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SOME FACTORS AFFECTING THE RATE OF  
CORROSION OF IRON

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By N. D. Clare, B. Sc.

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Being a thesis presented to  
The University of Manitoba,  
in partial fulfillment of the  
requirements for the degree of  
Master of Science.

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## THEORIES OF CORROSION OF IRON

### 1. HISTORY

The corrosion of iron, roughly follows one of two courses. In the presence of moisture, and an abundance of oxygen, the familiar, yellowish, flaky scale known as rust, and corresponding to  $\text{Fe}^{+++}$  appears. In conditions where the supply of oxygen is limited, however, such as in a sealed tube, this yellow substance gives way to a dark green or black substance corresponding to  $\text{Fe}^{++}$ . In a piece of cast iron in a solution or in the soil, if the corrosion product be ferrous, a large part of it may be dissolved away, leaving a mass of graphite, and some ferrous rust which appears much as the original iron. Examination shows it to be soft and pulverant and altogether changed. This process is referred to as graphitization.

Iron as a metal was one of the first to become known to mankind and, as it rusts very visibly when moistened and exposed to air, one phase of its corrosion must have been observed almost as soon as the metal was first used. Of the observation of graphitization, however, there is no record until much later. Graphitization has been observed in cannons and cannon balls raised from the sea, producing, incidently, some amusing theories, to account for it.

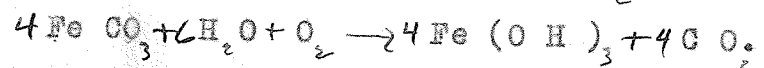
2.  
In 1817 it was shown by Daniell<sup>2.</sup> that graphitization might be produced rapidly by using dilute acids on cubes of grey cast iron.

The study of corrosion as a science begins with the work of Mallet,<sup>1.</sup> and since that time has been pursued with great vigor.

## 2. THEORIES

### Carbon Dioxide Theory

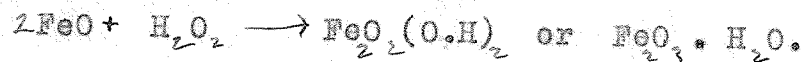
One of the first theories to gain general favor was the so-called "Carbon Dioxide Theory" <sup>3.</sup> This claimed that the basic processes of corrosion involved carbon dioxide, as follows:



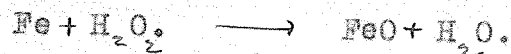
It received powerful support from Crum Brown, <sup>4.</sup> and later <sup>5.</sup> Moody showed that in the absence of carbon dioxide and other acids, that pure water and iron would not rust. This theory held sway for some time, and has many adherents today.

### Hydrogen Peroxide Theory

In 1905 <sup>6.</sup> a theory based on hydrogen peroxide being present as an intermediate product was put forth, and for some years constituted a powerful rival of the carbon dioxide theory. By it the corrosion of iron was explained as -



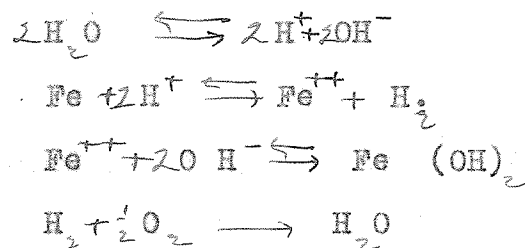
The excess hydrogen peroxide reacts with more ferrous oxide or with iron as -



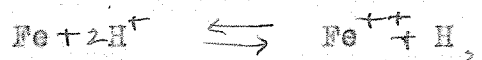
No evidence of the existence of hydrogen peroxide during corrosion was ever produced, the theory being based mainly on the fact that some substances such as potassium dichromate, etc., known to break down hydrogen peroxide, also rendered iron passive. This theory was disproved by evidence such as that of Moody (loc. cit.) and by showing that other substances, such as acids, <sup>which</sup> stabilize hydrogen peroxide accelerate corrosion. It is not accepted at present.

