A HYDROGEN ELECTRODE VIA FERROUS ION AND ULTRAVIOLET LIGHT

by

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Table of Contents

Introduction

The purpose of this research is to investigate the photoelectric properties of an acidified ferrous-sulfate solution. It is known that in the presence of ultraviolet light, the following equilibrium is shifted to the right:

$$2\ Fe^{++} + 2\ H^{+} = 2\ Fe^{+++} + H_2$$

The idea is proposed that the hydrogen gas produced by this reaction might be absorbed on a platinum grid, thereby creating a hydrogen electrode. A cell is thus proposed in which two platinum electrodes are immersed in the same solution of ferrous sulfate and sulfuric acid. The area surrounding one electrode is to be illuminated with ultraviolet light. Some of the hydrogen gas produced in that area will presumably be absorbed by the one platinum electrode and a potential across the two electrodes will be developed.

History

The first photoelectric cell involving the ferrous-ferric couple was that employed by Rideal and Williams (1). They were investigating the effect of invisible light and temperature on the ferrous-ferric iodine-iodide equilibrium.

$$2\ Fe^{++} + I_3^- \overset{\text{light}}{=} 2\ Fe^{+++} + 3\ I^-$$

To study the effect of temperature on rate of potential equilibrium, a cell was constructed consisting of two platinum electrodes placed in an equilibrium mixture. By illuminating one half of the cell and upsetting the equilibrium in that half, a potential resulted. While this particular cell did not produce a voltage high enough to be practical (10 mv.), the type of cell used has set a precedent.

Using basically the same type of cell, Rabinowitch (2) made a study of the photogalvanic effect using thionine, a reversibly reducible dyestuff, with the ferrous-ferric couple.

Thionine + Fe^{++} = (Semithionine + Leukothionine) + Fe^{+++}

A potential as high as 250 mv. was found. Potter and Thaller (3) worked with the same system and found that a voltage of 182 mv. could be developed in bright sunshine. The efficiency is found however, to be rather low because of electrode polarization, back reaction of reduced dye with the oxidizing agent and side chemical reactions which render the dye photochemically inactive." Work at Union College has also been carried out by Hofmann (4). While the voltages which he obtained are quite small, the photogalvanic effect was nevertheless shown to be present.

In 1962, it was reported (5) that hydrogen gas could be produced when a highly acidic (H_2SO_4) solution of ferrous sulfate was irradiated with ultraviolet light.

$$2\,Fe^{++} + 2\,H^{+} \overset{\text{light}}{=} 2\,Fe^{+++} + H_2$$

It was now conceived that by combining this reaction with the type of cell used by Rideal and Williams, a photoelectric cell could be produced.

Apparatus

As proposed in the introduction, the photosensitive cell consisted of two platinum electrodes, one being a strip of platinum and the other being a mesh electrode like those used for analytical determinations. To distinguish between the two, they were respectively named the plate and the grid. These electrodes were placed inside an airtight quartz container which was fitted with a glass stopper so that a vacuum could be pulled and nitrogen gas (oxygen-free) could be drawn into the cell. (figure 1)

Two modifications of the cell were later made. First, the grid was platinized so as to increase its surface area and therefore to increase its ability to absorb hydrogen. Second, a strip of fiberglas was placed between the two electrodes so as to prevent contact and to cut down on the amount of stray light in the area of the plate.

The potential of the cell was recorded using a Yellow Springs Instrument Corporation Model 80 Laboratory Recorder with a Millivac DC millivoltmeter, type MV-17B, as a check. The recorder was also used as a microammeter when current measurements were made. (figure 2)

The source of illumination was a 100-watt mercury arc lamp. A small opening in the metal surrounding the lamp allowed only a small beam of light to impinge upon the cell. Originally, the light was partially collimated by a two-foot piece of pipe (2" diameter) before striking the cell (figure 3); later the light was allowed to strike the cell directly (figure 4). In either case, the light was allowed to strike only in the area of the grid.

FIGURE #1

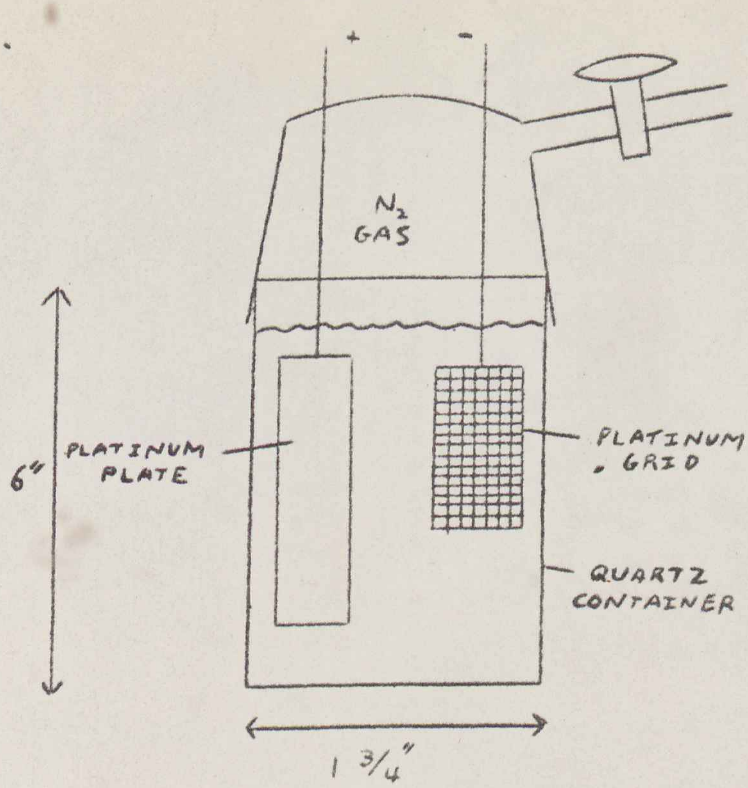


FIGURE #2

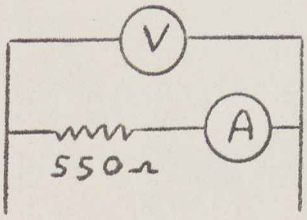


FIGURE #3

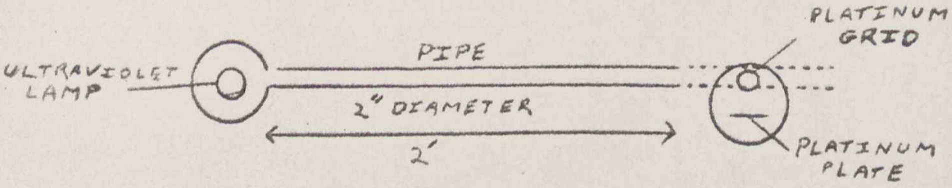
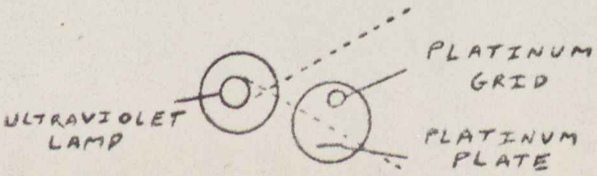


FIGURE #4



Procedure

Since the ferrous sulfate solution was to be 6 molar with respect to sulfuric acid, it seemed necessary to run at least one experiment with pure 6M H_2SO_4 in order to determine if a background potential were present. This background potential could be caused by inequalities or impurities in the electrodes, by the Becquerel effect (6), by changes in the ionic equilibria of the solution, etc.

