gradient, to the fluid property governing mass transfer by molecular diffusion due to a concentration gradient. The Reynold's number may be regarded as the ratio of fluid momentum per unit area per unit time (ρu^2), to the viscous drug force per unit area $(\eta U/I)$ against which it is balanced. In the case of moving fluid, the importance of Reynold's number can be more fully appreciated, as the transition from non turbulent or laminar flow to turbulent flow conditions is governed by its value.

Some aspects of surfaces under dynamic fluid flow conditions, referred to earlier in the previous paragraph deserves more detailed treatment. The particles of a real fluid in contact with a boundary have the same velocity as the boundary itself. As for instance, during flow over a flat plate, the fluid adheres to the wall , and frictional fordes retard the motion of the fluid in a generally thin layer near the walls. In this layer the local velocity of the fluid increases from zero at the wall to its full value in the un-disturbed flow as shown in Fig. 2.

The ratio of change of velocity at the vicinity of wass follows a definite law. The zone near the wall is known as the boundary layer. The

boundary layer thickness is considered as that distance normal to the wall where the local velocity is 99% of the undisturbed velocity. The velocity gradient is very large near the wall and gives rise to high shearing stresses. However, as the local velocity approaches the undisturbed velocity asymptotically the local shearing forces become smaller and smaller, and eventually become zero. As the fluid reaches the upstream edge of the plate, fluid particles may adhere to the plate. Shearing stresses are developed, and through the action of momentum transfer more and more fluid particles are slowed down and the boundary layer is developed. The flow within the boundary layer at the leading edge is laminar. Beyond this the flow becomes turbulent according to Re. In case of flow over a thin flat plate the value of the Reynold's number at which the flow becomes turbulent is approximately $5X10^5$. The transition from laminar to turbulent flow begins approximately at Re= $5X10^5$. Similar figures for flow through pipes are 3000 and 2100.

For the laminar type of flow, the velocity component parallel to the axis, depends only on the radial distanced from the axis. For turbulent flow, the velocity components have to be regarded as mean values taken over a long interval of time. Their actual values at any given point fluctuate with time owing to the movement of turbulent eddies through the fluid body.

The thickness of the hydrodynamic laminar boundary layer in case of flow over a thin flat plate is given by the Blassius equation :

$$\delta_{\text{hydrodynamic}} = \frac{5\,X}{Re} \quad \ldots\ldots\ldots \quad (17)$$

The thickness of the turbulent boundary layer is also given by the Blasius equation :

$$\delta \text{ hydrodynamic turbulent} = \frac{0.58X}{(Re)^{1/5}} \quad \ldots\ldots\ldots (17a)$$

(for X please refer to fig. 2)

Similar relations have been obtained for cases when a disc is rotating in a fluid of infinite boundaries (cf. previous discussion on Levich's work case of diffusion layer), and for flow through pipes (35).

In all cases of moving fluids of practical interest the Reynold's number is much greater than unity. The flow of fluid as detailed in the previous sections can be divided in to a region of unviscous flow and the boundary layer ~~xx~~ also called Prandtl boundary layer contigious to the surface of the solid.

To solve the problem of transport of matter in a stirred solution it is necessary first of all to find the distribution of concentration in the solution.

There is yet another dimensionless number which can be introduced in the present discussion. This is the Peclet number - (UI/D). It corresponds to the Reynold's number for the flow of liquid, and the regime of transport of matter is determined by the value of the peclet number. If this number is great compared to unity, molecular diffusion can be neglected in comparison with convective transport of matter, if it is small, on the contrary, molecular diffusion predominates. It might be of interest to note here that the ratio of the Peclet number and the Reynold's number is the dimensionless number called the prandtl number :

$$\frac{Pe}{Re} = Pr. = \frac{\nu}{D}$$

In the liquids the Prandtl number is always large in compared to unity, where as in gases it is in the order of unity.

Due to the smallness of the diffusion coefficient the Peclet number is large for the lowest values of the velocity, even when the corresponding Re is still small compared with unity. Molecular diffusion in liquids can, therefore, always be neglected in comparison with convective transport of matter. When the Peclet number is large convective diffusion can be treated in a manner analogous to that applied in hydrodynamics to the flow passed a body at large Reynold's number.

Thus at large P_e , as at large Re, the entire liquid can be divided into two parts; a region of constant concentration far from the surface of reaction and a region of rapid variation of concentration in the immediate vicinity of the surface. The zone adjacent to the surface is analogous to the hydrodyamic boundary layer referred to earlier. In the latter layer the viscosity of the liquid has to be taken into accounts, where as in the main bulk of the flow it does not come into play. Similarly in the liquid layer contiguous to the surface of the electrode likewise in a corroding surface, molecular diffusion must be considered. This layer is known as the diffusion boundary layer or the mass transfer boundary layer (84).

Although the concept of a mass transfer boundary layer may appear to be a generalisation of the Nernst's layer, discussed in chapter II, there is a fundamental difference between the two concepts. This difference lies in the fact that the velocity of flow of the liquid in the diffusion or the mass transfer boundary layer is not necessarily equal to zero. The

mass transport boundary layer is an analogue of thermal boundary layer in the theory of transport of heat in liquids but is several times thinner than the latter. Levich in his experiments with the rotating discs has shown that the mass transfer boundary layer equals the thickness of the layer dragged along on the region contiguous to the surface of the disc (i.e. the hydrodynamic boundary layer) divided by Prandtl number to the power 1/3 i.e. $(Pr)^{1/3}$.

CHAPTER - IV

PREVIOUS WORK

Natural Convection.

Significant work has been done by employing the principles of electrochemical mass transfer. Brunner (15) was the first electrochemist to study it with an engineering end inview. Work has been done employing the principles of hydrodynamics and boundary layer theory and for a few models experimental results were successfully correlated (1,2).

The effect of natural convection in electrolysis was studied by Wagner (5) and Wilke and coworkers (4) . Wagner showed that at a vertical electrode a well defined corrective flow due to the generally smaller density in the boundary layer and the resulting buoyancy force exists, analogous to natural convection in the course of heat transfer from a radiator to ambient air. The interplay between diffusion and convective flow determines the limiting current density which occurs if such a voltage is applied that the concentration of one of the reactants at the electrode drops to zero. Deviations from the vertical position of the electrode upto 15 degrees had no noticeable effect. The increase of convection due to the development of hydrogen was investigated. As long as the current flowing accross the lower section was so small that only copper was deposited, the current density of the upper section decreased with increasing current of lower section. When the current of lower section exceeded this value, copper as well as hydrogen ions were reduced and the current density of the upper section rose considerably. The ascending hydrogen bubbles increased the convection. Yet it is remarkable that the ascending hydrogen bubbles increase

the limiting current density no more than by a factor of two. This observation shows that natural convection alone is relatively effective and forced convection becomessignificant only when its intensity is fairly great.

Wagner (56) reported that for mass transfer due to natural convection in a laminar boundary layer, the current density is virtually constant, although concentration polarization at both the cathode and the anode varies from bottom to top. He found that the local limiting current density is proportioned to the fourth root of the distance from the leading edge of the electrode in accord of the experimental results(3,4,37,38). Approximate solutions of the differential equations for the concentration and the velocity distribution in the boundary layer have been obtained by using solutions for the analogous heat transfer problem (3,4,6,37,38,39,40).

Abramson and King (45) while studying the rate of dissolution of iron in acids in 1939, enslisted the following general criteria of a diffusion controlled reaction rate :

(1) Various solids dissolve in the same reagent at the same rate.

(2) In different reagents the rate is an exponential function of the diffusion coefficient.

(3) The rate increases with stirring speed, the exact function depending upon the type of stirring.

(4) The rate follows the same function of viscosity as the diffusion coefficient.

(5) The temperature coefficeint is generally less than 1.5 per 10°.