### Electrolytic Theory

The theory commonly known as the "Electrolytic Theory" was originated in 1903.<sup>7.</sup> It supposes that reaction between iron and water proceeds as follows:



and the ferrous hydroxide is oxidized to ferric hydroxide. The essential process being -



This theory is in close relation with the carbon dioxide theory since pure water and pure iron are practically never dealt with in practice, carbon dioxide, acids, salts, etc. usually being present. The theory is largely held today, and most of the work done on corrosion may be regarded as corroboration, since it is perfectly explained by this theory. The "Ferroxyl" indicator, a mixture of potassium ferricyanide and phenolphthalein, is also powerful support of this theory. The method is to place a piece of iron in an agar agar gel with which some of the ferroxyl indicator has been incorporated. If ~~one~~ one part of the iron be, for any reason, such as strain, segregation, etc., electropositive to another part, the ferroxyl indicator becomes pink in one place and blue in the other. The blue color indicates the presence of ferrous ferricyanide, due to the solution of iron, and the pink the presence of the hydroxyl ion owing to the plating out of hydrogen ions as hydrogen gas. This is almost proof of an entirely electrolytic action. The present results have been interpreted in the light of, and regarded as corroborating, this theory.

#### Colloidal Theory

Another theory which is of interest today, is the "Colloidal

Catalyst" theory of Friend. This theory is based mainly on the following considerations: Water which is flowing past an iron plate does not corrode the plate after a certain velocity of flow has been obtained.<sup>8</sup> A pure iron disc rotated in an acid corrodes at a rate directly proportional to the rim velocity of the disc, and does not seem to be affected by change of acid concentration between limits of 0.05% and 1% Sulphuric acid.<sup>9</sup> Friend's theory is as follows<sup>10</sup> -

- (1) Iron is passive towards distilled water in the absence of a catalyst and passes into solution, but with extreme slowness, owing to traces of electrolytes.
- (2) Dissolved iron is present as Ferrous ions which then become ferrous hydroxide sol.
- (3) This sol is then oxidized by dissolved oxygen to a sol of a higher oxide such as ferric or ferroso-ferric oxide.
- (4) The higher hydroxide sol acts catalytically by oxidizing iron rapidly and being itself reduced to the lower hydroxide sol which is, in turn, re-oxidized by dissolved oxygen.

Friend explains corrosion in acids by electrochemical solution and corrosion in neutral media by the above postulates. The retardation of corrosion by flowing water becomes a sweeping away of the colloidal ferric hydroxide sol. A moving acid, since acid corrosion is not dependant on the colloid catalyst, would not have a similar action but would corrode the iron faster owing to increased stirring. Friend has attempted to explain many things<sup>11</sup> by, and has adduced some new material in favor of, his theory, but in some cases the application of the colloidal theory appears strained, while most of the material which he claims cannot be explained by the electrolytic theory seems to be capable of such explanation.

In practically all of the work done on corrosion, however, the fact that iron, in the presence of a limited supply of water and in the absence of oxygen, shows no visible change, has been accepted as proof that no change has taken place, or can take place, between large amounts of water and iron, provided that oxygen be absent.

The composition of soils such as are present in Winnipeg suggest that they would be reducing in character. Also a study of the products of corrosion on pipes exhumed from this area shows that ferrous compounds and free graphite are almost universally present. These facts strongly suggest that oxygen, if present at all, played a very minor part in the production of this corrosion.

Normally, in a soil, oxygen would be provided in continual supply by the movement of soil waters. The soil under discussion is a heavy, gumbo clay, and offers great resistance to a flow of water through it. The presence of numerous streaks and patches of "alkali" or calcium and magnesium salts, points to an evaporation of water from capillary action in many places rather than a movement of soil solutions, and further strengthens the view that movement of soil waters is very slight in this district.

In relation to these considerations, a study of the behavior of iron with respect to solutions free from oxygen seemed desirable.

