FUEL CELLS:

EFFECT OF CURRENT ON THE GAS-SOLUTION-ELECTRODE INTERFACE CONTACT ANGLE

by

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Dear Sir:

A thesis entitled "Fuel Cells: Effect of Current on the Gas-Solution-Electrode Contact Angle" is herewith submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering.

Respectfully submitted,

Xavier L. Simon

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I. SUMMARY.

The object of this thesis was to study the effect that current density has on the contact angle associated with the gas-liquid-solid reaction zone interface found within a porous electrode of a fuel cell. Knowledge of this effect should permit better control of electrolyte penetration into porous electrodes. Concentration polarizations and the "drowning" of electrodes after long periods of operation can be avoided with proper control of electrolyte penetration.

The contact angle dependance on current was studied mainly by the Wilhelmy slide method, which permits direct measurement of the liquid surface tension and the cosine of the contact angle. This particular method provided extreme sensitivity to any changes in the angle.

In graphite surfaces, prepared on 30% porous graphite, two different phenomena were observed. When the graphite slide was the cathode, in 1N H_2SO_4, application of currents up to 0.91 ma/cm^2, for one minute, failed to change the angle. However, shorting the cell to discharge the back emf built up during this minute brought about a definite change in the contact angle of 2-12°, to a final angle of 67-72°. No penetration of electrolyte into the porous graphite was observed with the cathode.

When the porous graphite slide was the anode, application of currents of 0.5-2.0 ma/cm^2 caused the

contact angle to decrease from 75-85° to 45-60°, with both acidic and basic electrolyte. Furthermore, flooding takes place with 40-50% of the pores being filled when acidic electrolyte is used, and 15-25% when basic electrolyte is used.

The results obtained with copper and nickel failed to show any definite dependence of the contact angle on current density. The only other surface studied was platinum and here it was found that the contact angle is not a function of current density.

Finally, it was found that the changes in graphite surfaces were irreversible. However, the surface could be made lyophobic again by polishing or heating.

It is suggested that the changes in the anodic graphite surfaces are due to an oxidation of the outside layers followed by adsorption of the CO_2 and CO produced. For cathodic surfaces it is suggested that the changes are due to hydrogen adsorption during the discharging.

II. INTRODUCTION.

2.1. The Fuel Cell. A fuel cell may be defined as an electrochemical device in which the chemical energy of a fuel is converted directly and usefully into low-voltage direct-current electrical energy. In the traditional sense, the fuel cell is a power plant in that it consumes fuel, combines the fuel with an oxidant, and converts the resultant energy of combustion into a useful form of electrical power. The main attractiveness of the fuel cell is the directness with which it converts chemical energy into electrical energy. In the conventional heat engine the chemical energy of combustion is first degraded into heat with the consequence that the theoretical efficiency is limited to the Carnot-cycle efficiency. On the other hand, in the fuel cell, when functioning perfectly, the chemical energy is converted isothermally to electrical energy. Thus theoretical efficiencies of 100% are possible. With some experimental cells efficiencies of 80% have been reached.

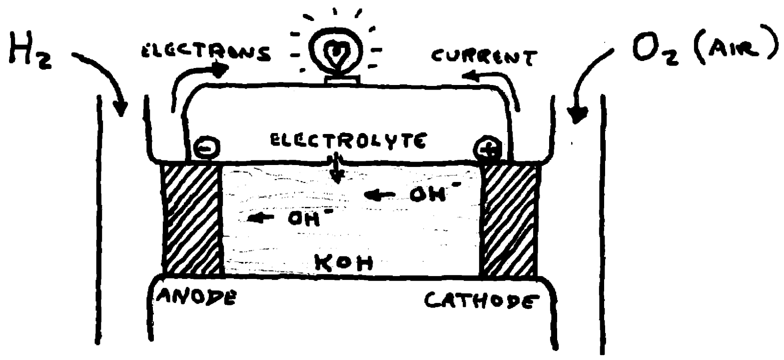
In addition to its high efficiency, the fuel cell has other potential advantages. In theory it can operate on cheap hydrocarbon fuels, and it appears to promise high power per unit weight and volume, low capital investment and upkeep, and long life. Presently, these and many more potentially attainable characteristics are being sought and in some cases have been achieved. However, the need for more research is imperative if the fuel cell is to operate at its theoretical optimum.(6)(7)(13)

2.2. Operation. The fuel cell does not differ fundamentally in its operation from the conventional battery. The difference lies in that the battery stores the energy that it converts while the fuel cell is a continuously feed device.

Depending on the projected applications, fuel cells have been designed to operate at low and medium temperatures using aqueous electrolytes, and at high temperatures using molten salt electrolytes. Cells of other types have also been designed.(13)

To illustrate how a fuel cell operates let us consider a hydrogen-oxygen fuel cell. It is the simplest type and combines all the basic characteristics. In addition it serves to illustrate some of the main variables and bottlenecks in present fuel cell technology.

In this cell, hydrogen (fuel) is fed to the anode, and oxygen (or air) to the cathode (Figure 2.1).



$$H_2 + 2OH^- = 2H_2O + 2e \qquad O_2 + H_2O + 2e = HO_2^- + OH^-$$

$$HO_2^- = OH^- + \tfrac{1}{2}O_2$$

Figure 2.1. The Hydrogen-Oxygen Fuel Cell.

At the anode, hydrogen combines with a hydroxyl ion to produce water and release electrons to the circuit. These electrons do work on the way to the cathode, where they combine with oxygen and water to produce hydroxide ions and undesirable peroxides. The circuit is completed through the electrolyte where hydroxyl ions are the main transport medium.

Since the reaction takes place at the surface of the electrode, it is desirable to have a high surface area to obtain high current densities. This is accomplished by use of porous electrodes.

The electrolytes usually employed are basic. Thermodynamically, it would be desirable to have acid electrolytes since the theoretical energy released would be higher. However, many irreversibilities have been encountered in the use of acidic mediums. Until these irreversibilities are overcome, basic electrolytes will continue to give better performance.

In the case of basic electrolytes, with the use of the proper peroxide decomposing catalyst at the cathode, the peroxide-forming reaction can be kept low enough to be neglected. In practice this has been achieved.

2.3. Performance. The open circuit potential is given by the Nernst equation and it is found to be 1.10 to 1.13 (depending on pH) volts, for low peroxide concentration.

In practice, however, the open circuit potential is not attained. This is due mainly to the nature of the electrode mechanism. Basically, three main types of polarization limit the efficiency of the cell. They are, activation polarization, concentration polarization, and ohmic resistance polarization.

Activation polarization can be divided into two main types, reaction activation polarization and activation polarization of chemisorption. The first has to do with the energy barrier that has to be overcome if the cell reactions are to proceed. A minimum activation energy has to be provided to the reactants before they combine.

If we consider the reaction taking place at the anode, we have,

$$H_2 + 2 \text{ active sites} = 2(H) \text{ chemisorbed}$$

$$(H) + OH^- = H_2O + e + \text{active site.}$$

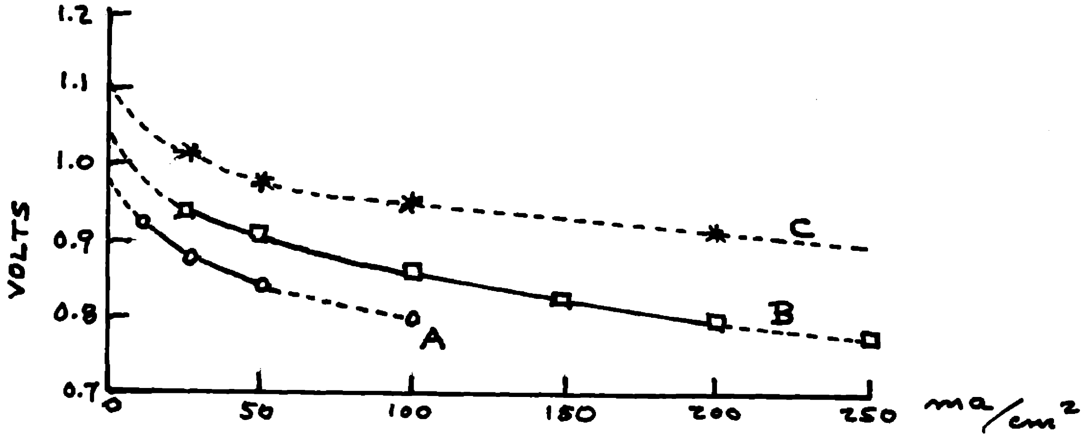
In other words, hydrogen is first chemisorbed into active sites of the electrode. If the chemisorption is slow during current flow, as could he the case for high currents, the electrochemical reaction comes into balance with the chemisorption and an additional polarization is introduced due to the free energy of chemisorption.(14)

Concentration polarization occurs when the areas near the reaction zone are depleted of reactant. This is noticeable especially at high current densities because reactants are consumed faster than they can be supplied to the reaction zone. This is particularly significant when we consider that transport to the reaction zone must take place within the pores of the electrodes. The transport process in the porous electrodes will be considered in more detail in the next section.