In 1952 Riddiford Ircumshaw (46) reported that kinetics of the dissolution of zinc in aqueous iodine solutions. In conformity with the criteria enlisted above, they found that zinc, copper, amalgamated copper, brass etc. dissolve in aqueous iodine solution at the same rate at the same experimental conditions.

FORCED CONVECTION

Lin and associates (7) made a systematic study of the transfer rates of ions and of other reacting species in diffusion controlled electrode reactions. They measured the transfer rates from a flowing electrolyte to the surface of an electrode. The reactions studied were the cathodic reduction of ferricynide ion, quinone and oxygen and the anodic oxydation of ferrocyanide at various flow rates. The results obtained were in remarkable agreement with the standard Leveque's equation for mass transfer in the stream line or laminar region and with Chitton-Colburn's emperical relation in the turbulent region.

Eisenberg and his associates (48,49) also took recourse to the ferri-ferrocyqnide system in their study of ionic mass transfer and concentration polarization at rotating electrodes. They also studied the mass transfer rate of solid cylinders rotating in solvents. They found that a general mass transfer correlation applied equally well to dissolution rates of rotating solids and to rates of ionic mass transfer at rotating electrodes. This correlation takes into account physical properties of the system as well as geometric and hydrodynamic factors.

The correlation allows prediction of limiting currents and concentration polarization at rotating electrode under a wide range of conditions. The nature of polarization involved in reduction of $Fe(CN)_6^{-3}$ and oxidation of $Fe(CN)_6^{-4}$ was also investigated. Polarization was found to depend strongly on presence of electrode positions. With freshly prepared solutions, under exclusion of light, and with cathodically treated nickel electrodes, relatively small chemical polarizations were determined. For rotational speed not exceeding Reynold's number 11,000, chemical polarization was found to be negligible in comparison with concentration polarization. Under such conditoons, the ferro-ferricyanide couple can be conveniently used to obtain mass transfer rates for various hydrodynamic conditions, or conversely, to varify the validity of mass transfer equations by a comparison of experimental and calculated values of limiting currents and concentration polarization.

The rotating electrode model used by them was found to be most suitable for studying the nature of electrolyte polarization phenomena because of uniformity of current distribution and the hydrodynamic diffusion layer at the electrode surface.

However, all these works reported above are recent. It was Brunner (15) in 1904 who first studied the effect of rotation upon the rate of mass transfer. He expressed his findings in the form of the diffusion layer thickness :

$$\delta = \frac{0.05}{(rpm)^{2/3}} \text{ cm} \quad \ldots\ldots\ldots \quad (23)$$

and is defined by $N = \frac{D\Delta C}{\delta}$

Since he did not take into consideration the effects of rotor diameter or those of the phyeical properties of the electrolyte, only quantative deductions can be made for different experiments.

Eisenberg and his associates (49) in a review of works on allied topics report that the methods of hydrodynamics were applied for the first time by Eucken to predict the effect of forced convection upon the rates of mass transfer at an electrode. During their own experiments, Eisengerg et al obtained results which lead to the conclusion that

$$\frac{K_1}{V} * S_c^{0.644} = \text{Constant } g(Re) \quad \ldots\ldots (22)$$

Where g (Re) represents a functions of the Reynold's number. The mass transfer correlation for the two electrolytic reactions, cathodic reduction of ferricyanide and enodic oxydation of ferrocyanide show the following general relationship :

$$\frac{K_1}{V} S_c^{0.644} \approx \text{Constant } Re^{-0.50} \quad \ldots\ldots\ldots (23)$$

Ibl (50) has reported that between $160 < Re < 1000$

$$Nu = 15.3\ Re^{0.44}$$

and for $1000 < Re < 12,600$, Wagner (66) reported

$$Nu = 5.96\ Re^{0.56}$$

The sharp change in transfer coefficients on transition from laminar to turbulent flow has also been observed by Lin and his associates (7).

The much employed rotating electrode technique was also used by Makrides in his study of anodic dissolution of iron in sulphuric acid and ferric sulphate solutions. In an analysis of the dissolution potential, he expressed the dependence of potential on hydrodynamic flow conditions as

$$E = b_a \log V^{(1-\beta)} + (\text{Constant}) \quad \ldots\ldots\ldots (24)$$

Where, V = Linear velocity

b_a = Tated slope

β = Constant

The rotating cylinder method of measurement is claimed to have the advantage that all parts of the surface move with equal velocity. Also, it is supposed to posses the added advantage of a uniform mass transport rate over the whole of its lateral surface. But it has not yet been possible to calculate δ as a function of rotational speed. It also hardly seems to represent a situation which can be found under ordinary practical conditions excepting of course the paddles, stirrers and other kind.

Recent investigators in the allied fields have been taking into consideration the importance of the gradual formation of boundary layer on an electrode. The investigation on this line has been carried out by Grassmal et al (57) in some detail and describes a novel technique for studying such effects. Wranglen and Nilsson also took into consideration this factor in their theoretical and practical analysis of mass transfer under forced laminar and turbulent convection at horizontal plane plate electrodes. They expressed their results as :

$$\text{Nu laminar} = 0.331 \; S_c^{1/3} \; Re^{\frac{1}{2}} \quad \ldots\ldots\ldots (25a)$$

$$\text{Nu turbulent} = 0.17 \; S_c^{1/3} \; Re^{3/5} \quad \ldots\ldots\ldots (25b)$$

CHAPTER - V

PRACTICAL WORK ON MASS TRANSFER AT ELECTRODES

The purpose of this experiment wasa to study the mass transfer rate at vertical electrode both in natural and forced convection including the effect of rotational speed of the electrode on mass transfer. The review of the literature presented in the last chapter shows that many authors have studied the mass transfer phenomena on an electrode surface - most common being that of surface acting cathodically. They have presented their results in the form of relationships between dimensionless groups. In the present case similar attempts were made with copper sulphate in sulphuric acid solution.

Experimental Details

a) Apparatus.

A concentric cylindrical cell, 7 in high, made of copper was incorporated as the mass transfer equipment. The anode was made of 4 m. 16 BWG pipe and the cathode of 1 in 16 BWG pipe (i.e. anode was kept sufficiently bigger than the cathode). The height of the cell was 7 in. The anodic cylinder was mounted on a grooved acrylic plastic (lucite) sheet. On the top was a similar grooved plastic sheet. The top and bottom sheets were made to hold the anode with the help of four long bolts. The cell was made water light with rubber gaskets placed in the grooves of the bottom sheet. The cathode was placed centrally through two ball bearings mounted at the ends of a gland, made of brass, fixed centrally in the top lucite sheet to facilitate frictionless revolution of the cathode.