# EXPERIMENTS.

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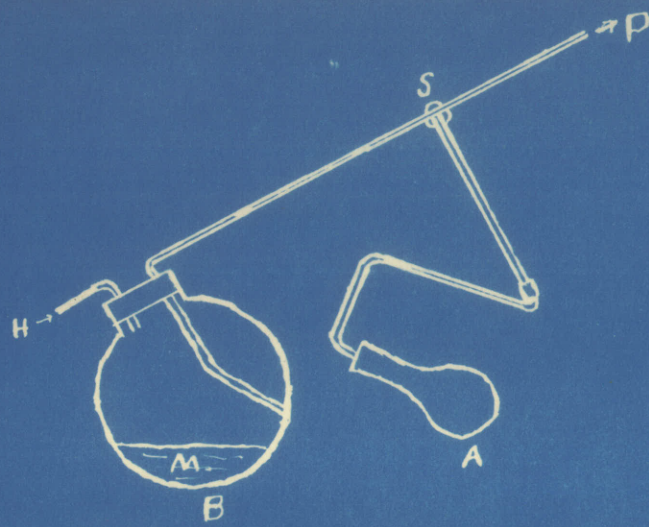


FIG. I

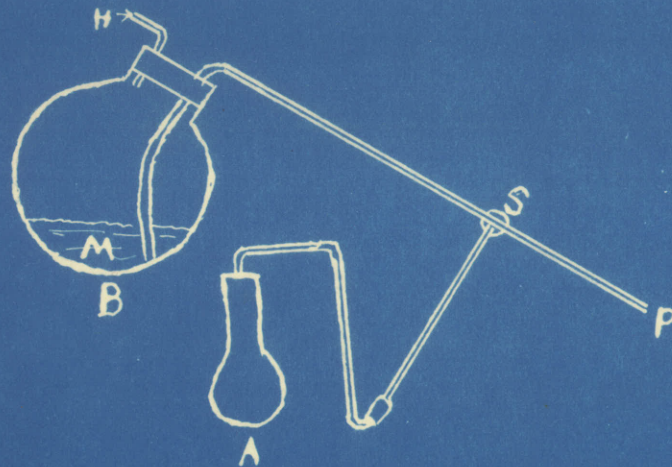


FIG. II

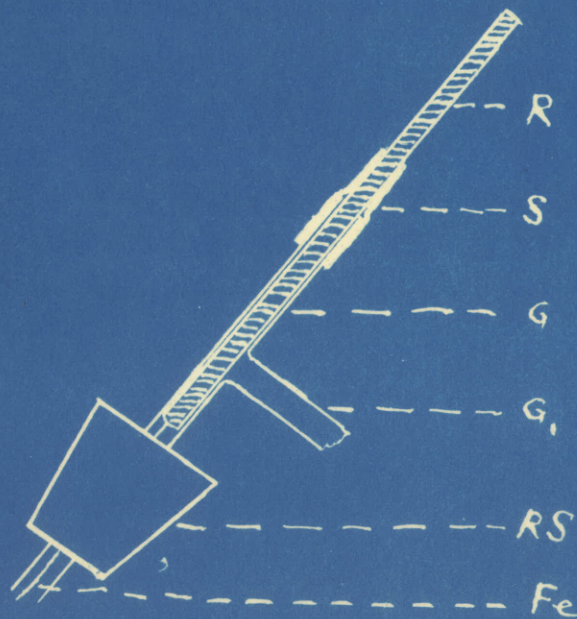


FIG. III

Description:

An experiment performed by I.R. McHaffie, <sup>12.</sup> was repeated modifying the form of iron used, so that the extent of surface could be determined, as anomalous results obtained by him were attributed to a probable difference of surface exposed.

An apparatus was constructed as follows: A large flask "B" was fitted with a two-holed cork and two glass tubes run through - a short tube was connected to the source of hydrogen "H" and a long one (bent as shown) was sealed to a three-way stopcock "S". To the other two arms of "S" were connected a vacuum pump "P" and the flask "A" which was to be filled. The whole could be rocked from position shown in figure 1 to that in Figure 11.