Ohmic polarization is due to an internal loss of potential due to the electrical resistance of the electrolyte.

These three types of polarization are by no means the only factors that lower the efficiency of the fuel cell. However, they are among the more important and present a picture of the problems yet to be solved by fuel cell technology.

Figure 2.2 illustrates some performance parameters obtained by Union Carbide fuel cells operating with basic electrolyte.(15)



A - $60^\circ C$ O_2/H_2, Atmospheric pressure (1958)
B - $60^\circ C$ O_2/H_2, 150 p.s.i.g. (1958)
C - $60^\circ C$ O_2/H_2, Atmospheric pressure (1959)

----- Denotes lack of long-time data.

Figure 2.2. Performance parameters of Union Carbide cells.

2.4. Transport Process in Porous Electrodes. The need for large surface area of reaction to obtain high current densities has made the use of porous electrodes necessary. Sintered porous metal electrodes and porous carbon electrodes are the most widely used. They consist of macropores (10^{-3} to 10^{-5} cm.), where the transport processes take place, and smaller pores or microcapillaries which provide extensive reaction area.

The reaction zone is usually wihtin the electrode. Furthermore, since the diffusion of ions in liquid is much slower than diffusion in gas, then, assuming that transport of reactants and products takes place mainly by diffusion, it is desired to keep the reaction zone close to the electrolyte side; otherwise electrolyte concentration polarization would be encountered at low current densities. (Figure 2.3).

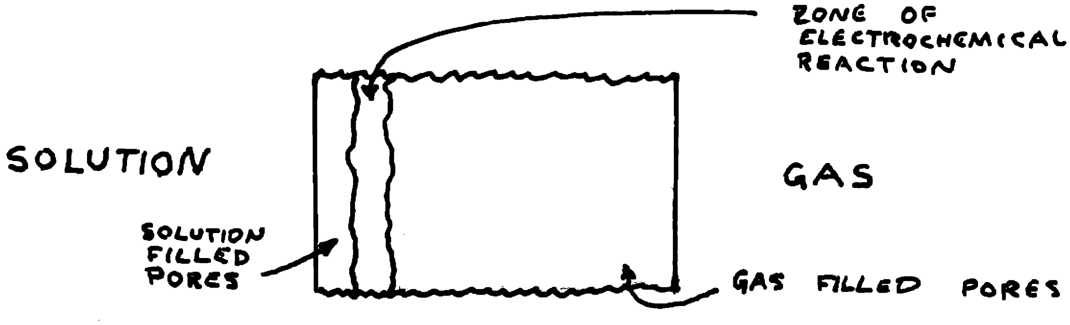


Figure 2.3. Model of porous electrode.

To avoid penetration of electrolyte into the electrode pores, the wetting properties of the electrolyte and electrode must be of such nature that low wetting prevails (lyophobic). If the electrode surface allows good wetting (lyophilic), a high pressure has to be mantained on the gas side of the electrode if penetration is to be kept at a minimum. (Figure 2.4).

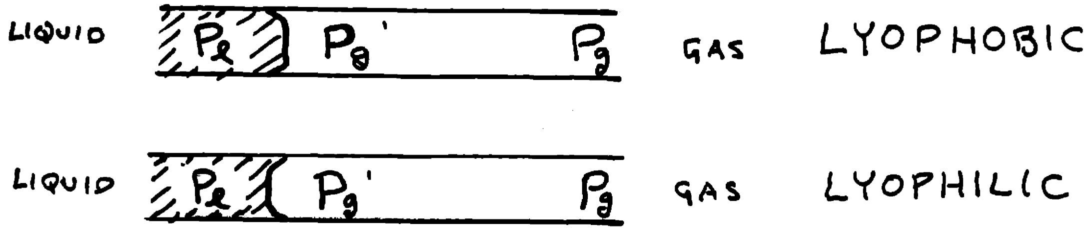


Figure 2.4. Gas-solution interface in capillaries.

Of the elctrodes used presently, it appears that metallic electrodes are lyophilic, while carbon electrodes are lyophobic. For either case the pressure difference between the gas phase and the liquid phase can be derived directly from Laplace's relationship(2), and is given by,

$$P_1 - P_g' = - \frac{2\gamma_{LA}}{r} \cos \theta \qquad (1)$$

where γ_{LA} is the liquid gas interfacial tension, r is the radius of the capillary, and θ is the contact angle associated with the gas-liquid-solid interface. For lyophobic surfaces, θ is between 90° and 180°, so that $\cos\theta$ is negative and the pressure in the gas phase is less than in the liquid phase. For the lyophilic case, clearly, the pressure would be higher in the gas phase.

Gas transport within the electrodes of the type described above can occur through the following mechanisms:

1) Viscous flow under a pressure gradient in the gas filled pores.

2) Bulk diffusion.

3) Knudsen diffusion (diffusion of molecules through pores smaller in diameter than the mean free path of the gas molecules).

4) Surface migration.

5) Diffusion of dissolved oxygen through the filled pores.

Viscous flow may be assumed non-functional, since it has been shown that, even for the purest gas fuels,some inerts accumulate within the electrode pores.

Under normal circumstances it can be assumed that diffusion is the primary transport mechanism. Bulk diffusion in particular is believed to be the principal mean of transport to within a few microns of the reaction zone. It is also believed to be the rate controlling mechanism for gas transport.

As the reaction proceeds, at the cathode, oxygen is consumed and a concentration gradient will be set up so that oxygen will diffuse from outside the electrode into the reaction zone. The oxygen will diffuse through the atmosphere of inerts that slowly accumulates within the pores. If oxygen can be supplied as fast as it is consumed there will be no change in the oxygen partial pressure at the reaction zone, and this pressure will be equal to the outside partial pressure, $P'_{O_2} = P_{O_2}$ (Fig. 2.4). However, if the current density is increased enough, the oxygen will be consumed faster than it can be supplied by the concentration gradient and the pressure of the oxygen at the reaction zone, P_{O_2}, will fall. When this happens, the emf of the cell drops due to what is called "gas transport concentration polarization", occurring. This emf drop, or concentration polarization, is given by the Nernst equation,

$$\eta_c = \frac{RT}{nF} \ln \frac{P_{O_2}}{P'_{O_2}} \qquad (2)$$

The reversible potential of the cell is for a pressure P_{O_2} and thus if this pressure falls to P_{O_2}', the reversible emf will drop by η_c. Therefore, increasing the current drain too much will give concentration polarization.

2.5. The Nature of the Problem.

With this background on fuel cells and the transport process in porous electrodes, it is now possible to present the problem that was studied in this thesis.

From the previous discussion two things are clear: one, that the reaction zone has to be mantained near the electrolyte side of the electrode; and, two, that the gas pressure required to do this is a function of the contact angle that the electrolyte makes with the walls of the capillaries (equation 1). It is also apparent that if the gas pressure is not sufficient the electrolyte may flood the electrode, while if the pressure is to high the gas will go through the pores and into the electrolyte. Control of the gas pressure is not simple and it can become extremely difficult if the contact angle changes during the operation of the fuel cell.

In actual practice, flooding of electrodes during operation has been encountered in at least one laboratory. Flooding has also been mentioned repeatedly, and just as often, it has been ascribed to contact angle changes.

Yeager(12) states that with high current densities in carbon electrodes, "chemical modifications will occur in the nature of the electrode surface and these modifications will result in contact angle changes which lead to penetration of the electrolytic solution further into the electrode systems." Yeager, however, gives no experimental data to support this statement.

In his work with hydrogen electrodes, Hunger(9) has encountered electrolyte penetration during operation. In experiments with electrodes wetproofed with paraffin, he found that the gas transportation pressure depends on the lenght of time that the electrodes have been operating. In his own words, "...the polarization of the hydrogen electrode increases while operating under constant loads (8 ma/cm^2), the gas pressure being kept constant. After some time (50 to 100 hours), the initial hydrogen pressure is no longer sufficient, and in order to avoid a total breakdown of the hydrogen electrode potential, the pressure has to be raised to a considerably higher value. This pressure effect seems to be due to a change in the contact angle which may be caused by a reduction of the hydrophobic layers. Although increasing the pressure causes an increase in the hydrogen potential, we have been unable to to overcome the continuous drop-off of the hydrogen electrode potential."

This problem has been one of the more important ones encountered in the design of reliable, long lasting, fuel cells. In this thesis the problem was studied further.

2.6. The Purpose of this Thesis. The purpose of this thesis was to study the effect that current density has on the contact angle associated with the gas-liquid-solid interface within the electrode of a fuel cell. Although it has been stated that the contact angle increases with current density, no specific experimental data has been presented to support this statement. It was the object of this project to obtain the experimental data to prove, or disprove, the statements made in the literature.