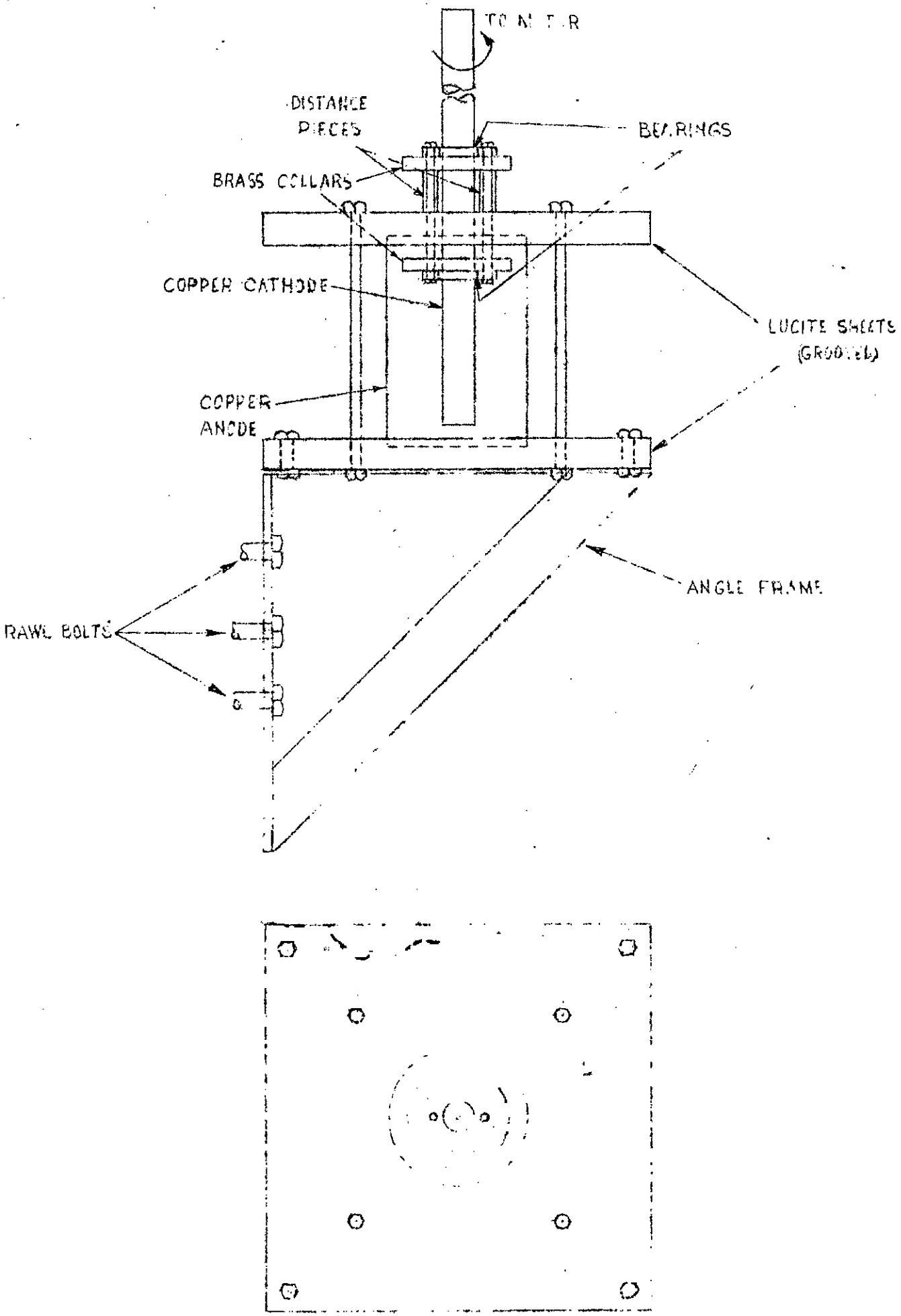
To avoid metal to metal contact of the cathode and the bearing, two PVC bushes were mounted on the cathode tube by heating. The bushes were then turned on lathe to exactly fit inside the innder face of the bearings. The entire cell was then fixed with the help of four bolts on two 2"X2"X¼" mes. angle frames mounted against the wass (see fig. 3) with the help of rawl bolts to avoid vibration. An arrangement was made to rotate the cathode by a fractional L.P. D.C motor mounted on to the was with the help of special fittings on the top of the cell.

Two 12 volts storage batteries were used to rotate the motor. The speed of the motor was controlled by controlling the supply voltage with the help of a 27 ohm rheostat. Coupling of the motor and the cahtode was made with the help of a ebonite rod to avoid short circuiting.

Two holes were drilled through the gland and the top of lunite sheet to carryout deseration before starting the experiment. Another hole was made in the bottom sheet to which one end of a transparent PVC pipe was inserted tightly (water tight). The other end of the PVC pipe was donnected with the bottom end of a stoppered funnel put on a stand into which the reference electrode was used.

The electrode length was maintained at 0.2 cm. The inside of the cathode was plugged with the help of a ebonite piece. The rest of the cahode length was protected by a heavy polysteryne coating.

One 6 volt storage battery was used to supply current to the cell through a series of variable resistances. milliammater and millivoltmeter were used to measure milliamperes and millivolts respectively.



SECTIONAL DRAWING OF THE CELL WITH PLAN

FIG. 3

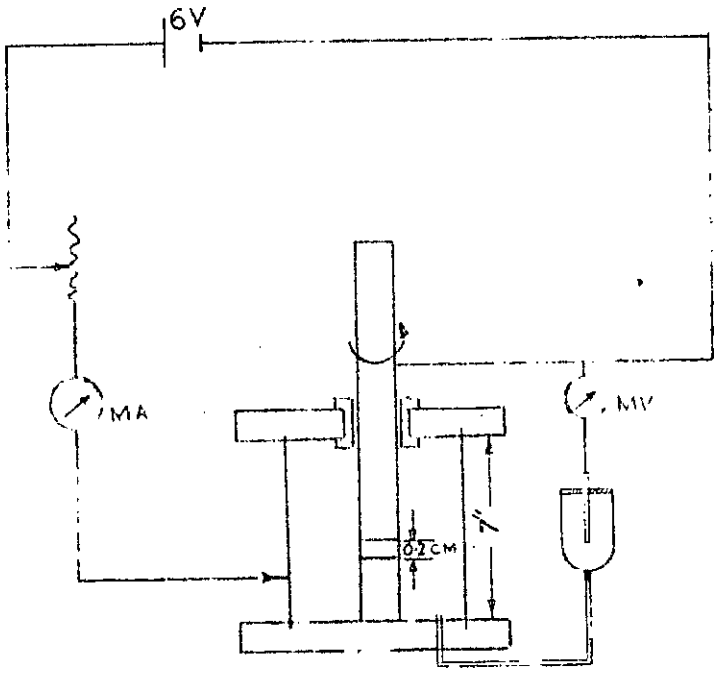
Millivolts were measured against a standard calomel electrode inserted in the solution.

b) Experiments.

At the beginning of each run the anode and the cathode were abraded with fine emery paper and thin degreased with acetone. Polysterine coating on the cathode was renewed as and when required. The cell was then reassembled and placed in prosition and filled in with freshly prepared copper sulphate and sulphuric acid solution of predetermined strength up to the required level at about 26°c. Nitrogen gas was then passed into the solution for 30 minutes to remove any dissolved oxygen in the solution. Presence of a considerable amount of dissolved oxygen in the cell would have interferred with electrode reactions.

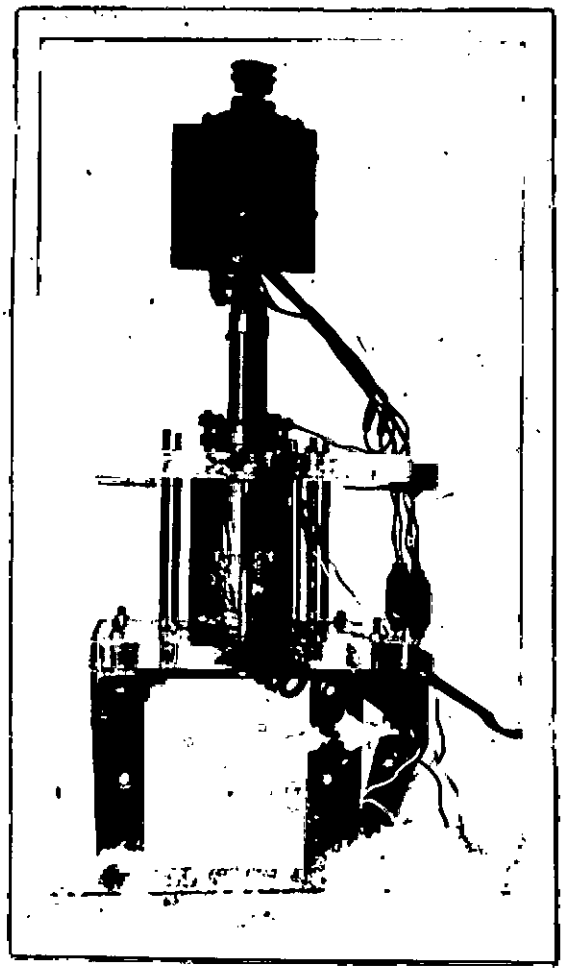
Value of the electrode potential with no current flow (ZCP) was measured with the reference. These were latter subtracted (with proper sign) from the 'at current values'. Thus any static potential differences due to variations in surface structure of the electrodes could be accounted for. A relatively small current was applied and the potential of the electrode was recorded by a millivoltmeter affect the steady state was achieved. current was increased in small increments until the liminting current noted by a sudden rise in potential was attained (in this experiment this could not be achieved clearly).