The solution to be used "M" was placed in "B", and the iron in Flask "A" and the apparatus was set in position as in Figure 1. Flask "B" was evacuated and filled with hydrogen several times. Next, "A" was evacuated, and then by connecting to "B" was filled with hydrogen. This was repeated five times. Finally "B" was evacuated and solution "M" boiled by warming slightly, hydrogen being gently passed meanwhile. The tube leading to the pump was then clamped off tightly to prevent any suck-back of air into either "A" or "B", and "B" was allowed to cool. When "B" was cold and once more under full hydrogen pressure, the apparatus was rocked to position as in Figure 11, "A" was evacuated and then connected to "B". Solution "M" was thus pumped into "A". "A" was evacuated again until vigorous boiling took place. A second connection with "B" usually filled "A" completely with solution free from oxygen.

One rubber connection was necessary, i.e. at the point where the delivery tube of "A" was joined to the stopcock arm. The glass tubes, however, were in contact, and heavy high pressure tubing was

used so that no leakage or chemical action is suspected at this point.

By this means flasks, each containing 5.0000 ~~g~~ .0010 gm. of Baker's iron wire 99.8% iron, and having a surface of  $111.90 \pm .02$  square centimetres, were set up, having in them solutions of Ph. 5.0, 5.9, 7.0, 8.0, and 9.0. The solution of Ph.5.0 was buffered with a mixture of potassium acid phthallate and potassium chloride prepared by hydrolysing phthallic anhydride with potassium hydroxide, (the anhydride being in excess) filtering, bringing to about Ph.5.6 with Hydrochloric acid, and finally boiling out the gases and bringing to exactly Ph. 5.0 with boiled hydrochloric acid. The solutions of ph.5.9, 7.0, 8.0, and 9.0, were prepared by adding boiled hydrochloric acid to a boiled solution of sodium phosphate. All the hydrogen ion concentrations were determined colorimetrically, the indicators used being for Ph.5.0 - methyl red, Ph.5.9 - Brom cresol purple, Ph.7.0 - brom thymol blue, checked with phenol red, Ph.8.0 - cresol red, checked with phenol red, Ph.9.0 - thymol blue alkaline.

This series was set up in a mercury trough and test tubes filled with mercury were arranged for the collection of gases evolved.

#### Results:

Ph. 5.9 filled the test tube with hydrogen in four days and then gave off no more gas at all. Consequently it was repeated, the titration in this case being to Ph.6.0. This second flask behaved more in conformity with the rest of the series.

The results of this series, neglecting Ph.5.9 and substituting Ph. 6.0, are seen on Page 9.

The solutions are seen to be evolving hydrogen in proportion to their hydrogen ion concentration. The complete cessation of action between Ph. 8.0 and Ph. 9.0 was of interest and suggested an intermediate series.

GAS RECORDSeries 1 A

| <u>P H</u> | <u>Days of Evolution</u> | <u>C.C.Evolved</u> | <u>C.C.Per Day</u> | <u>Mean</u> |
|------------|--------------------------|--------------------|--------------------|-------------|
| 5.0        | 6.                       | 10                 | 1.66               |             |
|            | 12                       | 20                 | 1.66               | 1.42        |
|            | 18                       | 17                 | 0.943              |             |
| . . . . .  |                          |                    |                    |             |
| 6.0        | 8                        | 20                 | 2.50               |             |
|            | 10                       | 17                 | 1.70               |             |
|            | 12                       | 10                 | 0.83               | 1.21        |
|            | 29                       | 17.5               | 0.60               |             |
|            | 39                       | 17.2               | 0.44               |             |
| . . . . .  |                          |                    |                    |             |
| 7.0        | 4                        | 6.0                | 1.50               |             |
|            | 144                      | 14.2               | 0.10               | 0.80        |
| . . . . .  |                          |                    |                    |             |
| 8.0        | 6                        | 4.0                | 0.66               |             |
|            | 116                      | 15.                | 0.13               | 0.39        |
| . . . . .  |                          |                    |                    |             |