A 6M H_2SO_4 solution was placed in the quartz container and flushed for 5-10 minutes with oxygen-free nitrogen. The top of the cell with the two electrodes was then set in place. In order to eliminate all oxygen from the cell, a vacuum was drawn and nitrogen was then allowed to fill the cell. This was normally done several times. This same procedure for eliminating oxygen was later followed in the making of every cell.

After experimenting with sulfuric acid, cells were also made containing 1) water, 2) 1M NaOH, and 3) benzene. The purpose of these cells was mainly to satisfy the author's curiosity, but they did yield interesting results.

The ferrous sulfate-sulfuric acid cells were then experimented with. The solution for these cells was to be .1M with respect to ferrous sulfate and 6M with respect to sulfuric acid. This solution was prepared by adding the proper amount of standard iron wire to a heated dil. sulfuric acid solution. The total amount of concentrated acid was usually not added until after the wire had dissolved so that other oxidation reactions were held to a minimum (such as oxidation of iron by reduction of sulfate).

Meanwhile, nitrogen was bubbled through the solution to stir the solution more than to eliminate the oxygen; the oxygen was more effectively removed by the fine bubbles of hydrogen which were being produced by the reaction of sulfuric acid on the iron. Finally however, nitrogen gas was used to eliminate all oxygen from the cell by a series of flushings and vacuums as described for the pure sulfuric acid cell.

Because of poor results with the original ferrous sulfate cells, the modifications mentioned in the "Apparatus" were now employed, i.e. the grid was platinized, the fiberglas was placed between the electrodes, and the cell was placed directly next to the light source to take advantage of the more intense light. Also, because of the precipitation of $FeSO_4$ in such concentrated sulfuric acid, the molarity of the acid was changed from 6M to 4M.

In all cases, the potential across the electrodes was measured as a function of time with the ultraviolet light being shuttered on and off to study the various effects of the light. At one point, several current measurements were also made simply to find out how much current a ferrous sulfate cell would produce.

Experimental Results

Graphs #1 and #2 were obtained for 6M H_2SO_4 solutions. Graph #1 shows the effect of having the light on for a short period of time and the subsequent "decay" when the light is turned off. Graph #2 shows the effect of leaving the light on for a long period of time. In all cases, the illuminated electrode was negative.

Graphs #3 and #4 are the graphs obtained for 1M NaOH and water respectively. Both contain curves with the light on for both long and short periods of time. Benzene was also tried in the cell but, as might be expected, no potential was developed.

Graph #5 was obtained from the first successful 1M ferrous sulfate-6M sulfuric acid cell. It was here that the grid was platinized and the cell was placed directly next to the light source. Before this, using the unplatinized grid and the collimator, no results were obtained. With these new conditions, sulfuric acid cells were again made up and the results similar to those in graphs #1 and #2 were found.

Some of the ferrous sulfate however precipitated out and poor response to the light resulted. With 4M sulfuric acid however, no precipitation took place and with this solution graph #6 was obtained. On following days, curves 7, 8, and 9 were also obtained from the same cell.

Some indication of the current which can be produced by the cell can be seen from the following two points taken from a 1M $FeSO_4$-6M H_2SO_4 cell.

R in ohms	V in mv.	I in µa
∞	~220	0
550	~34	57
550	~15	24

The voltage and current produced by the cell dropped fairly rapidly when the resistance and ammeter were connected into the circuit. With the light left on, the current tended to level out at about 20-25 µa.

Noteworthy results obtained from the graphs:

(1) Comparison of maximum potentials of 1) 6M H_2SO_4, 2) water, and 3) 1M NaOH cells.

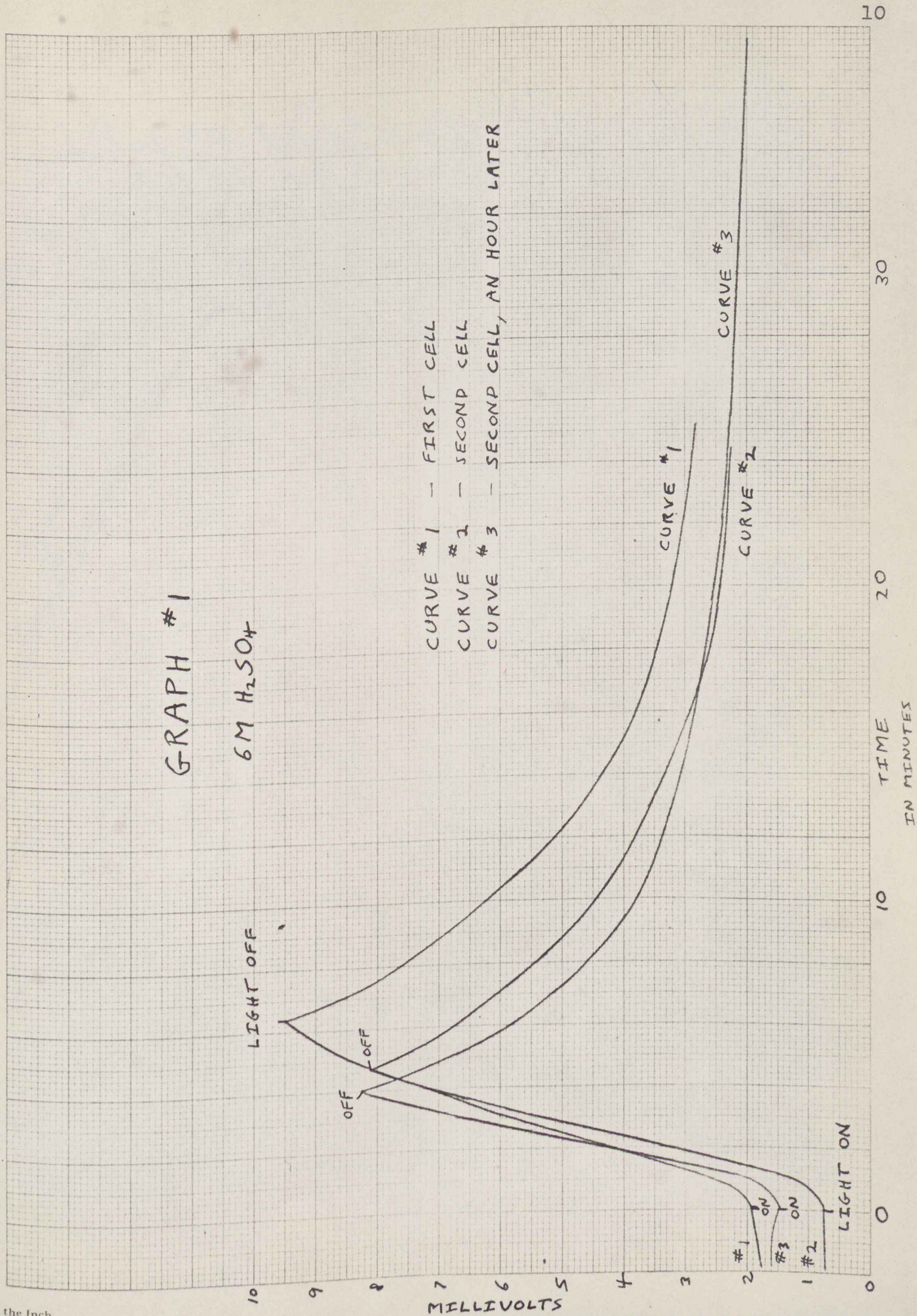
6M H_2SO_4	19.2 mv.
water	38 mv.
1M NaOH	22-24 mv.