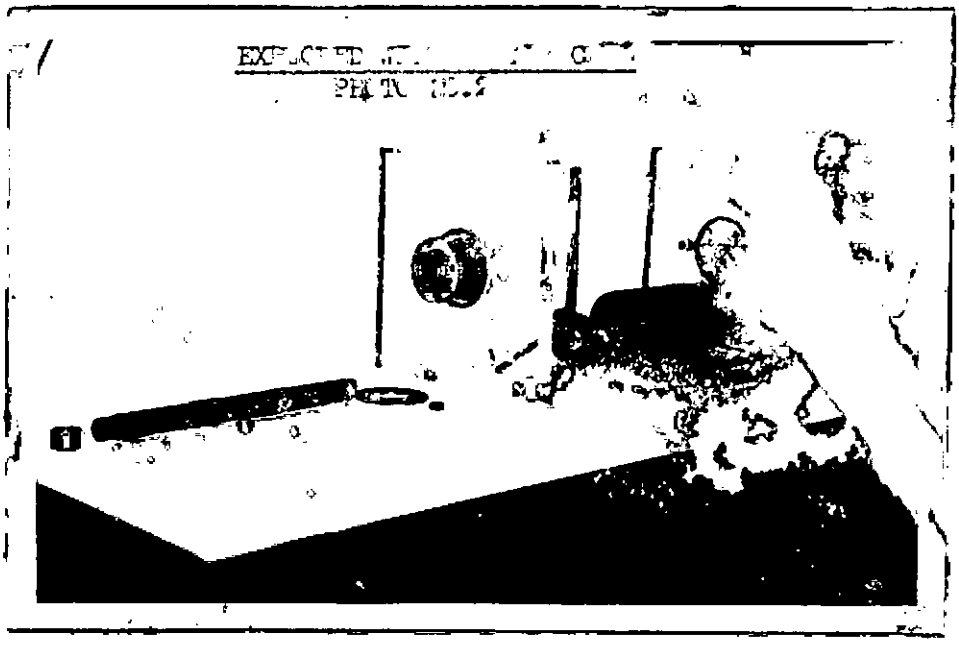
The experiment was carriedout at stagnent condition and at the different speeds with 0.1 mole copper sulphate in 1 mole sulphuric acid solution. With 0.2 mole copper sulphate in 1 mole sulphuric acid solution one



EXPERIMENTAL SETUP

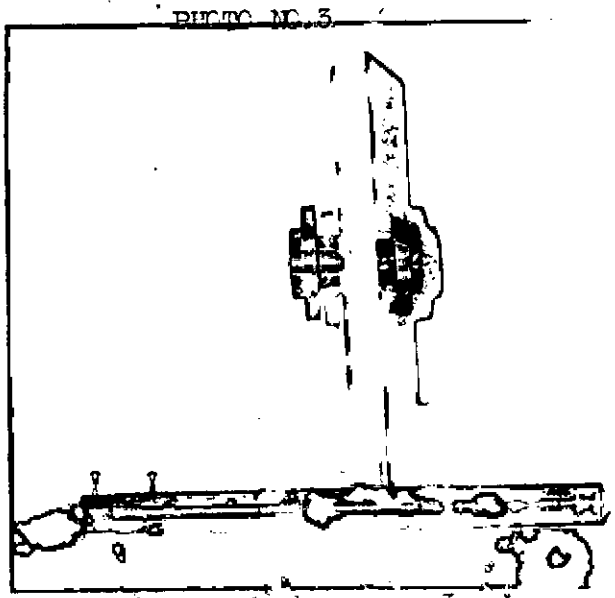
FIG. NO. 4




1

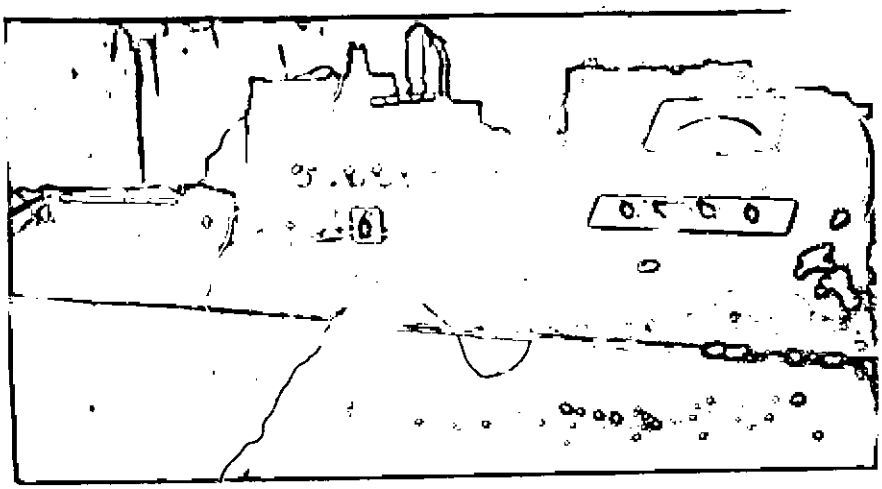
P[illegible]R(CATHODE) WITH P.V.C.INSULATING SLEEVES C[illegible]

PHOTO NO.3



[illegible]EASURING INSTRUMENTS,RHEOSTATS,AND WET CELLS

PHOTO.NO.4



run was carriedout at stagnent condition (limiting current could not be obtained at all.

Results and Discussions

Current densities were plotted against the electrode potential. The curves obtained were not at all satisfactory. Limiting currents could not be obtained distinctly. But the effect of mass transfer on rotational speed was to some extent clear (see graph No. 4) that is the higher the rotational speed the greater the current is mass transfer.

With 0.2 mole copper sulphate and 1 mole sulphuric acid solution at stagnent condition no trace of limiting current could be obtained and as such the experiment was not carriedout with rotating electrode (see graph No.2)

Once at stagnet condition, with 0.1 mole copper sulphate and 1N sulphuric acid solution limiting current was obtained very distinctly (graph No. 5). But after dismantelling the cell a large portion of polysterine coating at the bottom of the electrode (cathode) was found broken which might have happened at the time of assembling the cell. The protective coating was reapplied on the damaged portion and the same experiment was repeated when no distinct limiting current was obtained (graph - 5).

While investigating the reason for not getting the limiting current, it was found that instead of measuring the electode potential, IR drop accross the cell was being measured because the whole cathode was made of conducting material (copper) and the polysterine coating on it was acting as

resistance the electrode area considered for reaction was very small (0.2 cm) in comparison to the whole cathode area. This was the reason to get limiting current when a large portion of the polysterine coating was broken.

However, it must be mentioned here that the IR drop accross the solution was very insignificatnt as compared to that accross the thin polystyrene coating (an insulating material). As such in all the potential reading an error had crept in.

Due to the reasons mentioned above expected results could not be obtained. Sine limiting current is directly proportional to mass transfer coefficient (equation 8), mass transfer correlations could not be established.

Due to the shortage of time the experiment had to be postponed at this stage.

Suggestions for future work.

From the discussion it has been made clear that the cathode (rotor) should not be made of conducting material to avoid the situation the author faced. And as such it is felt that the cathode (rotor) should be made of an insulating material viz. ebruite, PVC. On the lower past of the insulating rod a detachable copper ring has to be mounted which will act as cathode. Special arrangment is to be made for making electrical connection with the said cathode ring.

The effect of mass transfer on electrode length may be studied by varying the weidth of the detachable copper ring.

With the same installation with little modification the effect of mass transfer on cylinder (anode) diameter may also be studied as done by Eisenberg, M, et, al, (45) on a different system.