Series 1 B

|           |     |       |      |      |
|-----------|-----|-------|------|------|
| 5.5       | 13  | 17.5  | 1.32 |      |
|           | 56  | 11.0  | 0.20 | 0.76 |
| . . . . . |     |       |      |      |
| 6.5       | 10  | 16.5  | 1.65 |      |
|           | 16  | 14.5  | 0.91 | 1.05 |
|           | 25  | 15.   | 0.60 |      |
| . . . . . |     |       |      |      |
| 7.5       | 21  | 14.5  | 0.69 |      |
|           | 6   | 14.75 | 2.46 | 1.08 |
|           | 41  | 3.7   | 0.09 |      |
| . . . . . |     |       |      |      |
| 8.2       | 15  | 14.75 | 0.98 |      |
|           | 5   | 14.25 | 2.85 | 1.91 |
| . . . . . |     |       |      |      |
| 8.6       | 100 | 5.0   | 0.05 | 0.05 |

SERIES 1 B.Description:

A second series of flasks was set up, using the same process for freeing from gases. The solutions were - Ph. 5.5 - potassium acid phthallate solution and carbon dioxide free sodium hydroxide ( prepared by metallic sodium), indicator Methyl red. Ph. 6.5, 7.5, 8.2, and 8.6, were sodium phosphate solutions as in the first series.

Results:

This series, however, worked in a very anomalous manner. In series 1.A. all started evolving gas soon after they were set up and evolved it slowly and continuously with the exception of Ph. 5.9 which was repeated. In Series 1.B. Ph. 6.5 started evolving gas shortly after being set up and behaved rather as did the members of Series 1.A. Ph. 5.5, 7.5, and 8.2, did nothing for a long time (two or three weeks) and then evolved gas at a great speed for a short time. They then practically ceased action. The results (Page 9) show that this series runs rather in the opposite direction to the first. It is considered that this may have been due to;

- (1) The variation in concentration of the buffer solution. No definite concentration of sodium phosphate was used and subsequent analysis showed that the solutions of Series 1.B. were more dilute than those of Series 1.A.
- (2) It will be noted that in setting up the members of Series 1, both A and B, that the iron was in its flask and in contact with air for from 14 to 30 minutes. Series 1.B. were set up in a much shorter time than was Series 1.A., and it is possible that minute traces of moisture were present in the flask when the iron was introduced. This would produce ferric oxide and might materially alter the subsequent behavior of the iron.

The results of Series 1.A. was taken as more probably representing the true course of corrosion because there was a more concentrated buffer solution and hence a greater buffer action, and there was less possibility of moisture being present before air was removed from the iron

Electrical Measurements:

13

A Bovie enclosed electro chamber, was used, containing in the four necks - the U arm of a calomel half-cell, a burette, a hydrogen electrode, and a combination iron electrode and outlet trap. This latter was arranged so that the arm could be kept above the solution and then dipped in without opening the chamber (See Figure 111.) The description is as follows:

R - An iron rod sliding through

S - A rubber sleeve fitting over

G - A glass tube with

G.- A T tube leading to the trap outlet

RS - A rubber stopper

Fe - The iron wire used for the electrode and soldered to "R"

Experiment 1.

A solution of sodium phosphate was placed in the electrode chamber, hydrogen bubbled for 25 minutes and then both electrodes read while titrating with acid.

| <u>E. M. F.</u><br><u>Hydrogen Electrode</u> | <u>P. H.</u> | <u>E. M. F.</u><br><u>Iron Electrode</u> |
|----------------------------------------------|--------------|------------------------------------------|
| .764 volts                                   | 8.79         | .457 volts                               |
| .711                                         | 7.89         | .365                                     |
| .691                                         | 7.56         | .380                                     |
| .680                                         | 7.37         | .772                                     |
| .669                                         | 7.18         | .765                                     |
| .661                                         | 7.06         | .757                                     |
| .650                                         | 6.90         | .751                                     |
| .621                                         | 6.40         | .736                                     |
| .582                                         | 5.71         | .711                                     |
| .435                                         | 3.22         | .646                                     |