There are various reasons for wanting to study this effect. First, as we have seen in previous sections, it is desired to keep the reaction zone close to the electrolyte for optimum operation. Penetration of electrolyte, then, has to be kept at a minimum. An increase in the contact angle would lead to further penetration. This would cause electrolyte transport concentration polarization.

Secondly, the life of the cell and the thickness of the electrode depend on the rate of penetration of the electrolyte into the electrode. "Drowning" of electrodes has been a source of many headaches.

Finally, if it is found that the current changes the contact angle, it will be of interest to know whether this change is reversible or irreversible. If a change in the wetting properties leads to electrolyte penetration and the change is irreversible, once the electrolyte solution has penetrated into a given region of the electrode, there will be little tendency for the solution to withdraw from this region when the current is released, since the region to the rear of the interface (i.e., within the section filled with electrolyte) has become substantially more lyophilic. If the change is reversible, however, when the current is decreased the pressure on the gas side will tend to push the solution to its original position. Hunger(9) apparently found this difficult to do.

III. STATE OF THE ART.

No evidence has been found in the literature of studies made of the effect of current on the contact angle or surface tensions. Surface tensions are mentioned because they are directly related to the contact angle through Young's equation,

$$\cos \theta = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}} \qquad (3)$$

where γ_{SA} is the solid-air interfacial tension, γ_{LS} the interfacial tension between solid and liquid, and γ_{LA} that of air and liquid. (Figure 3.1).

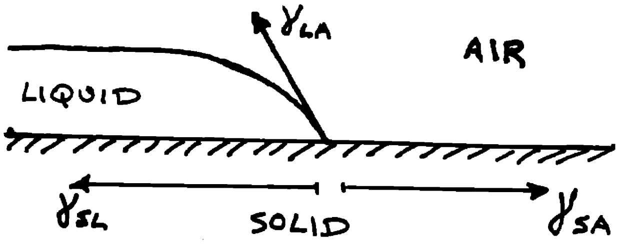


Figure 3.1. The contact angle.

Therefore, any effect that current has on surface tensions will be directly reflected on the contact angle.

Although no evidence was found of studies of the current effect, experimental data has been collected for the effect that potential, or emf, has on the solid-liquid interfacial tension of polarizable solid surfaces. This work has been done in connection with electrocapillarity. The electrocapillary curves obtained of interfacial tensions versus potential, in volts, are well known and can be found in any surface chemistry text.(1)(3)(5)

Plaksin and Kosukhova(9), according to the Chemical Abstracts, have studied the change in cosine of the contact angle and the time of wetting in the electroamalgamation of gold. They have noted that the changes of the contact angle with voltage between -o.2v and -6.5v are large, and that the cosine reaches a maximum at -2.0v.

The results obtained from studies of voltage dependence of interfacial tensions are not of any significance to this thesis because they were obtained on polarizable surfaces, i.e., mercury; this thesis is concerned with non-polarizable surfaces. The original paper of Plaksin and Kosukhova could not be obtained and thus the exact nature of their work could not be determined. However, the fact that they were amalgamating would indicate that they were dealing with polarizable surfaces. Of work done on non-polarizable surfaces, no evidence was found.

IV. PROCEDURE AND APPARATUS.

4.1. Introduction. It was seen in previous pages that the contact angle is a function of the interfacial tensions. The interfacial tensions and the contact angle were studied by the Wilhelmy Slide method. This method is very commonly used to measure the surface tension of liquids and it is treated in detail in most surface chemistry texts.

In addition to the Wilhelmy method, some contact angles were measured directly. This was done by looking at the angle that a drop or two of a liquid made with the surface on which it rested. A magnifying glass and a well marked protractor was all that was required.

4.2. Wilhelmy Slide Method. This method was chosen because of its flexibility and simplicity in operation. It allows direct measurements of the changes in the contact angle, and it is extremely sensitive to any change.

The apparatus for the Wilhelmy method consists of a thin plate, or slide, suspended from one arm of a chainematic balance and dipping into the liquid whose surface tension is to be measured. (Figure 4.1).

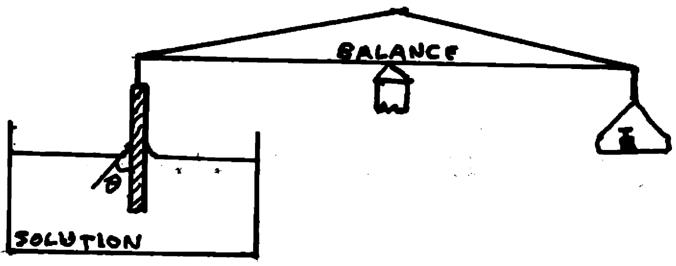


Figure 4.1. Wilhelmy Slide Method.

The weight of the slide hanging freely in the atmosphere is compared to the weight of the slide while immersed in the solution. The difference in weight will account for the liquid-air interfacial tension and its magnitude can be obtained from,

$$W_1 = W_s + 2\gamma_{LA}(t+w)\cos\theta - B \qquad (4)$$

where W_1 is the weight of the immersed slide; W_s, the weight of the slide when free; t and w, the thickness and width of the slide respectively; and B, a correction for the bouyancy effect. With this method the product $\gamma_{LA}\cos\theta$ can be measured directly.

The effect of current on the $\gamma_{LA}\cos\theta$ factor was measured directly by letting the slide be one electrode. A second electrode was immersed in the liquid near the slide, a current was then applied and changes in $\gamma_{LA}\cos\theta$, when they occurred, were read directly from the balance.

This information can be used in the following manner. It will be recalled that the contact angle is given by Young's equation,

$$\gamma_{LA}\cos\theta = \gamma_{SA} - \gamma_{SL} \qquad (3)$$

Since no current will be flowing across the solid-air and liquid-air interfaces, it will be assumed that γ_{SA} and γ_{LA} remain constant when current is applied. Therefore, if any changes in the balance readings are observed when current is applied, they will be caused solely by the liquid-solid interfacial tension changing. Furthermore, since the balance measures $\gamma_{LA} \cos\theta$, and γ_{LA} is assumed constant, any change in the balance reading will give the contact angle change directly.

How good is the assumption that γ_{LA} and γ_{SA} will not be affected by current? While Butler(5) and Adamson(9) claim that a voltage change will not affect γ_{LA} and γ_{SA} — while γ_{LS} will change if the electrode surface is polarizable — no mention is made of the effect of current. Nevertheless, I feel that it can safely be assumed that they will not be affected for there will be no current flowing across these interfaces. The validity of this assumption can be verified very simply. The ring method of measuring surface tensions could be used while a current is flowing through the solution; the current can be applied with two independent electrodes. In this thesis this was not done because it was felt that the nature of the results did not make it necessary to test the assumption. It will, however, be discussed further in a later section.

4.3. Experimental Procedure. The Wilhelmy method was used throughout most of the work. Four surfaces were used, platinum, copper, nickel, and graphite. For all four materials slides were prepared. These slides were small and thin, with average thickness of 0.01 to 0.06 cms. The width of the immersed section was about 4 cms. This provided an 8 cms. solid-liquid-air interface and minimum bouyancy.

These slides were hanged from one of the arms of the chainomatic balance. A specially designed hook was used for this purpose. The depht of slide immersion was controlled with a little jack on which the solution rested, and whose height could be varied at will.

Figure 4.2 shows the circuit used to apply the current to the Wilhelmy slide. It should be self explanatory. The sensitivity of the balance was not affected in any way.

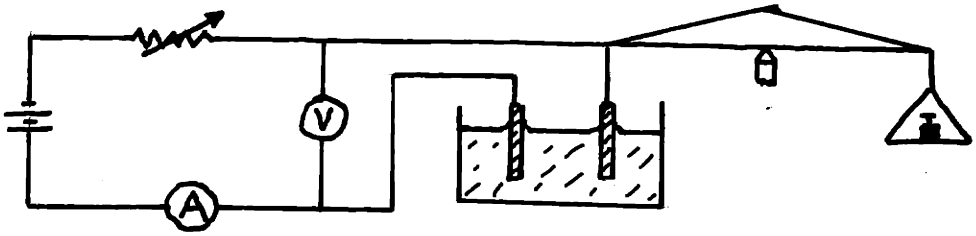


Figure 4.2. Circuit for current flow in Wilhelmy slide.

For a typical run the slide was cleaned and etched properly, it was then immersed to a depth of about o.5 cm. and the balance released. The current density through the immersed surface of the slide was then varied over a range usually between 0.5 and 50-100 ma/cm^2. Each new current, within the mentioned range, was applied for 10 to 20 seconds at least. For each run 10 to 20 different currents were used. Since the surfaces of the slides are not polarizable, there was no voltage drop across the liquid-solid interface; the current flowing through the interface was read directly on the ammeter shown in Fig. 4.2. Since the balance was at all times released, any change in the contact angle, occurring with current, would have caused an immediate and observable movement of the balance's needle pointer. The sensitivity of the system will be discussed in a later section. Eye estimates of the contact angle were made throughout. Bubbling, or gasing, was avoided. This limited the maximum current densities to those at which bubbling began. The reason for this is clear, bubbling would have made readings on the highly sensitive balance very difficult and inaccurate.