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APPENDIX

SOLUTION NO. 1.

0.1 Mole $CuSo_4$, $5H_2O$ in 1N H_2SO_4

Area of the Cathode = 1.81 cm^2

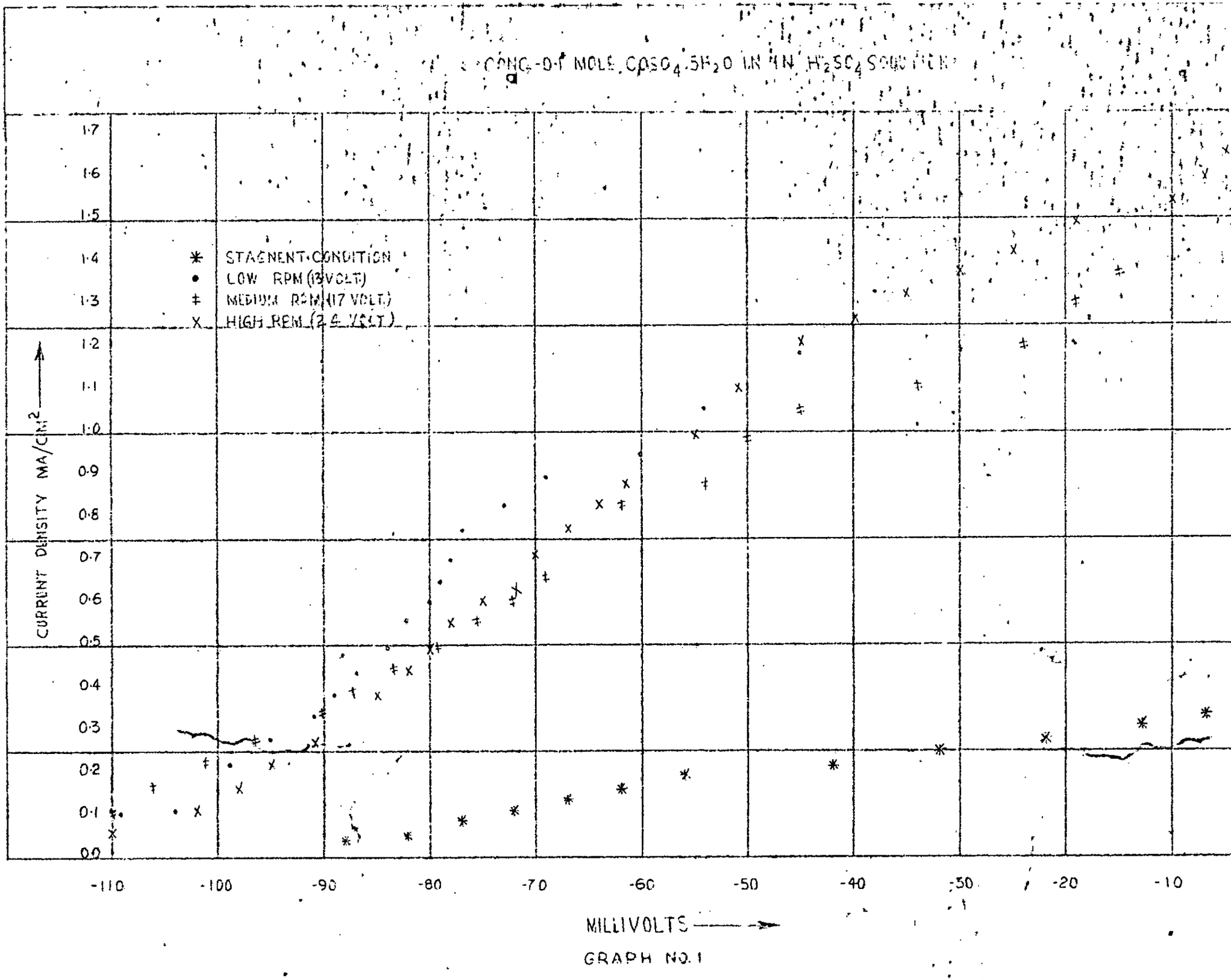
RPM	ZCP (mv)	Milli-Amps	Milli Volts	ma/cm^2	Corrected mv.	Milli-Amps	Milli volts	ma/cm^2	Corrected mv.
Medium RPM (17volts)	-59	0.025	-56	0.0138	-115	0.925	-20	0.5106	-79
		0.050	-55	0.0276	-114	0.950	-19.5	0.5244	-78.5
		0.075	-55	0.0414	-114	0.975	-17.5	0.5382	-76.5
		0.100	-55	0.0552	-114	1.000	-16.5	0.5520	-75.5
		0.125	-54.5	0.0690	-113.5	1.025	-16.0	0.5658	-75.0
		0.150	-55	0.0828	-112	1.050	-15.0	0.5796	-74.0
		0.175	-52	0.0966	-111	1.075	-14.5	0.5934	-73.5
		0.200	-51.5	0.1104	-110.5	1.100	-13	0.6072	-72
		0.225	-50.0	0.1242	-109	1.125	-12	0.6210	-71
		0.250	-49.5	0.1380	-108.5	1.150	-11	0.6348	-70
		0.275	-48	0.1518	-107	1.175	-10	0.6486	-69
		00300	-47	0.1656	-106	1.200	-9.9	0.6624	-68.9
		0.325	-46	0.1794	-105	1.500	-5	0.8280	-62
		0.350	-45	0.1932	-104	1.525	0	0.8418	-59
		0.375	-43	0.2070	-102	1.600	+5	0.885	-54
		0.400	-42	0.2218	-101	1.800	+9	0.995	-50
		0.425	-40	0.2346	-99	1.900	+14	1.05	-45
		0.450	-39.5	0.2484	-98.5	2.000	+25	1.105	-34
		0.475	-39	0.2622	-98	2.300	+55	1.27	-24
		0.500	-39	0.2760	-98	2.400	+40	1.325	-19
		0.525	-37.5	0.2898	-96.5	2.500	+44	1.380	-15
		0.550	-36	0.3036	-94	2.600	+47	1.435	-12
		0.575	-34	0.3174	-95	2.700	+51	1.490	-8
		0.600	-32	0.3312	-91				
		0.625	-30	0.3450	-89				
		0.650	-29.9	0.3588	-88.9				
		0.675	-29	0.3726	-88				
		0.700	-28	0.3864	-87				
		0.725	-27.5	0.4002	-86.5				
		0.750	-26	0.4140	-85				
		0.775	-25	0.4278	-84				
		0.800	-24.5	0.4426	-85.5				
		0.825	-23	0.4554	-82				
		0.850	-22	0.4692	-81				
		0.875	-21	0.4830	-80				
		0.900	-20	0.4978	-79				

SOLUTION NO. 1.

RPM	ZCP (MV)	Milli-Amps	Milli Volts	$\frac{ma}{cm^2}$	Corrected mv.
Low RPM (15volts)	-69	0.10	-55	0.555	-112
		0.20	-50	0.111	-109
		0.30	-45	0.166	-104
		0.40	-40	0.221	-99
		0.50	-36	0.276	-95
		0.60	-32	0.331	-91
		0.70	-30	0.386	-89
		0.80	-26	0.442	-87
		0.90	-25	0.497	-84
		1.00	-25	0.555	-82
		1.10	-21	0.607	-80
		1.20	-20	0.665	-79
		1.30	-19	0.718	-78
		1.40	-18	0.774	-77
		1.50	-14	0.830	-75
		1.60	-10	0.885	-69
		1.70	- 1	0.940	-60
		1.90	+5	1.05	-54
		2.10	10	1.16	-49
		2.20	14	1.216	-45
		2.40	21	1.325	-38
		2.50	25	1.38	-34

SOLUTION NO. 1.