Experiment 2

## Repeated Experiment 1.

| <u>E. M. F.</u><br><u>Hydrogen Electrode</u> | <u>P. H.</u> | <u>E. M. F.</u><br><u>Iron Electrode.</u> |
|----------------------------------------------|--------------|-------------------------------------------|
| .755 volts                                   | 8.65         | .495 volts                                |
| .719                                         | 8.01         | .674                                      |
| .680                                         | 7.37         | .755                                      |
| .662                                         | 7.05         | .754                                      |
| .658                                         | 7.00         | .748                                      |
| .650                                         | 6.87         | .737                                      |
| .636                                         | 6.64         | .732                                      |
| .625                                         | 6.48         | .727                                      |
| .606                                         | 6.14         | .715                                      |
| .598                                         | 6.00         | .711                                      |
| .593                                         | 5.91         | .709                                      |
| .581                                         | 5.70         | .701                                      |
| .564                                         | 5.40         | .695                                      |
| .535                                         | 4.92         | .686                                      |

Experiment 3.

## Repeated Experiment 2.

| <u>E. M. F.</u><br><u>Hydrogen Electrode</u> | <u>P. H.</u> | <u>E. M. F.</u><br><u>Iron Electrode.</u> |
|----------------------------------------------|--------------|-------------------------------------------|
| .730                                         | 8.21         | .383                                      |
| .683                                         | 7.44         | .322                                      |
| .662                                         | 7.06         | .756                                      |
| .645                                         | 6.80         | .748                                      |
| .631                                         | 6.56         | .737                                      |
| .615                                         | 6.30         | .725                                      |
| .582                                         | 5.70         | .706                                      |
| .553                                         | 5.21         | .693                                      |
| .382                                         | 2.34         | .605                                      |

The presence of a large jump in the voltage of the iron electrode will be noted near the beginning of each experiment. This, it was suspected, was due to an equilibrium being reached after starting i.e. that the voltage of the iron electrode tended to rise to a certain point without the addition of acid while the addition of acid tended to depress the voltage. The jump represents the success of the rising tendency. With this in mind, the system was set up without the acid burette and the electrode read against time, hydrogen being bubbled through meanwhile and also before the iron was inserted, as in Exps. 1, 2 and 3.

Experiment 4.

| <u>E. M. F.</u><br><u>Hydrogen Electrode</u> | <u>Time</u> | <u>E. M. F.</u><br><u>Iron Electrode.</u> |
|----------------------------------------------|-------------|-------------------------------------------|
| .763 volts                                   | 5.06        | .5743 volts                               |
|                                              | 5.07        | .6845                                     |
|                                              | 5.08        | .7608                                     |
|                                              | 5.09        | .7855                                     |
|                                              | 5.10        | .7940                                     |
|                                              | 5.11        | .7966                                     |
|                                              | 5.12        | .7972                                     |
|                                              | 5.13        | .7975                                     |
|                                              | 5.14        | .7969                                     |
|                                              | 5.15        | .7968                                     |
|                                              | 5.16        | .7973                                     |
| .758                                         | 5.17        | .7966                                     |

This shows that the iron electrode reaches an equilibrium potential in the solution.

Experiment 5.

The arrangement was that of Exps. 1, 2 and 3, but the iron electrode potential was established before any acid was used.

E. M. F.  
Hydrogen Electrode

.766 volts

Time

E. M. F.  
Iron Electrode.

.687 volts

3.19

.716

3.20

.733

3.21

.744

3.22

.751

3.23

.755

3.24

.758

3.25

.761

3.26

.762

3.27

.765

3.28

.766

3.29

.767

3.30

.768

3.31

.773

3.36

.775

3.41

.777

3.46

.778

3.51

Then adding acidP. H.

.762

8.75

.778

.720

8.04

.769

.703

7.76

.765

.686

7.47

.762

.679

7.35

.761

.665

7.10

.756

.655

6.95

.753

.646

6.81

.748

.638

6.68

.743

.637

6.66

.738

.626

6.47

.735

(Cont'd)

|            |      |            |
|------------|------|------------|
| .617 volts | 6.31 | .729 volts |
| .602       | 6.06 | .720       |
| .593       | 5.90 | .716       |
| .582       | 5.71 | .709       |
| .562       | 5.37 | .700       |
| .519       | 4.64 | .686       |

Experiment 6.