In addition to the Wilhelmy slide method, data was obtained by other means in later runs.

The rest of the measurements were of simple nature. It was observed that in graphite the contact angle changed with current, and, furthermore, that the pores of the graphite (30% porous) being used were absorbing the electrolyte. It was then desired to try to determine the rate of electrolyte penetration with time at a constant current. This was done by preparing a number of slides which were totally immersed in electrolyte while current was being applied. The current was applied for a determined period of time, then the slide was removed from the solution and after its outer surface had been carefully dried, the slide was weighted. After weighting, the slide was re-immersed and the procedure repeated at the same current. For runs at different currents new slides were used in most cases.

Finally, the contact angle on the outside surface of the slides was determined. This was done by the simple technique of allowing a drop of electrolyte to rest on the surface of the treated slide and determining the angle with the aid of a magnifying glass and a protractor.

4.4. Procedure Discussion. Two important points merit further discussion at this point.

First. A very important precaution was taken throughout the use of the Wilhelmy method; this was to keep the slide in the exact same position at all times during an entire run while the current was being varied. The need for this is dictated by the histerisis of the contact angle. Usually the advancing angle is far from being the same as the receding angle. If the slide had been allowed to move up and down, the angle could have changed within the receding and advancing limits, resulting in false measurements of angle changes. With a steady slide any change in angle with current can be measured regardless of the particular initial angle.

Keeping the slide fixed could be accomplished by keeping the balance needle pointer in the exact same position, by fast and proper control of balancing weights, when there was a change in the pull on the slide. During the early runs it was difficult keeping up with the changes; however, in time sufficient ability was developed to accomplish keeping the slide fixed.

Second. There is an important difference between the contact angle changes measured by the Wilhelmy method ond those measured by the "drop method". The difference is important and it will become apparent in the discussion of results; however, it must be emphasized here so that no doubts arise later.

In the Wilhelmy method the contact change is being measured at the interface between the treated surface of the electrode (immersed portion) and the untreated surface. If the current decreases the contact angle, and the slide remains fixed, the tip of the electrolyte (formed by the contact angle) will advance towards the untreated surface. Therefore, if the angle change is due to a surface change (as appears to be the case in graphite), the fact that the angle advances to a non-treated surface will cause the angle decrease being measured to be smaller than it would otherwise be if it had been measured on the fully treated surface. When the drop method was used on the slides which had been treated while fully immersed, the angle was being formed on a surface which had been treated in its entirety. This means that the contact angle changes measured by the drop method, or Wilhelmy method on a fully treated surface, can be expected to be larger decreases than those measured by the regular Wilhelmy method.

4.5. Sensitivity. The balance used was the so-called chainomatic balance. This type of balance permits measuring weights with an accuracy of one or two tenths of a miligram. As all two-pan balances, the chainomatic balance has a needle pointer. A change in weight of one or two tenths of a milligram can be registered instantly by the needle pointer. Therefore a change in pull on the Wilhelmy slide of one or two tenths of a milligram can be measured. How big a change in weight will a one or two degree angle change cause?

We can find the weight change caused by an angle change if we put numbers into equation (4). All the slides used made a solid-liquid interface of about 8 cms. (2t + 2w = 8). The surface tensions of the liquids were all within 2-3 dynes/cm. of 72 dynes/cm., the surface tension of water at 25°C. Using these numbers the following is found:

From	80 to 79°	is equivalent to	0.0159 gms.
"	45 to 44°	" " "	0.0072 "
"	10 to 9°	" " "	0.0023 "

It can be seen that a one degree angle change can be measured with no difficulty.

4.6. The Slides. The platinum, copper, and nickel slides were cut from regular metal sheet. They were cleaned by etching.

The graphite slides were cut from stock 0.75 in. cylindrical electrodes. The slide was then polished with very fine sandpaper until all the rough spots were removed and the surface appeared smooth. The porosity of the graphite used was reported as 30%. To check this, some slides were weighed and their volume determined to obtain their density. Comparing this density to that of pure homogeneous graphite, the porosity obtained was 30%.

V. RESULTS.

Four different surfaces were used. These were platinum, copper, nickel, and graphite. The Wilhelmy slide method was used on all four. On graphite, the drop method and penetration measurements were also made. In every case where the Wilhelmy method was used bubbling was avoided. For all runs the second electrode was of the same material as the first, or slide.

5.1. Platinum. Measurements were made by the Wilhelmy method on both the advancing and receding angles (80-90° and 30-45° respectively, by eye observation). The electrolytes used were a one normal solution of ferrous-ferric sulfate, and a one normal solution of ferrous-ferric chloride. Currents were varied between one and 40-45 ma/cm^2. In all runs the final conclusion was that the current did not have an effect on the contact angle within the ranges of current used and the sensitivity of the equipment. The balance needle pointer did not move at any time during any of the runs. See table 8.1 in the Appendix.

5.2. Copper. For the copper slide two different electrolytes were used. Both contained one normal copper sulfate, but one of them was made one normal in sulfuric acid as well. The sulfuric acid allowed greater current densities, and since the hydrogen overpotential is high on copper electrodes, bubbling was not a problem. All copper measurements were made for receding angles (5-20° by eye estimate). The slide was made both anode and cathode for both electrolytes. In the copper sulfate electrolyte current densities were varied between 1.5 and 33 ma/cm^2. In the acidic electrolyte, current densities went from 2 to 100 ma/cm^2.

With copper we have a system in which electroplating, or corrosion, depending on polarity, will take place; thus, changes in weight can be expected. This changes can be estimated using Faraday's law. In the experiments it was found that for the cathode the weight increased and for the anode it decreased as expected. In table 8.2 (Appendix) it can be seen that for four out of six runs the changes were within those expected. For the two runs where the change in weight was greater than could be accounted for by plating, or corrosion, the excess change could be explained by a contact angle change of about 2-4°. This angle change could be due to the change in the nature of the surface that occurs with plating, or corrosion. However, as will be seen in the Discussion of Results, these changes in the pull on the slide could also be accounted for by concentration gradients near the electrode surface. Finally, it was noted that the rate of change of weight was higher at the higher currents.

The accuracy of the calculated angle changes is in the order of one degree; the accuracy is limited by the estimate of total coulombs passed during each run.

5.3. Nickel. With the nickel slide, one normal nickel sulfate electrolyte was used. Again in some runs the nickel sulfate was made acidic, to unit normality, with sulfuric acid. Only three runs were performed on the nickel surface and all for receding angles. With the pure nickel sulfate solution only one run was made and in this run the slide was the cathode. Current densities ranged from 0.9 to 7.5 ma/cm^2. In this run no change of weight was noticed at all. (Table 8.3 in Appendix).

In the two runs for which acidic electrolyte was used, the slide was the anode both times. Current densities as high as 48.5 ma/cm^2 were used. For both runs the changes in weight were larger than could be accounted for by corrosion (Table 8.3). If contact angle changes were responsible, contact angle increases of 2-3° would have been necessary. It is possible that corrosion caused the surface to increase in roughness, which in turn caused an increase in the contact angle. As in the case for copper, however, concentration gradients affecting the liquid surface tension could also be responsible for the excess change.

5.4. Graphite. In graphite it was found that the contact angle changed with current. When the graphite was the cathode the angle would not change when the current was applied for one minute. However when the cell was shorted, after current had been applied for one minute, the angle would decrease with no evidence of electrolyte penetration into the pores of the porous graphite slide. When the graphite was the anode the angle would decrease and the pores would drown upon application of current. It was not possible to determine with quantitative conclusiveness whether the rate of drowning increased with increasing current density. Howevsr, eye observation of big bubbles formed on the surface of the slide due to drowning was possible; this qualitative observation seemed to indicate that drowning was much faster the higher the current density. Graph # 2 also seems to indicate this.

A variety of measurements were made with the porous graphite. These can be summarized as follows:

Cathode: 1N H_2SO_4 - Wilhelmy method.
Anode: 1N H_2SO_4 - Wilhelmy method.
1N H_2SO_4 - Penetration & Angle by Wilhelmy.
1N H_2SO_4 - Penetration vs. Time.
1N H_2SO_4 - Penetration & Angle by Drop.
1N KOH - Penetration vs. Time & Angle by Drop Method.

Each of these will be treated separately and briefly.

Note that all the angle measurements were for advancing angles. No receding angles were used.

Cathode: 1N H_2SO_4 - Wilhelmy method.