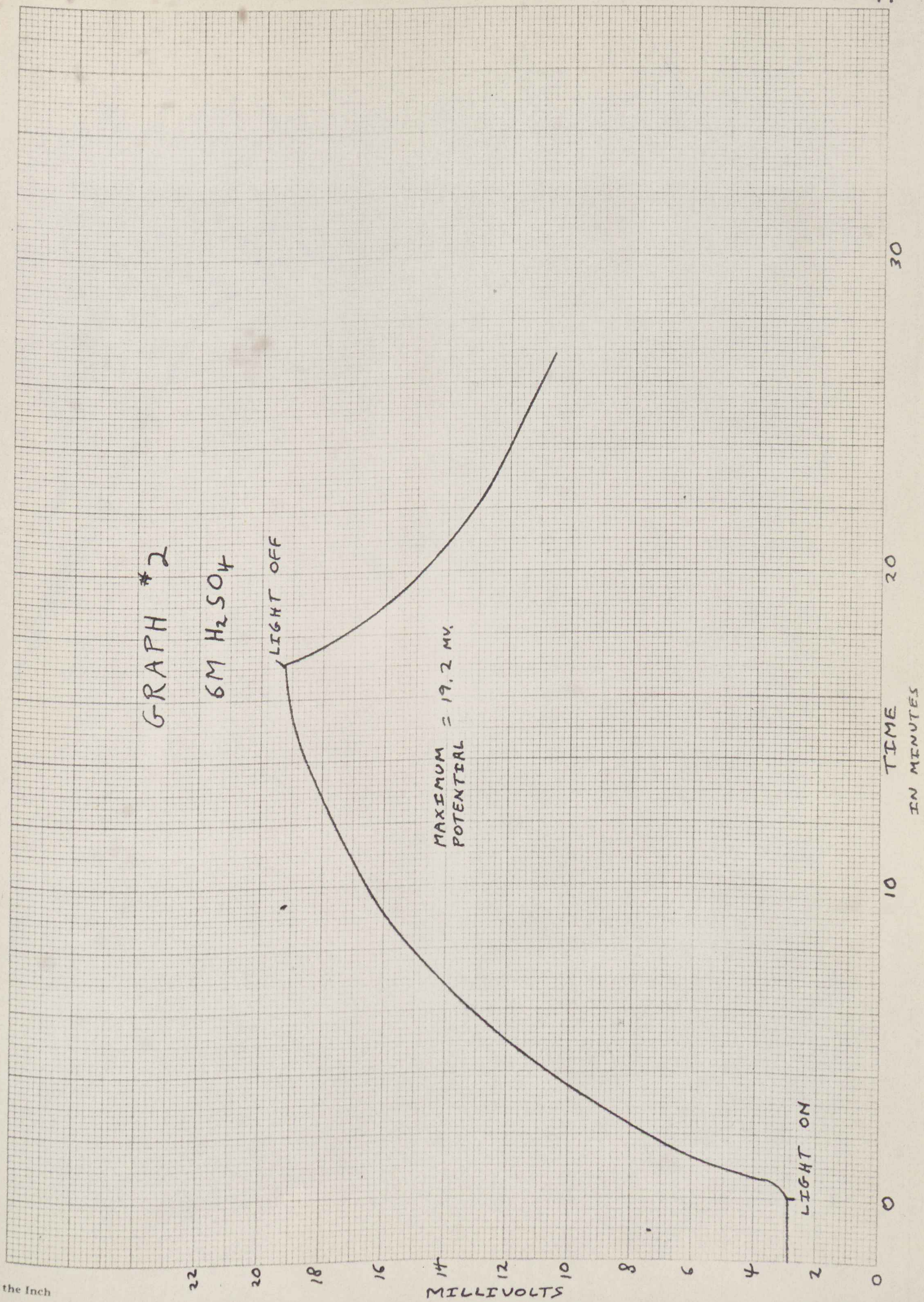
(2) Comparison of maximum potentials of the ferrous cells with different acid concentrations.

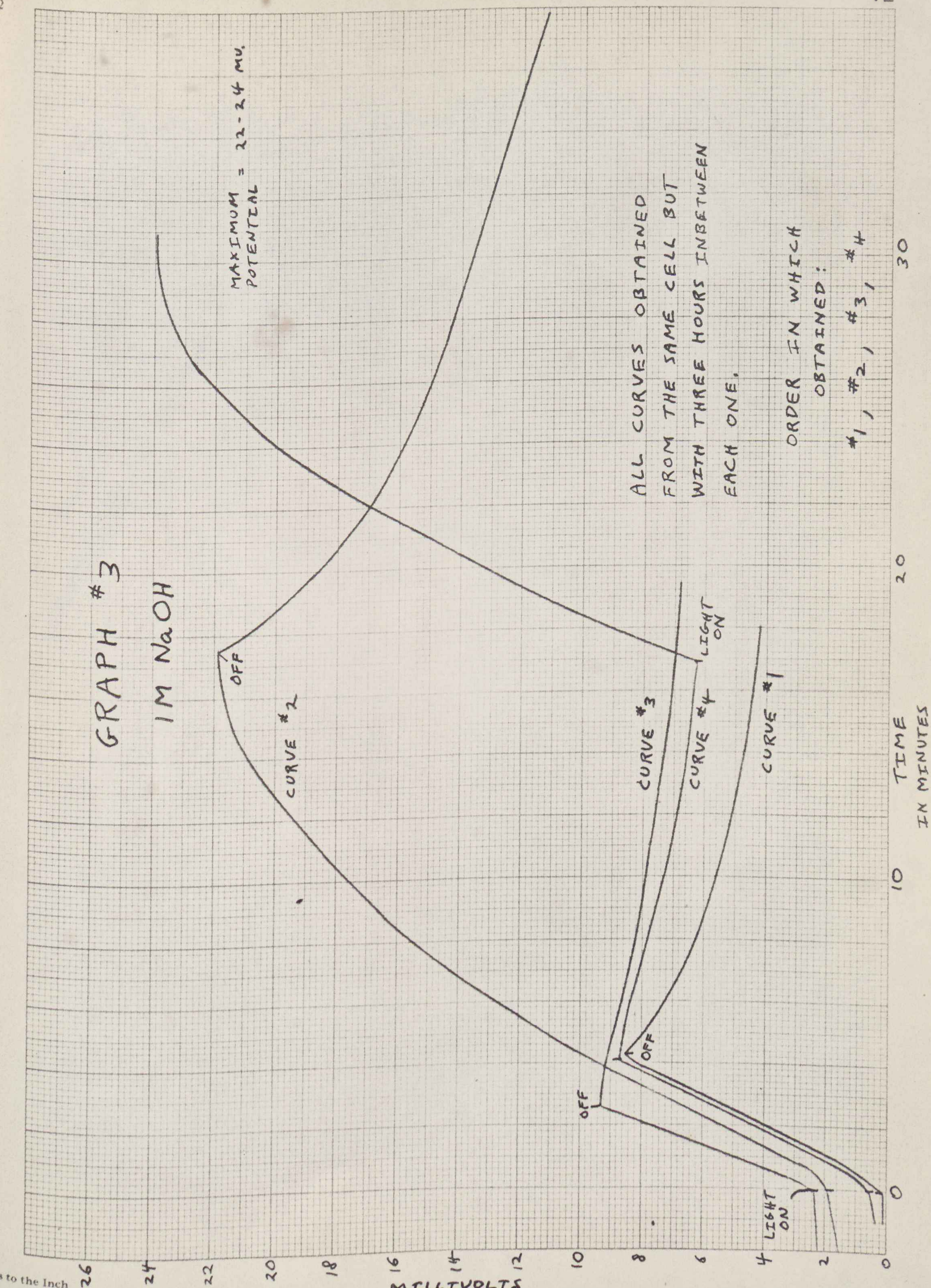
.1M $FeSO_4$-6M H_2SO_4	240 mv.
.1M $FeSO_4$-4M H_2SO_4	185+ mv.