A solution was then titrated to Ph. 7.0, the iron electrode inserted, and its voltage read against time.

| <u>E. M. F.</u><br><u>Hydrogen Electrode</u> | <u>P. H.</u> |
|----------------------------------------------|--------------|
| .762                                         | 8.75         |
| .687                                         | 7.50         |
| <u>.657</u>                                  | <u>6.98</u>  |

| <u>Time</u> | <u>E. M. F.</u><br><u>Iron Electrode.</u><br>(From .4 to .748 to<br>rapidly to follow) |
|-------------|----------------------------------------------------------------------------------------|
| 12.25       | .748                                                                                   |
| 12.26       | .7504                                                                                  |
| 12.27       | .7508                                                                                  |
| 12.28       | .7510                                                                                  |
| 12.29       | .7513                                                                                  |
| 12.30       | .7519                                                                                  |
| 12.31       | .7524                                                                                  |
| 12.36       | .7535 H -.656                                                                          |
| .....       |                                                                                        |
| 2.35        | .7552 .653                                                                             |

Experiment 7

Experiment 6 was repeated except that the solution was titrated to Ph. 5.0

| <u>E. M. F.</u><br><u>Hydrogen Electrode</u> | <u>P. H.</u>                              |
|----------------------------------------------|-------------------------------------------|
| .558 <i>volts</i>                            | 5.31                                      |
| .549                                         | 5.16                                      |
| .537                                         | 4.96                                      |
| <u>.540</u>                                  | <u>5.00</u>                               |
| <u>Time</u>                                  | <u>E. M. F.</u><br><u>Iron Electrode.</u> |
| 3.52 $\frac{1}{2}$                           | .688 <i>volts</i>                         |
| 3.53                                         | .690                                      |
| 3.54                                         | .6920                                     |
| 3.55                                         | .6928                                     |
| 3.56                                         | .6940                                     |
| 3.57                                         | .6945                                     |
| 3.58                                         | .6953                                     |
| 3.59                                         | .6958                                     |
| 4.00                                         | .6966                                     |
| 4.01                                         | .6968                                     |
| 4.06                                         | .6988                                     |

During all these experiments, the iron had been suspended over the solution while the acid was added. There was thus a possibility of splashing the iron electrode. The experiment was varied by titrating the solution to the desired hydrogen ion concentration, and then rapidly removing the burette and inserting a cork bearing the iron electrode. All subsequent experiments were carried out on this plan.

#### Experiment 8.

Titrated a solution to Ph. 5.0 and then inserted the iron electrode.

| <u>Time</u> | <u>E. M. F.</u><br><u>Iron Electrode</u> | <u>E. M. F.</u><br><u>Hydrogen Electrode</u> | <u>P. H.</u> |
|-------------|------------------------------------------|----------------------------------------------|--------------|
| 5.03        | .6858 volts                              | .540 volts                                   | 5.00         |
| 5.04        | .6874                                    |                                              |              |
| 5.05        | .6897                                    |                                              |              |
| 5.06        | .6908                                    |                                              |              |
| 5.07        | .6906                                    |                                              |              |
| 5.08        | .6915                                    |                                              |              |
| 5.09        | .6924                                    |                                              |              |
| 5.10        | .6924                                    |                                              |              |
| 5.15        | .6934                                    | .546                                         | 5.10         |

Experiment 9.

Experiment 8 was repeated, titrating to Ph. 7.5

| <u>Time</u> | <u>E. M. F.</u><br><u>Iron Electrode</u> | <u>E. M. F.</u><br><u>Hydrogen Electrode.</u> | <u>P. H.</u> |
|-------------|------------------------------------------|-----------------------------------------------|--------------|
| 3.58        | .4073                                    | .6875                                         | 7.50         |
| 3.59        | .6890                                    |                                               |              |
| 4.00        | .751                                     |                                               |              |
| 4.01        | .764                                     |                                               |              |
| 4.02        | .766                                     |                                               |              |
| 4.03        | .7663                                    |                                               |              |
| 4.04        | .7661                                    |                                               |              |
| 4.11        | .7642                                    | .6886                                         | 7.52         |