For these runs currents of 0.5-0.9 ma/cm^2 were used. Upon aplication of current and while current was flowing in no case was there a change in contact angle. Current was applied for one minute in all cases. During this minute the cell became charged and upon shorting the cell a definite contact angle change took place. The change took place suddenly and rapidly two or three seconds after initial shorting. In two cases (Run 23 B & K, Table 8.5) the changes were observed visually, as well as through the balance.

There was no evidence of flooding, or penetration, by the acidic electrolyte. This was checked by weight difference of the free slide before and after the runs. To check if the slide was capable of absorbing electrolyte, after the final run it was made anodic and current was applied: the slide was flooded by the 1N H_2SO_4 electrolyte.

The cell was shorted and allowed to discharge until no further changes with time took place. In this period the angle changed from about 1-2° in some runs to as much as 11-12° in two (Tables 8.4 & 8.5). The angle would change the most when the initial angle was largest. Interestingly, the final angle was always between 68 and 72°. The accuracy can be summarized as follows: for absolute angles it is good to about 2-3°; for relative angles between runs about 1-2°; and for the angle changes much better than one degree.

Finally, it was noted that if the slide was allowed to dry for a few minutes between runs, after a few runs it was not possible to reproduce the original large contact angle (Run 22, Table 8.4). However, if the slide was left overnight or the surface rubbed with soft paper between each run, the original large contact angle could be partly reproduced (Run 23, Table 8.5). Heatingthe surface between runs made it possible to totally reproduce the original large contact angle. Heating was done in an 80°C oven.

__Anode__: __1N H_2SO_4 - Wilhelmy method.__ For this series of runs (Table 8.6) current densities of 0.9-1.2 ma/cm^2 were used in all cases. It was found that the contact angle decreased with current and that the pores of the slide were flooded. The changes occurred suddenly and rapidly two or three seconds after the current was initially applied. All these changes were instantaneously registered by the balance pointer and there is no doubt of their occurrence.

The total flooding and the change in angles were measured in three runs. The changes, after correcting for flooding, were between 2 and 13° (Table 8.6). For all three the final angle was between 75 and 80°. The accuracy again is about 2-3° for absolute angles, about 1-2° for relative angles between runs, and much better than one degree for angle changes.

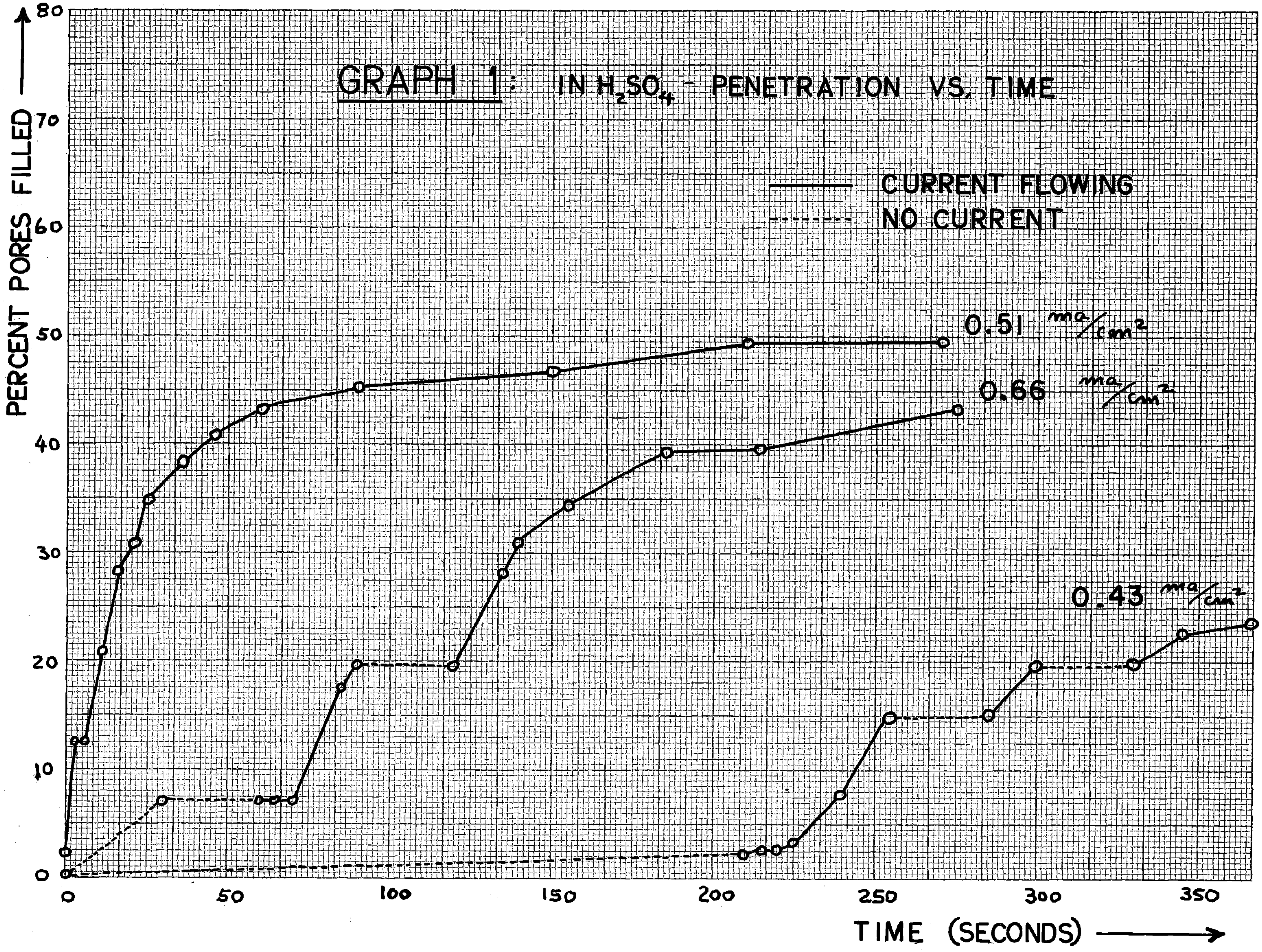
Percent of flooded pores was not calculated since there was no way of telling how much of the portion not immersed was also drowned. However, results of experiments focusing on penetration follow.

Anode: 1N H_2SO_4 - Penetration and Angle by Wilhelmy.

In this run the slide was totally immersed and current was then applied for three minutes. The percent of pores flooded, based on 30% porous graphite, was determined by weight difference. Finally, the angle on the treated surface was measured by Wilhelmy method. Current densities of about 0.56-0.80 ma/cm^2 were used. It was found that 45-55% of the pores were flooded and that the contact angle changed from 85-90° on the new surface to 40-50° on the surface of the flooded slides. Increasing the current density to 62.8 ma/cm^2 did not cause the flooded slide to take up additional electrolyte. (Table 8.7 in Appendix).

Anode: 1N H_2SO_4 - Penetration vs. time.

For this series of runs the graphite slide was totally immersed in the elctrolyte and current was applied. Graph 1 shows the percentage of pores filled with time for various currents. To check for penetration without current, the slide was immersed in the electrolyte without applying current (broken lines in graph) at various times during each run. There was no flooding without current.


GRAPH 1: IN H_2SO_4 - PENETRATION VS. TIME

Anode: 1N H_2SO_4 - Penetration and Angle by Drop Method.

In these runs three new slides were subjected to a constant current for a period of time to determine penetration. The results are shown in Table 5.1.

Table 5.1. Percent pores flooded by 1N H_2SO_4.

Slide	Current Density	Time	% Pores Filled
A	0.31 ma/cm^2	30 min.	47
B	0.28 "	5 "	40
C	0.10 "	5 "	38

The contact angles on the new surfaces — determined by drop resting on the surface — were 75-85°. The angles on the surface of the flooded slides were 40-50°.

At this point in the work a check was made to determine the penetration of electrolyte into the graphite without current flowing. A new slide was immersed in electrolyte for 20 hours. In this 20 hours 24% of the pores were filled. The first few minutes of immersion, however, showed no evidence of flooding. A further check was made to determine if polishing the surfaces of the slides had changed the flooding characteristics. Four "chunks" of graphite broken from the main body of the graphite were immersed for 30 to 60 minutes in the electrolyte. During this time only 1-3% of the pores were filled.