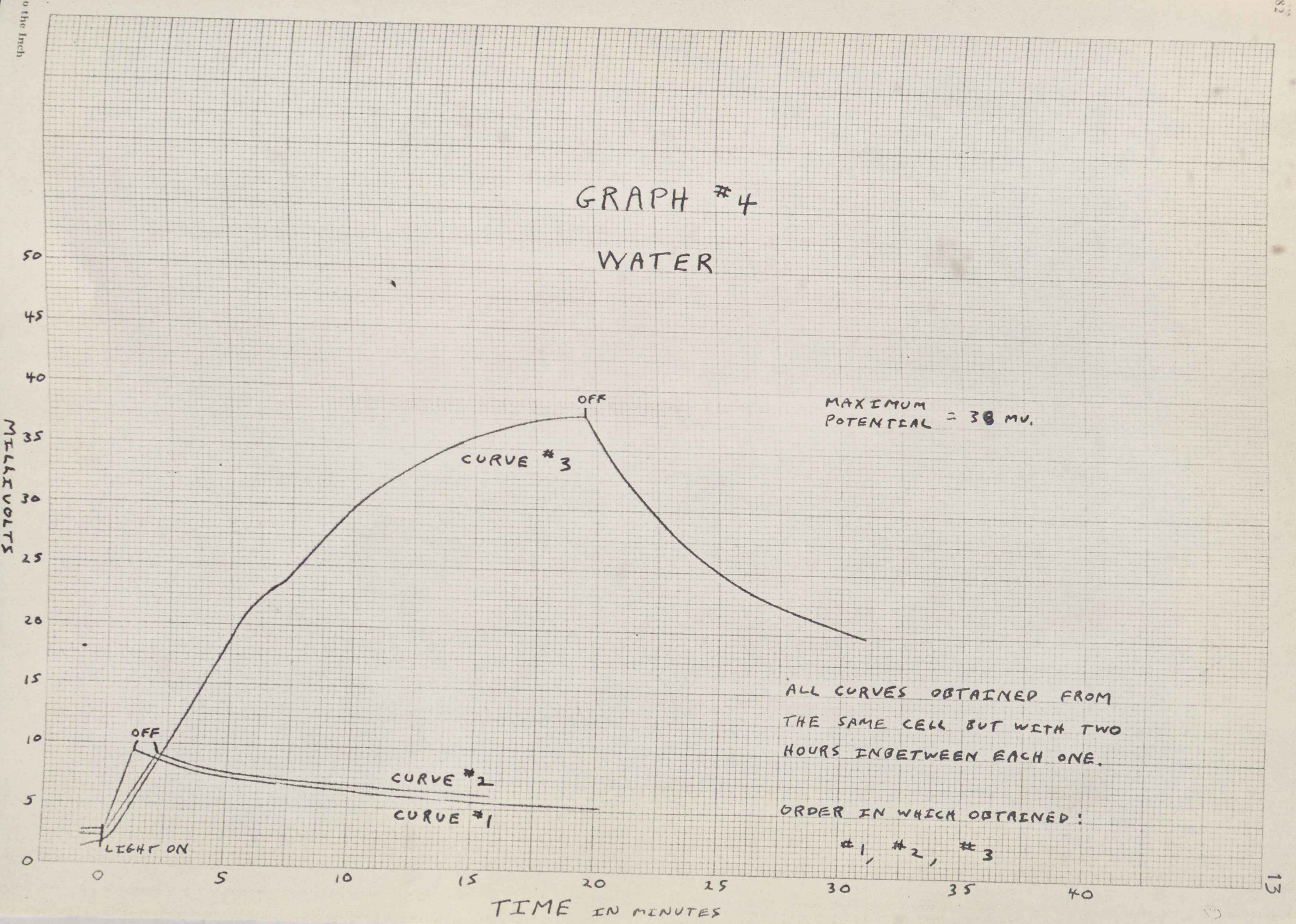
(3) Comparison of maximum potentials of the .1M $FeSO_4$-4M H_2SO_4 cell on consecutive days.

first day	185+ mv.
second day	126 mv.
third day	4.1+ mv.
fourth day	<1 mv.


GRAPH #1
6M H_2SO_4
CURVE #1 — FIRST CELL
CURVE #2 — SECOND CELL
CURVE #3 — SECOND CELL, AN HOUR LATER
LIGHT OFF
OFF
OFF
LIGHT ON
ON
ON
#1
#3
#2
CURVE #1
CURVE #2
CURVE #3
MILLIVOLTS
10
9
8
7
6
5
4
3
2
1
0
TIME
IN MINUTES
0
10
20
30
10


GRAPH #2
6M H_2SO_4
LIGHT OFF
MAXIMUM POTENTIAL = 19.2 MV.
LIGHT ON
TIME IN MINUTES
0
10
20
30
MILLIVOLTS
0
2
4
6
8
10
12
14
16
18
20
22


GRAPH #3
1M NaOH
MAXIMUM POTENTIAL = 22-24 MV.
ALL CURVES OBTAINED FROM THE SAME CELL BUT WITH THREE HOURS INBETWEEN EACH ONE.
ORDER IN WHICH OBTAINED:
#1, #2, #3, #4
CURVE #1
CURVE #2
CURVE #3
CURVE #4
OFF
OFF
OFF
LIGHT ON
LIGHT ON
0
10
20
30
TIME IN MINUTES
0
2
4
6
8
10
12
14
16
18
20
22
24
26
MILLIVOLTS