RPM	ZCP (MV)	Milli-Amps	Milli Volts	$\frac{ma}{cm^2}$	Corrected mv.
High RPM (24volts)	-60	0.10	-50	0.0555	-110
		0.20	-42	0.1110	-102
		0.30	-38	0.166	-98
		0.40	-35	0.221	-95
		0.50	-31	0.276	-91
		0.60	-30	0.331	-90
		0.70	-25	0.386	-85
		0.80	-22	0.442	-82
		0.90	-20	0.497	-80
		1.00	-18	0.555	-78
		1.10	-15	0.607	-75
		1.20	-12	0.663	-72
		1.30	-10	0.718	-70
		1.40	-7	0.774	-67
		1.50	-4	0.830	-64.8
		1.60	-1.5	0.885	-61.5
		1.70	0	0.94	-60
		1.80	+5	0.995	-55
		2.00	9	1.105	-51
		2.10	11	1.16	-49
		2.20	15	1.216	-45
		2.30	20	1.27	-40
		2.40	25	1.325	-35
		2.50	30	1.38	-30
		2.60	35	1.435	-25
		2.70	41	1.49	-19
		2.80	50	1.545	-00
		2.90	53	1.60	-7
		3.00	55	1.66	-5
		3.10	60	1.715	- 0
		3.30	65	1.82	+ 5
		3.40	60	1.88	0


CONC-0·1 MOLE $CoSO_4.5H_2O$ IN 1N H_2SO_4 SOLUTION
* STAGNENT CONDITION
• LOW RPM (13 VOLT)
‡ MEDIUM RPM (17 VOLT)
X HIGH RPM (2.5 VOLT)
CURRENT DENSITY MA/CM²
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
-110
-100
-90
-80
-70
-60
-50
-40
-30
-20
-10
MILLIVOLTS

GRAPH NO. 1

SOLUTION NO. 1.

RPM	ZCP (MV)	Milli-Amps	Milli Volts	$\frac{ma}{cm^2}$	Corrected MV
Stagnent Solution (broken Polyste-rine Coating)	-55	0.025	-51	0.0138	-106
		0.050	-50.5	0.0276	-105.5
		0.075	-50.0	0.0414	-105
		0.100	-50.0	0.0552	-105
		0.125	- 50.0	0.0690	-105
		0.150	-50.0	0.0828	-105
		0.175	-50.0	0.0966	-105
		0.200	-50.0	0.1104	-105
		0.225	-49.9	0.1242	-104.5
		0.250	-49.3	0.1380	-104.6
		0.275	-49	0.1478	-104
		0.300	-48	0.1616	-103
		0.325	-48	0.1754	-103
		0.350	-48	0.1892	-103
		0.375	-47.5	0.2030	-102.5
		0.400	-47.5	0.2168	-102.5
		0.425	-47.5	0.2306	-102.5
		0.450	-47	0.2444	-102
		0.475	-47	0.2582	-102
		0.500	-46.5	0.2720	-101.5
		0.525	-46.5	0.2858	-101.5
		0.550	-45	0.2996	-100
		0.575	+40	0.3154	-15
		0.600	45	0.3272	-10
		0.625	20	0.3410	-35
		0.650	25	0.3548	-35
		0.675	20	0.3686	-30
		0.700			
		0.750	20	0.4100	-35
		0.775	10	0.4218	-45

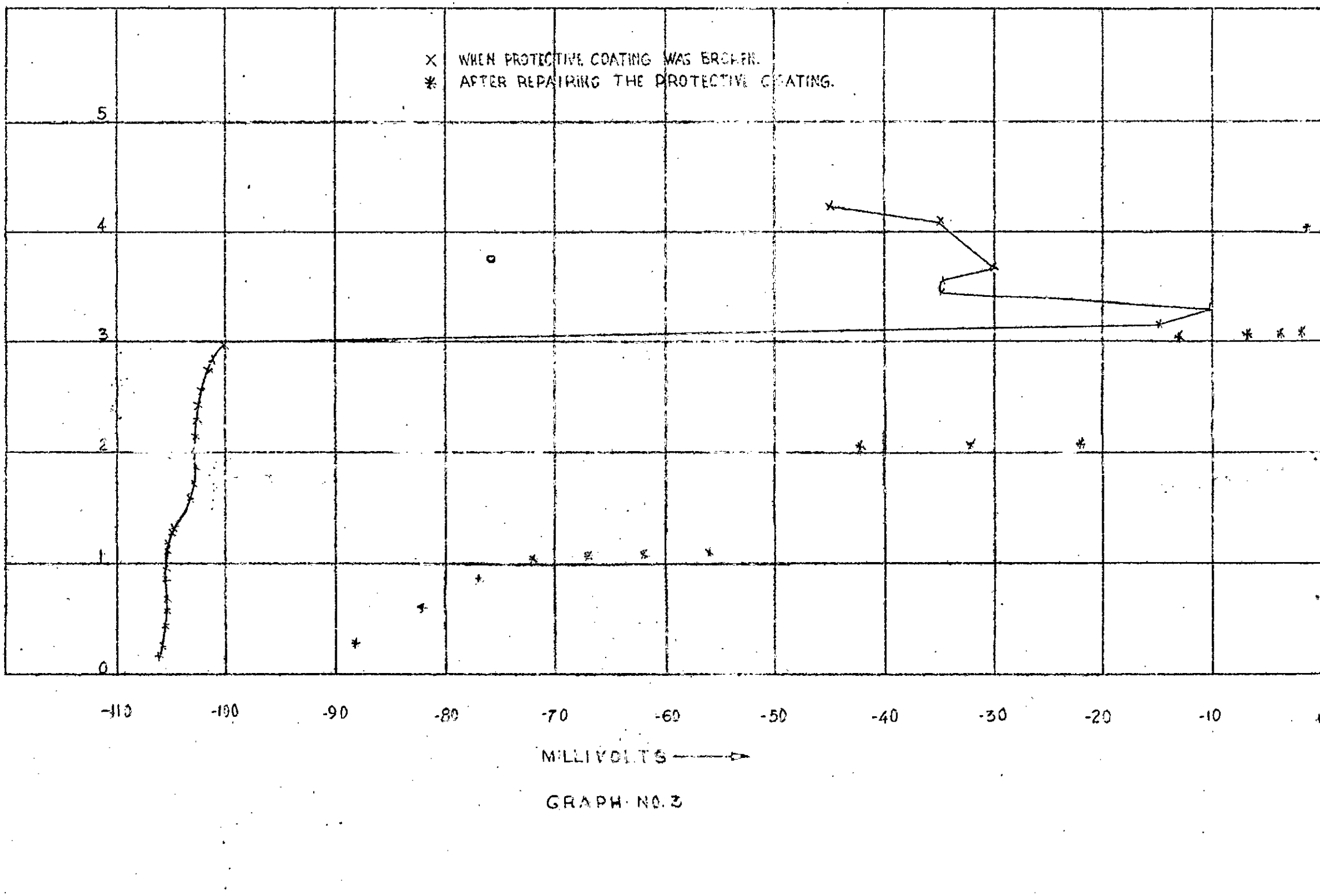
SOLUTION NO. 1.

RPM	ZCP (MV)	Milli-Amps.	Milli Volts	MA / CM²	Corrected MV
Stagnent Solution (after repairing the Pâlys-terine Coating)	-52	0.050	-56	0.0276	-88
		0.100	-50	0.0555	-82
		0.150	-25	0.0851	-77
		0.200	-20	0.111	-72
		0.250	-15	0.138	-67
		0.300	-10	0.166	-62
		0.350	-4	0.1955	-56
		0.400	+10	0.221	-42
		0.450	20	0.2486	-32
		0.500	30	0.276	-22
		0.550	39	0.304	-13
		0.600	45	0.331	-7
		0.650	48	0.359	-4
		0.700	50	0.386	-2
		0.750	50.5	0.415	-1.5

STAGNENT SOLUTION

CONC.-0·1 MOLE, $CUSO_4, 5H_2O$ IN 1N H_2SO_4 SOLUTION

LIMITING CURRENT = 0·3 MILLIAMPERE/CM^2



GRAPH NO. 3

SOLUTION NO. 2.