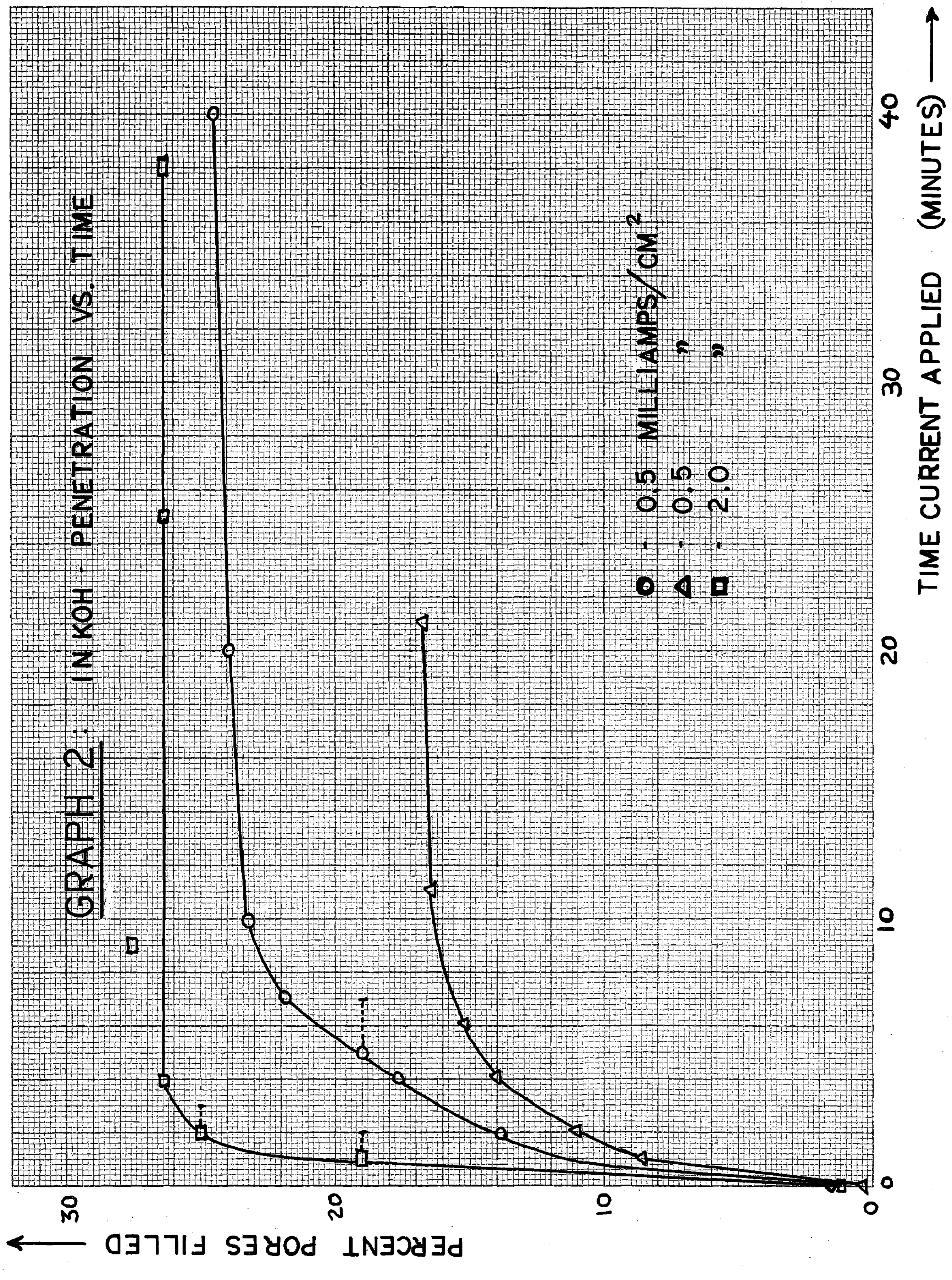
Anode: 1N KOH - Penetration vs. Time & Angle by Drop.

These were the only runs for which basic electrolyte was used. Current was applied while the slide was totally immersed. Penetration was determined by weight difference. For each run a new slide was used. The results are shown in Graph 2. Unlike Graph 1, Graph 2 shows only the time during which current was applied. The three dotted lines departing from two of the curves show time during which the slide was immersed without current flowing; in all three it was found that no further penetration would occur without current. In addition, at time zero in the graph, the slide had already been immersed without current for five minutes.

The penetration rate at 2.0 ma/cm^2 appears to be greater than at 0.5 ma/cm^2. More data, however, would be necessary to conclude that penetration is in effect higher at 2.0 ma/cm^2.

The contact angle that a drop of solution made on the new surface of the slides was 70-80°. The angle on the surface of the flooded slides was 40-50°.

To conclude, it will be noted that the maximum of pores filled by basic electrolyte (based on 30% porous graphite) was 15-25%, while it has been seen that with acidic electrolyte 40-55% of the pores were flooded.


GRAPH 2: IN KOH - PENETRATION VS. TIME
● : 0.5 MILLIAMPS/CM^2
▲ : 0.5 "
■ : 2.0 "
TIME CURRENT APPLIED (MINUTES)
PERCENT PORES FILLED
0
10
20
30
40
0
10
20
30

VI. DISCUSSION OF RESULTS.

6.1. Concentration Gradients. The question of concentration gradients will be discussed first. When current is applied there will be a depletion, or increase, of some of the ions near the electrode surface. This can have an effect on the surface tension and thus on the pull on the slide since the pull is due to $\gamma_{LA} \cos\theta$ directly. To determine the effect that the possible changes of surface tension may have it is only necessary to substitute numbers into equation (4). When the surface tensions of the various electrolytes are looked up in the literature it is found that the maximum tension changes that can be expected are not small. For the KOH and H_2SO_4 electrolytes the maximum changes that can be expected are about 0.5 dynes/cm. For the rest of the electrolytes the maximum is about 1.5 dynes/cm. These maximums are determined by considering how far from the surface tension of water the surface tensions of the various electrolytes are. Equation (4) is now used to calculate the effect on the slide pull. For a 1.5 dyne/cm change (using $2t+2w=8$ cm., and $\gamma_{LA} = 72$ dynes/cm. as reference), the difference in pull will be 0.0043 gms. when the absolute angle is 80°, and 0.0240 gms. when the absolute angle is 10°. It can be seen that the effect becomes considerable at the smaller angles. Note that the effect of a change in γ_{LA} is much bigger, on the pull on the slide, directly, than it would be through the angle itself. This, then, could also account for the excess weight changes that were observed with the copper and nickel slides. On the other hand, the concentration effect is far to small to explain the results obtained with the graphite slides in acidic and basic electrolytes. In any case, some of the data obtained for graphite was independent of concentration gradients. It can be concluded that the effect is important in the nickel and copper cases but negligible in the case of graphite.

6.2. Platinum. With the platinum slide absolutely no changes in the $\gamma_{LA} \cos\theta$ factor were observed. Enough runs were made with sufficient precautions taken to permit as a final conclusion that the contact angle is not a function of current density. This conclusion is limited to the current densities and systems used. It is interesting to note that concentration gradients, if they occurred, had no effect. This would seem to indicate that the concentration effect is probably not even as big as was suggested.

6.3. Copper and Nickel. For these two metals it will be recalled that in some of the runs the weight changes were greater than could be accounted for by corrosion or plating. In these cases the excess change was equivalent to an angle change of two or three degrees. However, the changes can also be accounted for by a change in liquid surface tension of one dyne per centimeter. The change in liquid surface tension of course will also affect the contact angle. However, Young's equation tells that a change of one dyne per centimeter would only change the angle about half a degree. On the other hand the change in the surface tension itself has a big effect on the pull of the slide, since the pull is given by $\gamma_{LA} \cos \theta$. If the concentration gradients do not explain the changes, then it is possible that they were due to a change in the nature of the surface due to plating or corrosion. This could have increased the roughness and at the same time the contact angle. Thus, two equally plausible explanations present themselves to explain the excess change in the pull on the slide: electrolyte concentration gradients,and/or changes in the physical nature of the metal surfaces due to plating or corrosion.

6.4. Graphite. It is with this system that the most striking and interesting results were obtained. Two different phenomena were observed. When the graphite slide is the cathode, upon application of the current the angle did not change during the minute that the current was flowing; however, upon shorting the cell, two or three seconds after shorting the angle decreases suddenly and rapidly. This decrease in angle is not enough to cause flooding of the graphite pores. On the other hand, when the graphite is the anode, upon application of current the angle decreases from 75-85° to 45-55° with both acidic and basic electrolyte. Furthermore, flooding takes place, with 40-50% of the pores filled with acidic electrolyte, and 15-25% with basic electrolyte. The only case reported of a similar phenomena was discussed in the chapter on the State of the Art. It will be recalled that Dr. Hunger(9) observed that hydrogen electrodes were flooded with time, at constant current; this time usually being in the order of 50 to 100 hours.

At this point it may be recalled that one of the purposes of this thesis was to determine whether the angle change was irreversible. From the results obtained it appears that the angle change is irreversible. In the case of the cathode the changes were permanent. The pull on the Wilhelmy slide remained constant after initially changing. With the anode again the angle changes appeared permanent. However, this 'permanency' or irreversible change only appeared to be effective over short periods of time and it appearently could be removed by polishing or heating. Between runs 22 and 23, it will be recalled, THE SLIDE recovered its lyophobic character after standing two nights, and in run 23 after polishing and heating.