GRAPH #4

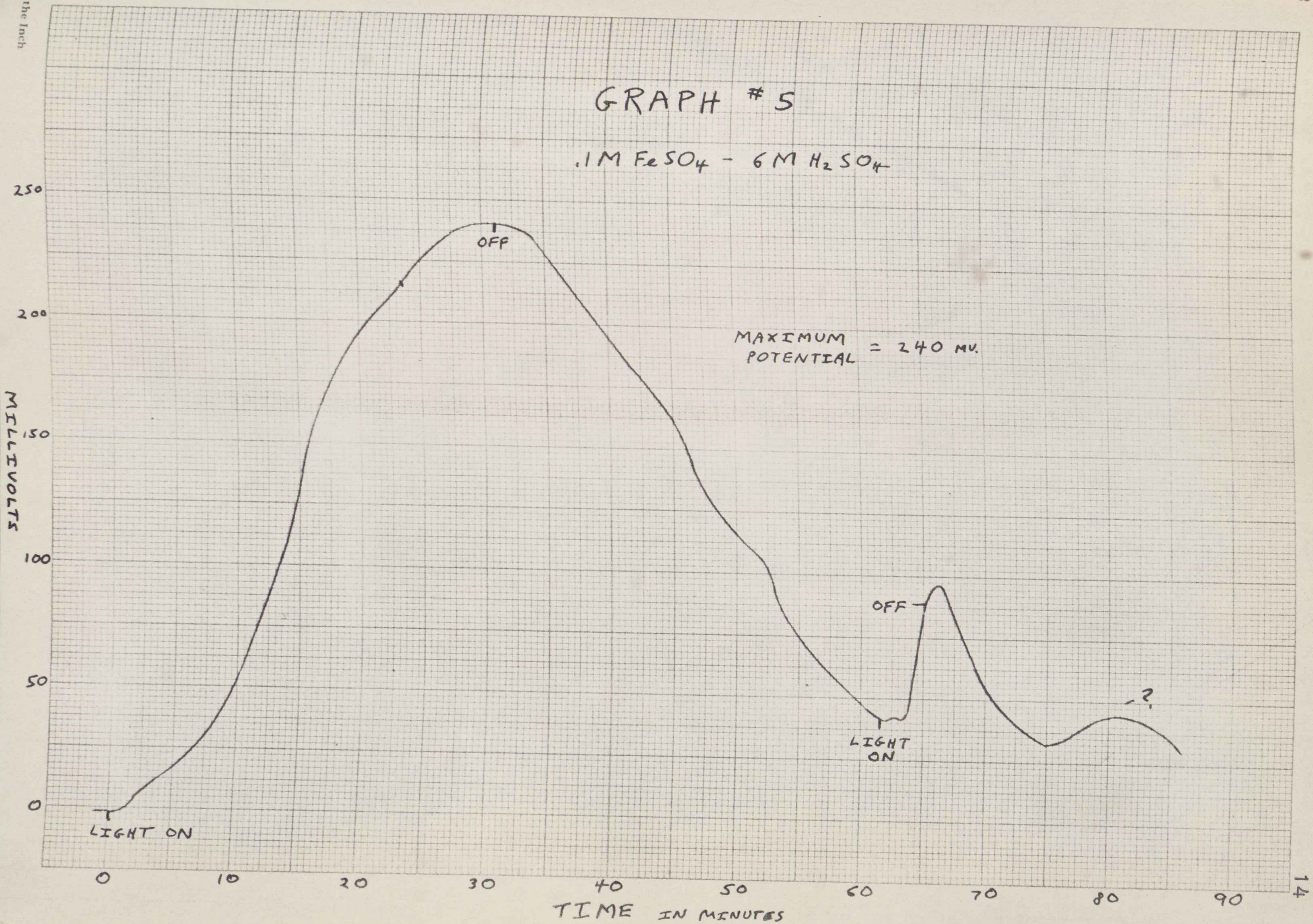
WATER

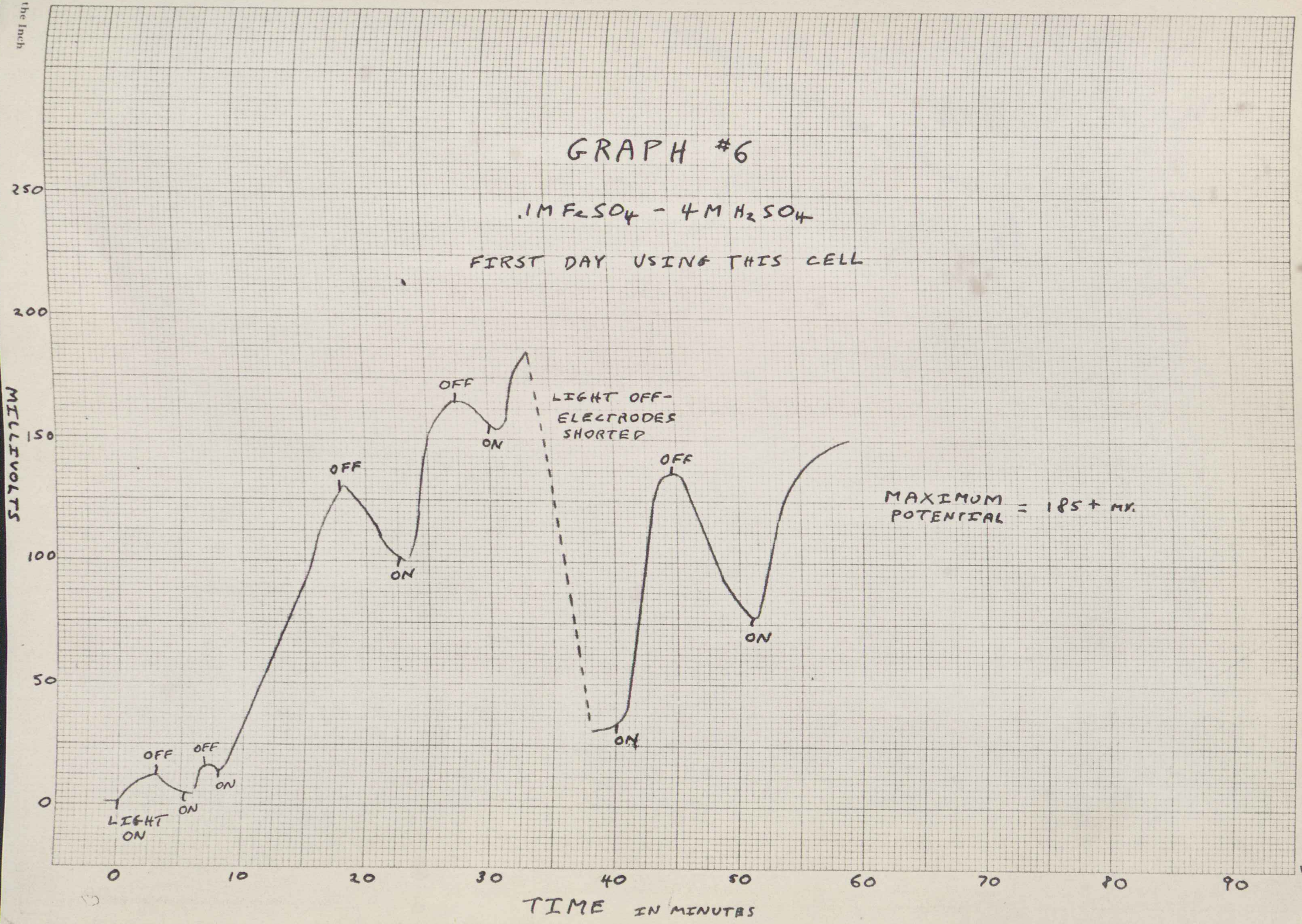
MAXIMUM POTENTIAL = 38 MV.

ALL CURVES OBTAINED FROM THE SAME CELL BUT WITH TWO HOURS INBETWEEN EACH ONE.