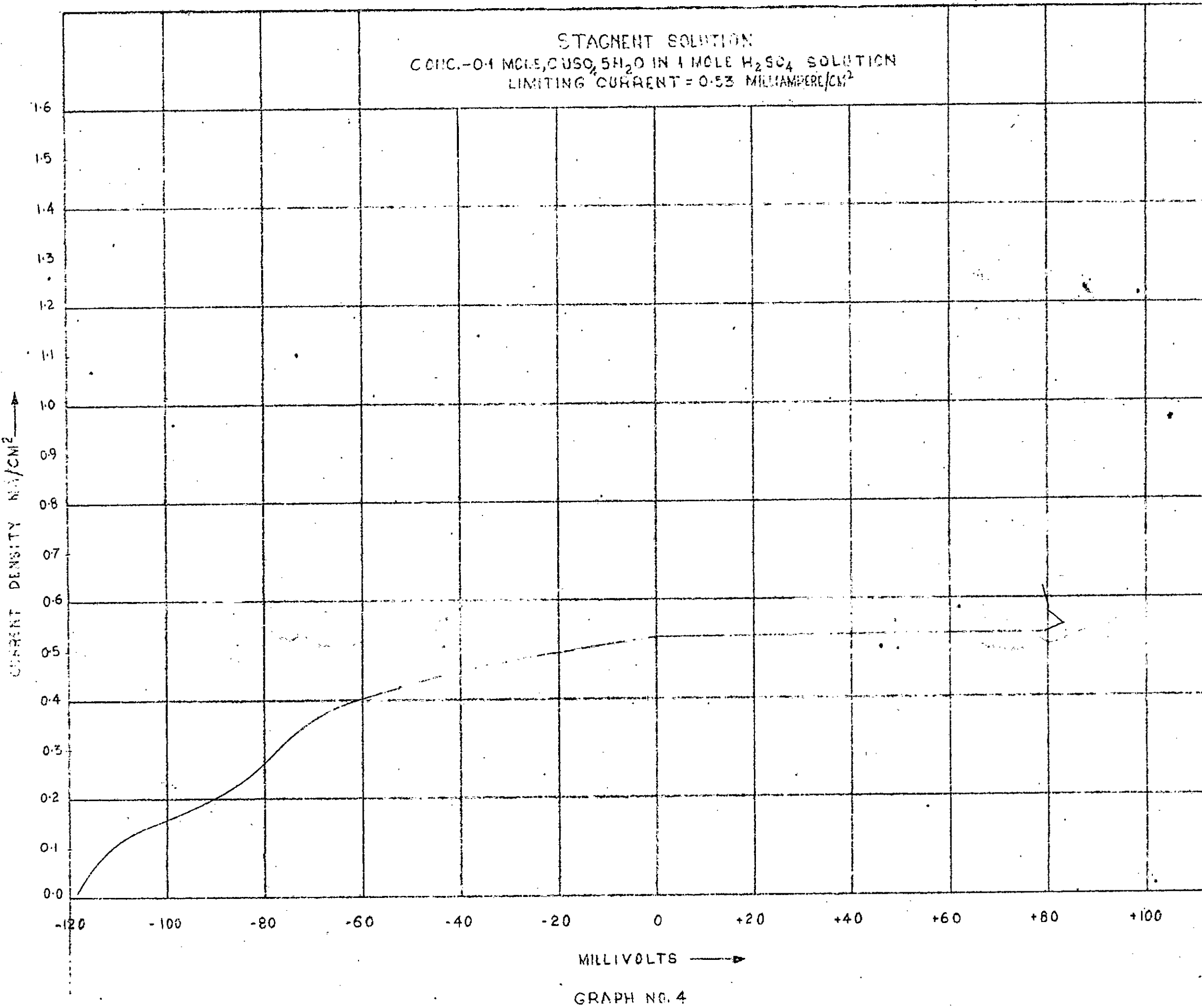
0.1 Mole $CuSo_4$, $5H_2O$ in 1 Mole H_2SO_4

RPM	ZCP	Milli-Amps.	Milli Volts	$\frac{MA}{CM^2}$	Corrected MV	Milli-Amps.	Milli Volts	$\frac{MA}{CM^2}$	Corrected MV
Stagnant Condition	-60	0.025	-58	0.0138	-118	0.875	80	0.4790	-30
		0.050	-57	0.0276	-117	0.900	40	0.4926	-20
		0.075	-56	0.0414	-116	0.950	60	0.5204	0
		0.100	-55	0.0552	-115	0.975	159	0.5342	+79
		0.125	-54	0.0690	-114	1.000	145	0.5480	65
		0.150	-53	0.0828	-113	1.025	141	0.5618	81
		0.175	-51.5	0.0966	-111.5	1.050	140	0.5756	80
		0.200	-50	0.1104	-110	1.075	140	0.5894	80
		0.225	-48	0.1242	-108	1.100	159	0.6032	79
		0.250	-45	0.1380	-105				
		0.275	-42.5	0.1478	-102.5				
		0.300	-38	0.1616	-98				
		09325	-35	0.1754	-95				
		0.350	-32	0.1892	-92				
		0.375	-28.5	0.2050	-88.5				
		0.400	-27	0.2168	-88				
		0.425	-25	0.2306	-85				
		0.450	-25.5	0.2444	-85.5				
		0.475	-22	0.2582	-82				
		0.522	-21	0.2720	-81				
		0.525	-20	0.2858	-80				
		0.550	-18	0.2996	-78				
		0.575	-15.5	0.3134	-75.5				
		0.600	-14	0.3272	-74				
		0.625	-12	0.3410	-72				
		0.650	-10	0.3548	-70				
		0.675	-8	0.3686	-68				
		0.700	-5	0.3824	-65				
		0.725	-2	0.3962	-62				
		0.750	+5	0.4100	-57				
		0.775	7	0.4238	-55				
		0.800	17	0.4376	-45				
		0.850	22	0.465	-38				

STAGNENT SOLUTION

CONC.-0·1 MOLE, $CuSO_4 5H_2O$ IN 1 MOLE H_2SO_4 SOLUTION

LIMITING CURRENT = 0·53 MILLIAMPERE/CM^2



GRAPH NO. 4

SOLUTION NO 5.