The specific causes of the changes of angle and the flooding of the anodic slide are not yet clear. However, some hypotheses are possible.

When the graphite is the anode it is very likely that oxidation of the graphite surface layers to CO and CO_2 occurred. Sihnoven(11), who has done extensive work in this area, has found that the electrolytic oxidation of a carbon anode in NaOH solution at high current densities density yields O_2, CO_2, and a little CO. In H_2SO_4 solution at low current densities, Sihnoven continues to say, the marginal atom chains are attacked and an equimolar mixture of CO and CO_2 is produced; further action resulting from use of higher currents or polished surfaces will yield more CO_2.

It is possible that what Sihnoven discusses occurred and that there remained in the graphite surface an adsorbed layer of CO and CO_2 that caused the contact angle to change. Sihnoven's work also points to this adsorption. He found that polishing the surface would allow more CO_2 to be evolved. It will be reaalled that it was also found that penetration, or flooding, was larger with H_2SO_4 than with KOH. Sihnoven found that oxidation with H_2SO_4, as opposed to NaOH, was possible at lower current densities.

Therefore, in the case of the graphite anode it is very possible that oxidation coupled with adsorption of the CO and CO_2 produced, occurred. This may explain the contact angle decrease.

In the case of the cathode the following could have occurred. Upon application of the current some hydrogen was formed which remained absorbed within the pores of the graphite. Upon shorting the cell this hydrogen, which reacted to produce the back emf, was first chemically adsorbed to the outside surface. This chemisorbed hydrogen could have caused a decrease in the contact angle.

These are presented as posible explanations of the phenomena observed. Other hypotheses are possible and further work would be necessary before a final explanation can be given.

Finally, one may wonder if the angle changes observed in the outside surface are large enough to cause the flooding observed with anodic graphite. In the introduction the equation,

$$P_l - P_g' = - \frac{2\gamma_{LA}}{r} \cos \theta$$

was given for the pressure difference on the liquid surface within a capillary. The important factor is the inverse proportionality of the pressure gradient with pore radius. The pore radius of the porous graphite is in the micron range and therefore in the case of the smaller pores not much of an angle change would be necessary to cause a considerable pressure gradient. This pressure gradient could cause electrolyte penetration.

To conclude, it is recommended that further work be done to determine the reasons behind the observed phenomena. Determination of the causes of angle changes may permit steps towards avoiding the changes. This would permit design of more reliable fuel cells.

VII. CONCLUSIONS AND RECOMMENDATIONS.

The most striking results were those obtained for graphite surfaces. Two different phenomena were observed. When the slide is the cathode, in 1N H_2SO_4 electrolyte, upon application of the current the angle did not change during the minute that the current was flowing; however, upon shorting the cell and allowing the back emf to discharge, two or three seconds after shorting, the angle decreases $5-10^{\circ}$ suddenly and rapidly. The decrease in angle was not sufficient to cause flooding of the graphite pores.

When the slide is the anode, upon application of currents of about one milliampere per square centimeter, the angle decreases from $75-85^{\circ}$ to $45-55^{\circ}$ with both acidic and basic electrolyte.

In addition, it appears that the angle changes in graphite are irreversible. The flooded surfaces lose their lyophobic nature. The slide, however, can be made lyophobic again by allowing it to dry and letting it stand a few days, or by polishing and/or heating to $60-100^{\circ}C$.

The results obtained with copper and nickel failed to show any dependence of the contact angle on current. In the few runs where changes of the pull on the Wilhelmy slide were observed, the maximum angle change that could account for this would have been about three degrees. But the change in pull on the slide, it was seen, could be explained just as well by electrolyte concentration gradients.

The only other surface used was platinum. Here it was found that the contact angle is not affected by current density.

It is recommended that further work be undertaken to determine the causes of the phenomena observed in graphite surfaces. This may permit steps towards avoiding contact angle changes. Control of contact angle changes on graphite surfaces would make possible the construction of more reliable fuel cells.

Data on flooding and angle changes with current applied for long periods of time should prove interesting. It is recommended that this data be obtained.

VIII. APPENDIX A: SUMMARY OF DATA AND CALCULATED VALUES.

In this appendix results already mentioned will be presented in more detail. A brief discussion of how the numbers were obtained will be given with each table. Each run will be referred to with the same number, or letter, used in the notebook of original data.

Table 8.1. Platinum slide data.(next page).

Runs 3 to 6 were with 1N Fe^{++}, Fe^{+++}, $SO_4^{=}$.

Runs 7 to 12 were with 1N Fe^{++}, Fe^{+++}, Cl^{-}.

Slide dimensions: lenght = 4.44 cm.

thickness = 0.0109 cm.

In all runs slide was immersed 0.5 ± 0.05 cm.

The weights in column 5 are not absolute weights; only difference in weight of significance.

The voltage drop in the cell ranged from about 0.1v at 2 ma/cm^2, to about 1.8v at 45 ma/cm^2.

The current density at which voltage drifts begin was usually around 12 to 20 ma/cm^2 (0.50 to 0.85 voltage drop). This current is mentioned because it might indicate when concentration gradients began to develop.

In the table only the minimum and maximum currents are presented. Between these limits measurements were made at 10 to 20 different currents. For each measurement the current was applied a minimum of 10 seconds.

The balance was at all times free during each entire run. Any change would have been registered by the balance needle pointer.

Table 8.1. Platinum slide data.

Run	Polarity of slide	Current ma/cm^2 From	To	Free slide (grs.)	Immersed slide (grs.)	Eye estimate of angle R: receding A: advancing	Angle change
3	+	1.12	32.7	2.2356	2.3232	A: 80 ± 10°	zero
4	+	1.63	35.0	"	2.6980	R: 40 ± 10°	"
5	+	1.67	45.0	"	2.6980	R: 40 ± 10°	"
6	-	2.10	45.0	"	2.7438	R: 35 ± 10°	"
7	-	2.14	22.5	2.2322	2.6540	R: 40 ± 10°	"
8	+	1.65	42.5	2.2290	2.2732	A: 85 ± 10°	"
9	+	"	43.0	"	2.6384	R: 45 ± 10°	"
10	+	"	43.0	"	2.6475	R: 45 ± 10°	"
11	-	"	39.5	"	2.3625	A: 80 ± 5°	"
12	-	"	37.2	"	2.6364	R: 40 ± 5°	"

Table 8.2. Change in weight of the copper slide

Run	Polarity of slide	Angle estimate	Current ma/cm^2		Total weight change (grs.)	Estimated coulombs	Expected wt. change (grs.)	Angle change that would justify excess weight change.
			From	To				
13	+	10-20°	1.6	33.7	-0.0129	13	0.0044	3°
14	-	10-20°	1.6	31.6	+0.0010	11	0.0036	0
15*	-	5-15°	2.2	72.5	+0.0212	25	0.0083	4°
16*	+	5-15°	2.2	93.5	-0.0054	25	0.0083	0
17*	+	5-15°	2.2	105.	-0.0036	28	0.0092	0
18*	-	5-15°	2.2	100.	+0.0042	27	0.0090	0

* acidic electrolyte

Table 8.2. Change in Weight of Copper Slide.

All runs were done using 1N $CuSO_4$.

Runs 15 to 18 were done with acidic electrolyte, (1N H_2SO_4).

All angles were receding and estimated with the eye.

Slide dimensions: lenght = 4.28 cm.
thickness = 0.0127 cm.

Slide was immersed 0.5 ± 0.05 cm.

Again, as for the Pt case, between the limiting currents 10 to 20 different currents were used for at least 10 seconds. The balance was free at all times.

The expected change in weight due to plating or corrosion is given in column eight and it was calculated using Faraday's law. The coulombs passed were estimated by multiplying the number of different currents used for each run by tens seconds, this was then multiplied by the average current for each run. It is estimated that the accuracy is about 25%. When calculating the angle cahnge that would account for the excess weight change, this 25% margin would make a difference of about one degree. Therefore, conclusion that angle could have changed is not affected at all.

The rate of change inweight of the slide was considerably larger at the higher currents.

Table 8.3. Change in weight of the nickel slide.

Run	Polarity of slide	Angle estimate	Current ma/cm² From	Current ma/cm² To	Total weight change (grs.)	Estimated coulombs	Expected wt. change (grs.)	Angle change that would justify excess weight change
19	-	20-30°	o.9	7.5	o	1.5	0.0005	0
20*	+	35-45°	2.0	48.5	-0.0219	14	0.0043	2.5°
21*	+	10-20°	2.0	22.0	-0.0105	5	0.0015	3°

* acidic electrolyte

Low contact angle of run 21 obtained through cleaning surface slide extremely well.

Table 8.3. Change in Weight of Nickel Slide.

All runs were done using 1N $NiSO_4$.

Runs 20 and 21 were done with acidic electrolyte, (1N H_2SO_4).

All angles were receding and estimated with the eye.

The slide dimensions were: lenght = 4.02 cm.

thickness = 0.0272 cm.