ORDER IN WHICH OBTAINED:

#1, #2, #3

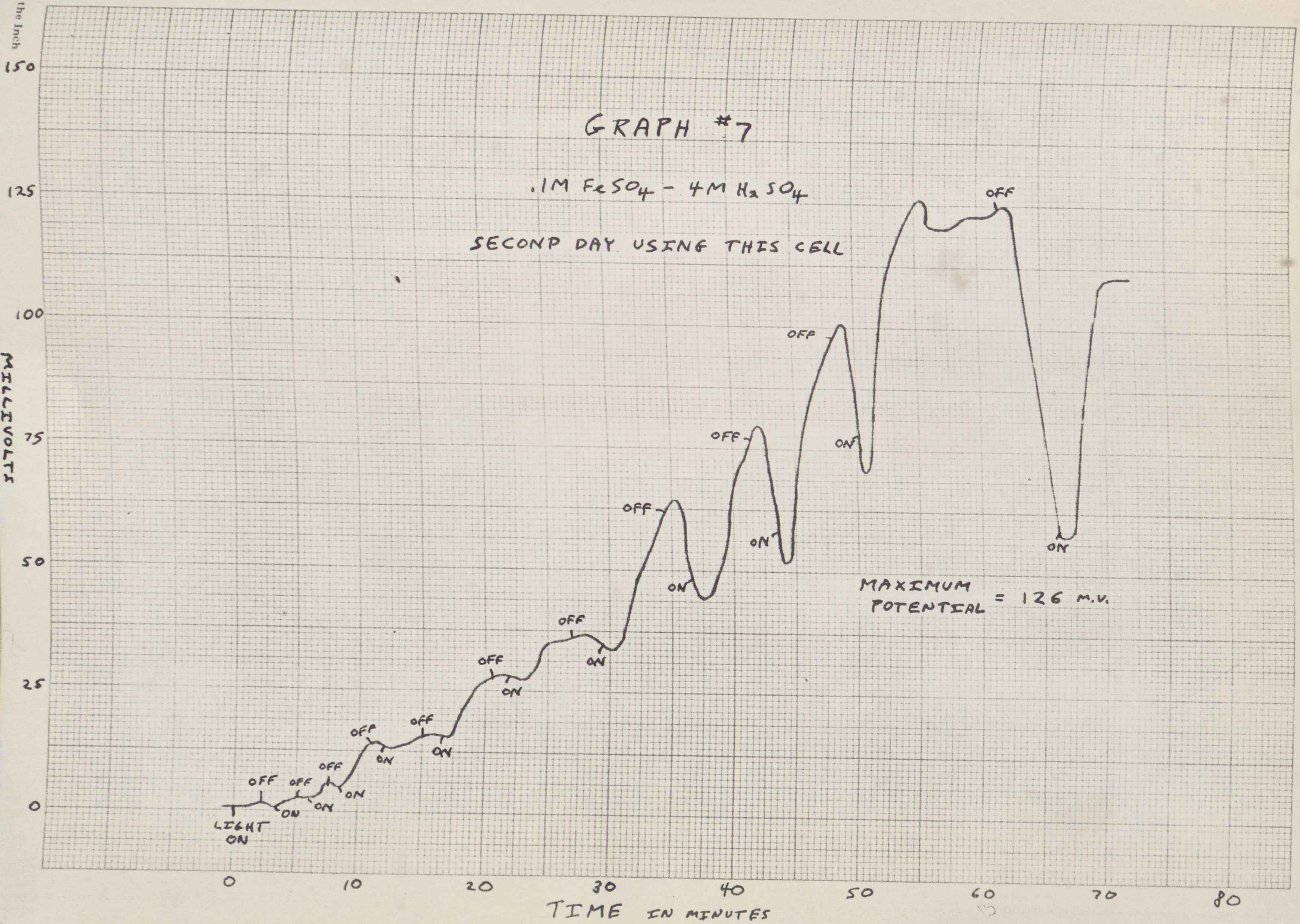

GRAPH #5
.1M $FeSO_4$ - 6M H_2SO_4
MAXIMUM POTENTIAL = 240 MV.
OFF
OFF
LIGHT ON
LIGHT ON
?
MILLIVOLTS
250
200
150
100
50
0
TIME IN MINUTES
0
10
20
30
40
50
60
70
80
90



GRAPH #6

$.1M\ FeSO_4 - 4M\ H_2SO_4$

FIRST DAY USING THIS CELL

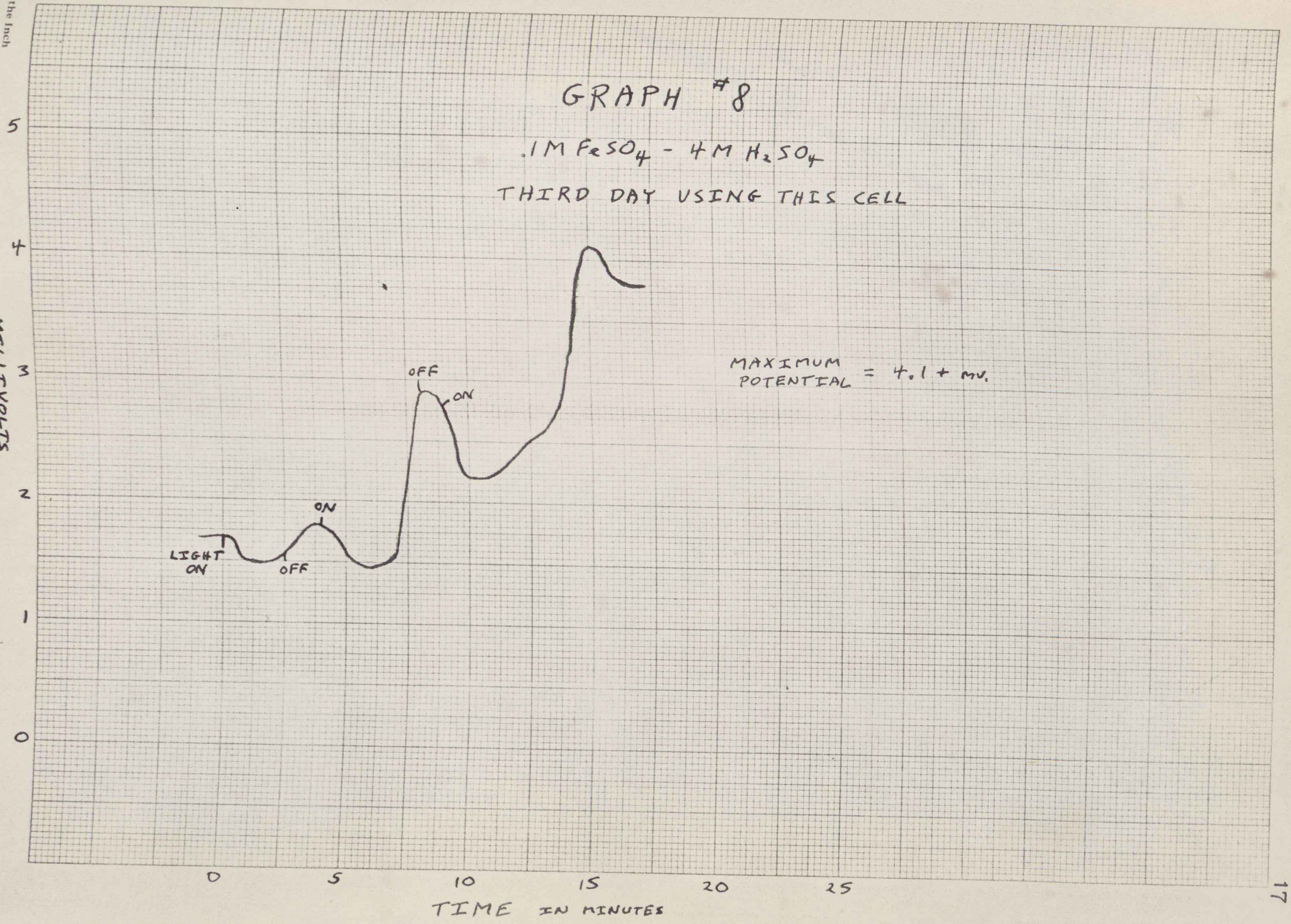


GRAPH #7

.1M $FeSO_4$ - 4M H_2SO_4

SECOND DAY USING THIS CELL

MAXIMUM POTENTIAL = 126 M.V.