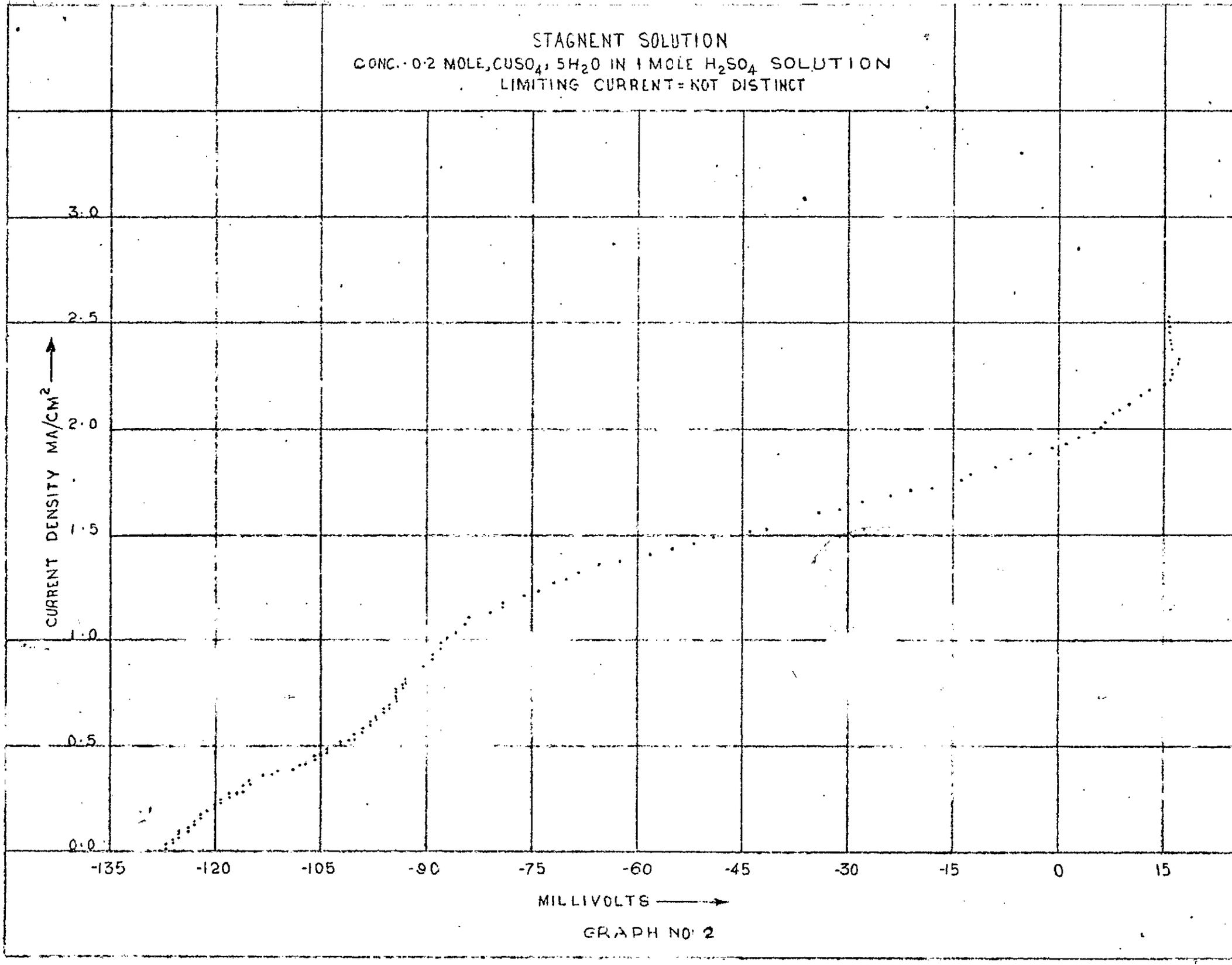
0.2 Mole $CuSo_4, 5H_2O$ in 1N H_2So_4

RPM	ZCP	Milli-Amps.	Milli Volts	$\frac{MA}{CM^2}$	Corrected MV	Milli-Amps.	Milli Volts	$\frac{MA}{CM^2}$	Corrected MV
Stag-nent Condi-tion	-64	0.025	-63	0.0138	-127	0.850	-41	0.4652	-105
		0.050	-63	0.0276	-127	0.875	-40	0.4790	-104
		0.075	-62	0.6414	-126	0.900	-40	0.4978	-104
		0.100	-62	0.0552	-126	0.925	-38	0.5066	-102
		0.125	-61	0.0690	-125	0.950	-38	0.5204	-102
		0.150	-61	0.0828	-125	0.975	-37	0.5342	-101
		0.175	-61	0.0966	-125	1.000	-36	0.5480	-100
		0.200	-60	0.1104	-124	1.025	-36	0.5618	-100
		0.225	-60	0.1242	-124	1.050	-35	0.5756	-99
		0.250	-59	0.1340	-125	1.075	-35	0.5994	-99
		0.275	-59	0.1478	-125	1.100	-34	0.6032	-98
		0.300	-58	0.1666	-122	1.125	-34	0.6170	-98
		0.325	-58	0.1754	-122	1.150	-33	0.6308	-97
		0.350	-57	0.1892	-121	1.175	-33	0.6446	-97
		0.375	-56	0.2550	-120	1.200	-32	0.6584	-96
		0.400	-56	0.2168	-120	1.225	-32	0.6722	-96
		0.425	-55	0.2306	-119	1.250	-31	0.6860	-95
		0.450	-55	0.2444	-119	1.275	-31	0.6998	-95
		0.475	-54	0.2582	-118	1.300	-30	0.7136	-94
		0.500	-54	0.2720	-118	1.325	-30	0.7274	-94
		0.525	-53	0.2858	-117	1.350	-30	0.7412	-94
		0.550	-52	0.2996	-116	1.375	-30	0.7550	-94
		0.575	-52	0.3134	-116	1.425	-29.5	0.7826	-93.5
		0.600	-51	0.3272	-115	1.450	-29.5	0.7964	-93.5
		0.625	-51	0.3410	-115	1.475	-29	0.8102	-93
		0.650	-49	0.3548	-113	1.500	-29	0.8240	-93
		0.675	-48	0.3686	-112	1.600	-28.5	0.8842	-90.5
		0.700	-47	0.3824	-111	1.650	-25	0.9118	-89
		0.725	-45	0.3962	-109	1.700	-25	0.9394	-89
		0.750	-44	0.4100	-108	1.750	-24.5	0.9670	-88.5
		0.775	-45	0.4238	-107	1.800	-24	0.9946	-88
		0.800	-42	0.4376	-106	1.850	-23	1.0222	-87
		0.825	-42	0.4514	-106	1.900	-22	1.0498	-86

Contd.

SOLUTION NO. 5 (Contd)

RPM	ZCP	Milli-Amps.	Milli Volts	MA/CM²	Corrected MV	Milli-Amps.	Milli Volts	MA/CM²	Corrected MV
		1.950	-20.5	1.0774	-84.5	3.750	71.5	2.0710	7.5
		2.000	-20	1.1050	-84.0	3.800	72.5	2.0986	8.5
		2.050	-17	1.1326	-81.0	3.850	74.0	2.1262	10.0
		2.100	-15	1.1602	-79.0	3.900	75.5	2.1538	11.5
		2.150	-15	1.1878	-79.0	3.950	77.5	2.1814	13.5
		2.200	-12.5	1.2154	-76.5	4.000	79.0	2.2090	15.0
		2.250	-10.5	1.2430	-74.5	4.050	79.5	2.2366	15.5
		2.300	-8.0	1.2706	-72	4.100	80	2.2642	16
		2.350	-6.0	1.2982	-70	4.150	80	2.2918	16
		2.400	-4	1.3258	-68	4.200	81	2.3194	17
		2.450	-1	1.3534	-65	4.250	81	2.3470	17
		2.500	+2	1.3810	-62	4.300	80	2.3746	16
		2.550	5.5	1.4086	-58.5	4.350	80	2.4022	16
		2.600	9	1.4362	-55	4.400	80	2.4298	16
		2.650	12	1.4638	-52	4.450	80	2.4574	16
		2.700	15	1.4914	-49	4.500	80	2.4850	16
		2.750	20	1.5190	-44	4.550	80	2.5126	16
		2.800	25	1.5466	-41	4.600	80	2.5402	16
		2.900	50	1.6018	-54				
		2.950	35	1.6294	-31				
		3.000	36	1.6570	-28				
		3.050	40	1.6846	-24				
		3.100	42.5	1.7122	-21.5				
		3.150	46	1.7398	-18				
		3.200	50	1.7674	-14				
		3.250	51.5	1.7950	-12.5				
		3.300	55	1.8226	-9				
		3.350	57	1.8520	-7				
		3.400	60	1.8774	-4				
		3.450	65	1.9054	-1				
		3.500	65	1.9330	+1				
		3.550	67	1.9606	3				
		3.600	69	1.9882	5				
		3.650	70	2.0158	6				
		3.700	70.5	2.0434	6.5				


STAGNENT SOLUTION
CONC.-0·2 MOLE, $CUSO_4$, $5H_2O$ IN 1 MOLE H_2SO_4 SOLUTION
LIMITING CURRENT = NOT DISTINCT
CURRENT DENSITY MA/CM²
3·0
2·5
2·0
1·5
1·0
0·5
0·0
-135
-120
-105
-90
-75
-60
-45
-30
-15
0
15
MILLIVOLTS

GRAPH NO: 2