Slide was immersed 0.5 ± 0.05 cm.

The number of coulombs passed was calculated as explained for copper case (Table 8.2).

Tables 8.4 and 8.5. (next two pages). Graphite cathode slide in 1N H_2SO_4.

Tables 8.4 and 8.5 were obtained using a graphite slide, made of 30% porous graphite, in 1N H_2SO_4. The slide was the cathode. Same slide used in both runs: Slide dimensions: lenght = 3.86 cm.

thickness = 0.0516 cm.

Slide was immersed 0.6 ± 0.05 cm.

Current was applied for one minute. During this minute no change in weight occurred. However, a back emf was built up by the cell and upon shorting the cell to discharge it, the weight did change. It is this weight change that is recorded in column six. Changes began suddenly and rapidly two or three seconds after shorting. The cell was allowed to discharge until no more changes in weight occurred with time.

Table 8.4. Graphite cathode slide in 1N H_2SO_4 electrolyte. Data for run 22 using Wilhelmy slide method. Current was applied one minute followed by shorting of cell.

Run	ma/cm^2	Calculated initial angle	Weight immersed before current	Highest back emf.	Increase in weight after shorting	Calculated final angle	Change in angle that occurred after shorting
A	0.91	84°51'	0.9833	0.8	"Big"	-	"Big"
B	0.84	72°	1.0896	-	-	-	-
C	0.68	76°25'	1.0470	0.6	0.0525	70°55'	5°30'
D	0.89	73°30'	1.0748	-	0.0311	70°15'	3°15'
E	0.82	72°30'	1.0851	0.7	0.0219	70°10'	2°20'
F	0.82	72°	1.0902	0.6	0.0220	69°40'	2°20'
G	0.64	70°30'	1.1039	-	0.0219	68°10'	2°20'
H	0.46	71°25'	1.0955	0.3	0.0225	69°5'	2°20'
I	0.46	69°20'	1.1150	"Small"	0.0012	69°10'	10'

Table 8.5. Graphite cathode slide in IN H_2SO_4 electrolyte.
Data for run 23 using Wilhelmy slide method.
Current was applied one minute followed by shorting the cell.

Run	ma/cm²	Calculated initial angle	Weight immersed before current	Highest back emf	Increase in weight after shorting	Calculated final angle	Change in angle that occurred after shorting
A	0.91	$82^\circ 50'$	0.9734	0.5	"Big"	-	"Big"
B	0.75	$84^\circ 20'$	0.9581	0.6	0.1150	$72^\circ 40'$	$11^\circ 40'$
C	0.73	$79^\circ 25'$	1.0076	0.7	0.0889	$69^\circ 40'$	$9^\circ 45'$
D	0.66	$78^\circ 15'$	1.0187	0.6	0.0663	$71^\circ 25'$	$6^\circ 50'$
G	0.75	$74^\circ 50'$	1.0521	0.7	0.0692	$67^\circ 35'$	$7^\circ 15'$
H	0.78	$76^\circ 20'$	1.0374	0.8	0.0620	$69^\circ 50'$	$6^\circ 30'$
I	0.82	$70^\circ 10'$	1.0966	0.8	0.0105	$69^\circ 5'$	$1^\circ 5'$
J	0.82	$88^\circ 30'$	0.9200	0.8	0.0754	$82^\circ 20'$	$6^\circ 10'$
K	0.91	$98^\circ 50'$	0.8203	0.8	0.0973	$88^\circ 10'$	$10^\circ 40'$

The absolute angles given in columns three and seven were calculated using equation (4), based on the surface tension of 1N H_2SO_4 at 25°C, 72.2 dynes/cm. All the angles are advancing angles.

For the entire run 22 the slide surface remained untouched. Between each sub-run it was allowed to dry for a few minutes in the atmosphere. Between run 22 and run 23 (Tables 8.4 and 8.5 respectively), the slide was left to dry for two days. Between runs 23-A and 23-I the slide was dried by rubbing with soft paper. Before runs 23-J and 23-K the slide was dried by placing it in a 60°C oven for five minutes.

Finally, no evidence of pore flooding was found during any of these runs. Apparently the angle changes were not great enough to cause flooding of the pores. To check if the slide was capable of being flooded it was made anodic and a current was applied. The slide did flood upon application of the current.

In runs 23-B and 23-K the change in the contact angle was observed visually as well as through the balance's needle pointer!

Table 8.6. Graphite anode slide in 1N H_2SO_4. Data for Run 24 using Wilhelmy method.

Run	ma/cm²	Time current applied (sec.)	Weight initial immersed	Weight final immersed	Calculated angles		Weight increase due to electrolyte take up	Corrected weight increase	Angle change
					Initial	Final			
A	1.21	15	1.0992	-	$78^{\circ}45'$	-	0.0124	-	-
B	1.07	50	1.0645	1.1546	$82^{\circ}20'$	$75^{\circ}10'$	0.0196	0.0705	$7^{\circ}10'$
C	1.09	10	0.9312	-	$95^{\circ}10'$	-	0.0155	-	-
D	0.97	40	0.9829	1.1217	$90^{\circ}35'$	$77^{\circ}35'$	0.0221	0.1167	13°
E	0.97	40	1.0664	1.1146	$82^{\circ}20'$	$80^{\circ}35'$	0.0311	0.0171	$1^{\circ}45'$

Table 8.6. Graphite anode slide in 1N H_2SO_4.

All angles are advancing angles.

The angles given were calculated using equation (4) after having substracted from the total weight change the weight due to electrolyte in pores. Again the surface tension used was 72.2 dynes/cm.

The slide used for these runs was 3.86 cm. long and 0.0588 cm. thick. It was immersed to a depth of 0.5 ± 0.05 centimeters.

Table 8.7. Penetration of electrolyte into graphite. Data for Run 25. Slide was anode in 1N H_2SO_4.

ma/cm^2	Additional time applied	Additional electrolyte take up	Percent pores flooded	Calculated final angle
-	-	-	-	89°
0.56	3 min.	0.0603	49	54°
0.59	3 "	0.0019	50	35°
0.83	3 "	0	50	47°
0.79	3 "	0.0059	55	48°
62.8	3 "	-0.0025	52	44°

In this run the slide was totally immersed in the one normal sulfuric acid electrolyte. The slide was the anode and current was applied for three minutes. The increase in weight due to electrolyte flooding was determined and the contact angle on the flooded surface determined by the Wilhelmy method. The percent of pores flooded is calculated based on 30% porous graphite. After each sequence of steps, the flooded slide was re-immersed in the electrolyte and current was applied for three more minutes to see if any further flooding occurred. Finally, an extremely high current was applied with no further effect. The angles were calculated using equation (4) based on a surface tension of 72.2 dynes/cm.

The accuracy of the angles, absolute angle and relative between runs, is limited to the accuracy with which the slide could be re-immersed to the same depth for each measurement. This was usually done with an accuracy of about ± 0.05 cm. The important numbers to note is that initially the angle was about 90° and it decreased to 35-55° approximately.

VIII. APPENDIX B: SAMPLE CALCULATIONS.

1. Calculation of contact angle by Wilhelmy equation:

$$gG = gW + 2\gamma_{LA}(t + w)\cos\theta - gh\rho tw \qquad (4)$$

Run No. 23-B:

Weight free slide	$W = 1.0236 \pm 0.0002$ gms.
Weight immersed slide	$G = 0.9581 \pm 0.0002$ gms.
Surface tension of acid	$\gamma_{LA} = 72.2 \pm 0.1$ dynes/cm.
Depth slide immersed	$h = 0.6 \pm 0.05$ cm.
Width slide	$w = 3.86 \pm 0.01$ cm.
Thickness slide	$t = 0.0516 \pm 0.0003$ cm.
Density of acid	$\rho = 1.023 \pm 0.003$ gms/cc.
Gravitational constant	$g = 980$ cm/sec^2.

$$\cos\theta = \frac{g(G - W + \rho htw)}{2(t + w)\gamma_{LA}}$$

$$\cos\theta = \frac{980[(0.9581 \pm 0.0002) - (1.0236 \pm 0.0002) + (1.023 \pm 0.003)(0.6 \pm 0.05)(0.0516 \pm 0.0002)(3.86 \pm 0.01)]}{2[(0.0516 \pm 0.0002) + (3.86 \pm 0.01)](72.2 \pm 0.1)}$$

$$\cos\theta = \frac{980(-0.0655 \pm 0.4\% + 0.1220 \pm 8\%)}{2(3.911 \pm 0.3\%)(72.2 \pm 0.2\%)}$$

$$\cos\theta = \frac{980(0.0567 \pm 17.5\%)}{2(282.5 \pm 0.5\%)} = 0.0983 \pm 17.5\%$$

$$\theta = 84^\circ 20' \pm 1^\circ$$

VIII. APPENDIX C: BIBLIOGRAPHY.

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