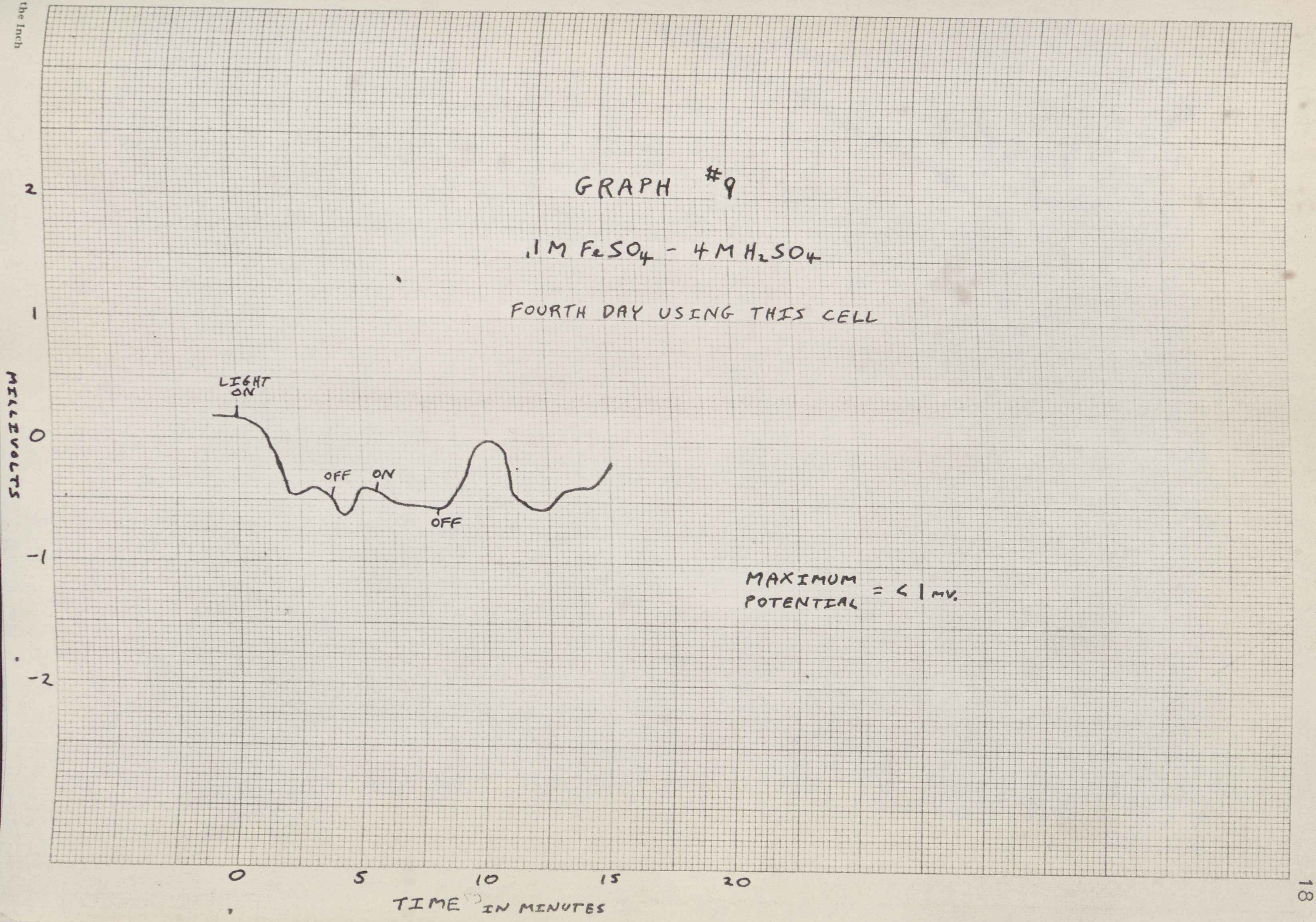


GRAPH #8

$.1M\ FeSO_4 - 4M\ H_2SO_4$

THIRD DAY USING THIS CELL

MAXIMUM POTENTIAL = 4.1 + mv.



GRAPH #9

.1M $FeSO_4$ - 4M H_2SO_4

FOURTH DAY USING THIS CELL

MAXIMUM POTENTIAL = < 1 MV.

Conclusions

(A) Cells without ferrous ions

The results of the sulfuric acid cells were at first somewhat puzzling. No change in potential had been predicted because no oxidation-reduction system was present. However, it was later found that Becquerel (6) in 1839 also discovered that a potential was produced when ultraviolet light was allowed to impinge on one of two platinum electrodes which had been placed in a dilute H_2SO_4 solution. Neither his original work nor a discussion of his work (7) were available at the time of writing, and consequently no comparison of results could be made.

The explanation of this potential and of potentials derived from similar cells is apparently not clearly understood. It has been described both as the result of electrode-electrolyte interaction and as a modification of the electrolyte in the presence of light (8). In some cells, new species were produced in the presence of light and then concentration cells resulted. In every case however, no specific details of the individual half-cell reactions were given.

An attempt was made to explain the potentials by ascribing it to a higher amount of ionization of water and sulfuric acid in the illuminated half of the cell. However, nothing definite could be found, especially that would account for the fact the illuminated electrode was negative, (a source of electrons).

Another suggestion was that hydrogen gas could be produced and perhaps absorbed by the platinum electrode. With the light on, the amount of hydrogen in solution and absorbed would gradually increase and thus the potential would also increase. With the light off, the hydrogen gas would slowly revert back to hydrogen ion and the potential would decay to zero. A problem with this theory immediately arose. If the hydrogen ion was forming hydrogen gas, then obviously something in the solution must be oxidized. There seemed however, very little in the solution which could be oxidized, except perhaps the water itself.

$$2\ H_2O = O_2 + 4\ H^+ + 4\ e^-$$

The possibilities of this theory were discussed but again no definite conclusions were drawn.

One other explanation involved photon interaction directly with the electrode. If light did interact with the electrode, then when the light was turned on or off, an immediate jump in potential should be found, Since this was not found, this explanation was considered incorrect. However, this theory called attention to the slow build up and decay. It was decided that the only way of explaining this slow build up and decay was to assume that some chemical species had to be produced in the presence of light.

While the theory of photon-electrode interaction was considered incorrect, it did yield this interesting bit of information.

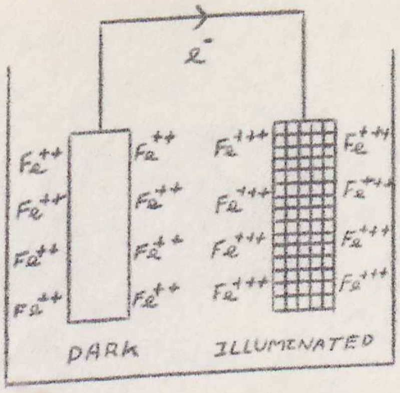
Finally, it was thought that impurities in the sulfuric acid may have been the cause of the potential. This was also ruled out when the potential of the distilled water was noted. It was furthermore interesting to note that the pure water cell produced the highest potential among the three cells: 6M H_2SO_4, water and 1M NaOH. Once more, no sound explanations for this could be given.

Obviously, these theories did not explain the data. These have been offered however so that future work in this field may have any benefits of thoughts which may be present here.

(B) With ferrous ions present

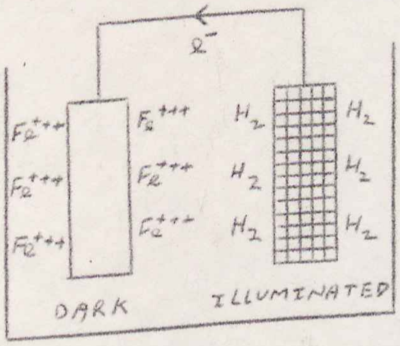
The first noticeable observation from the ferrous sulfate-sulfuric acid cell is that the maximum potential is an order of magnitude greater than the maximum potential with the plain sulfuric acid-240 mv. compared with 19 mv. The ferrous ion, being the only addition to the cell, must be responsible for this large increase. As for the sulfuric acid case, complete explanations for this potential were now sought.

The first explanation was that the illuminated half of the cell would have an excess of ferric ion and a potential would arise which would tend to equalize the ferric ion concentration in the two halves of the cell.



This implies that electrons would tend to flow toward the illuminated electrode, making the illuminated electrode positive. Since this electrode was found to be negative, the ferric ion cannot be the cause of the potential.

Originally, a hydrogen electrode had been proposed and it was here that a semi-reliable explanation was found. Immediately, one can see that a hydrogen electrode (the illuminated electrode) vs. a ferrous-ferric electrode would create a potential with the illuminated electrode being negative.



The half-reactions would be:

$$H_2 = 2\ H^+ + 2\ e^-$$

$$2\ Fe^{+++} = 2\ Fe^{++} - 2\ e^-$$

and the total reaction would be:

$$2\ Fe^{+++} + H_2 = 2\ Fe^{++} + 2\ H^+$$

In order to test this theory, it now remained to calculate the amount of hydrogen necessary to produce the 200 mv. peak potential and to see if this amount of hydrogen could reasonable be produced within the cell. The following Nernst equation was used to do this:

$$E = E_o - \frac{.0591}{2} \log \frac{(Fe^{++})^2\ (H^+)^2}{(Fe^{+++})^2\ (H_2)}$$

where $E_o = E^o_{H_2} - E^o_{Fe} = 0.000 - (-.771) = .771$

In order to solve this equation, several assumptions and approximations had to be made.

(1) The standard potential for the ferrous-ferric half-cell (-.771) was not actually the correct standard potential to use. The solution was composed of sulfate complexes and not of free ions and thus the standard potential for the complexes should have been used. This standard potential could be found experimentally, but since it has not as yet been done to our knowledge, the standard potential of the free ions was used in approximation.

(2) The concentration of ferric ion around the dark electrode was taken to be 10^{-5}M. It has been found that this is approximately the concentration which is introduced through the oxidation of ferrous by sulfate ion and oxygen from the air and through impurities in the sulfuric acid. It was further assumed that this concentration did not change appreciably even though some ferric ion may have diffused over from the illuminated half of the cell.

(3) One final assumption was that the activities equaled the concentrations.

Since only magnitudes were disired in the calculations, these assumptions were considered valid. Furthermore, to try and use actual valves would be virtually impossible.

To see if hydrogen gas could produce the required potential, it was necessary to know how much hydrogen gas would have to be produced. The amount produced would equal the amount present when the 200 mv. potential was measured minus the amount present when the potential was zero.

$$E = .771 - \frac{.0592}{2} \log \frac{(Fe^{++})^2\ (H^+)^2}{(Fe^{+++})^2\ (H_2)}$$

At zero potential, the hydrogen concentration would be approximately:

$$0 = .771 - \frac{.0591}{2} \log \frac{(.1)^2\ (6)^2}{(10^{-5})^2\ (H_2)}$$

$$(H_2) \cong 3.6 \times 10^{-17}\ M$$

At a potential of 200 mv., the hydrogen concentration would be approximately:

$$.200 = .771 - \frac{.0591}{2} \log \frac{(.1)^2\ (6)^2}{(10^{-5})^2\ (H_2)}$$

$$(H_2) \cong 3.6 \times 10^{-10}\ M$$

This meant that approximately 10^{-10} moles/liter of hydrogen gas had to be produced to result in a potential of 200 mv. This seemed entirely reasonable.

It also was noted that at this concentration, hydrogen gas is soluble in water, and therefore to produce a potential it would not have to be absorbed by the electrode but it could merely remain around the electrode much as any other ion in solution would. This conclusion was important because it was first assumed that only a small amount of hydrogen would diffuse toward the electrode and therefore only a small potential would be produced. This assumption was now considered incorrect.

By varying the concentration of the ferric ion, this theory could be further tested. By increasing the amount of ferric ion and assuming that the amount of hydrogen produced remained approximately constant, the Nernst equation would predict that the peak potential would decrease. If however the ferric ion concentration became too great, it would absorb the light and the hydrogen gas production itself would decrease and lower the potential.

Two other conclusions were also drawn from the graphs. Comparing the ferrous cells, the peak voltage for the 6M H_2SO_4 cell is higher than that for the 4M H_2SO_4 cell. This is apparently in line with the fact that more hydrogen gas was found to be produced in solutions of higher acid concentrations(5). One can also see that the ferrous-4M sulfuric cell lost its photoelectric ability as indicated by less potential on illumination on subsequent days. This may have been caused by oxygen leaking into the cell and oxidizing the ferrous ion. No further explanation of this could be offered although further explanation seemed necessary, since the cell was thought to be air-tight.

The final conclusion was that the amount of current produced by the cell would never enable it to be of any practical value. The power produced by this cell is approximately 3.6×10^{-7} watts. Since a 100-watt lamp was used, this cell would be 3.6×10^{-7} percent efficient. Much however could be done to increase the efficiency (a reflector for the ultraviolet light, better methods of keeping the plate in the dark, etc) but it would probably not reach the point of being practical.

Hopefully the true explanations for the results presented here will someday be found.

Summary

Potentials were found for (1) sulfuric acid, (2) water, (3) sodium hydroxide cells but no suitable explanation has been found for them.

A much higher potential was found for the ferrous sulfate-sulfuric acid cell. It was concluded from calculations using the Nernst equation that the potential might have been due to the production of a hydrogen electrode.

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