Experiment 10

The run was repeated, titrating a solution of potassium acid phthallate to ph 5.0 with base approximately .37 N.

| <u>Time</u> | <u>E. M. F.</u><br><u>Iron Electrode</u> | <u>E. M. F.</u><br><u>Hydrogen Electrode</u> | <u>P. H.</u> |
|-------------|------------------------------------------|----------------------------------------------|--------------|
| 5.17        | .6582                                    | .5404                                        | 5.00         |
| 5.18        | .6608                                    |                                              |              |
| 5.19        | .6602                                    |                                              |              |
| 5.20        | .6597                                    |                                              |              |
| 5.30        | .6658                                    |                                              |              |
| 5.40        | .6664                                    | .5388                                        | 4.99         |

Experiment 11.

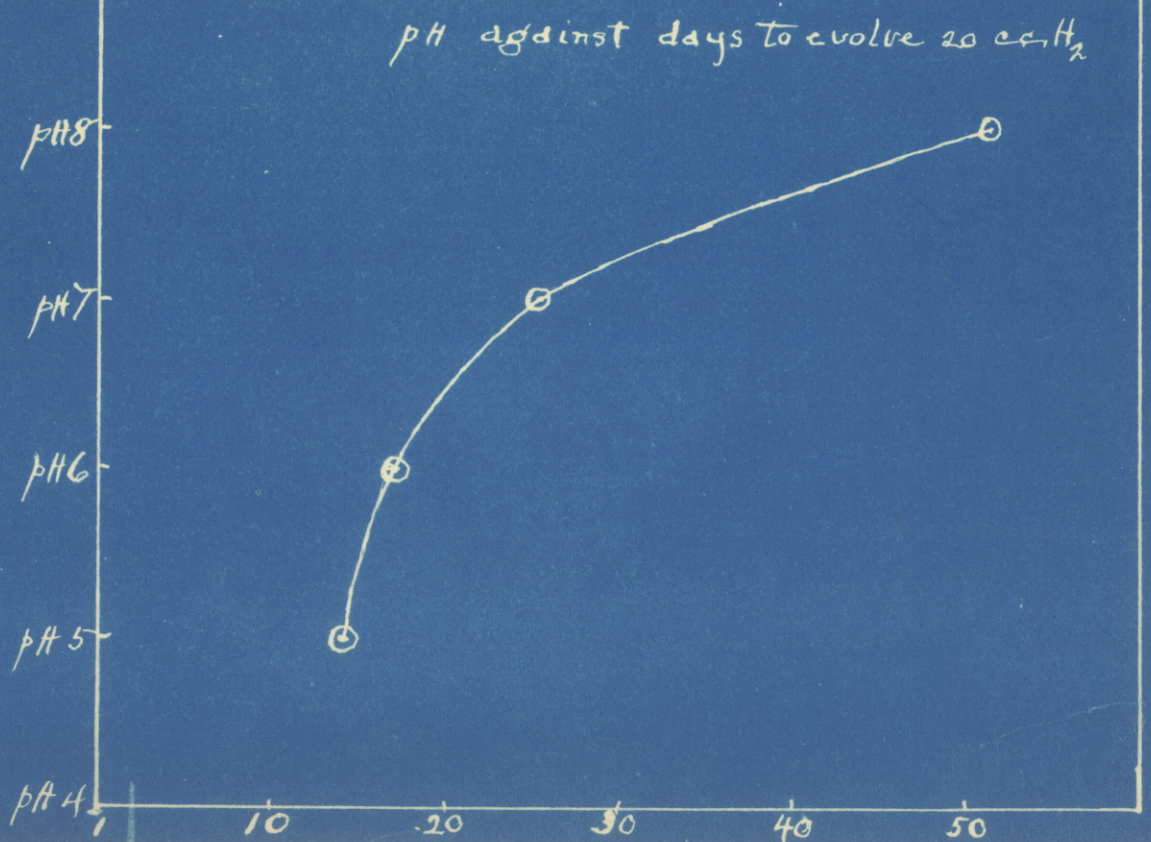
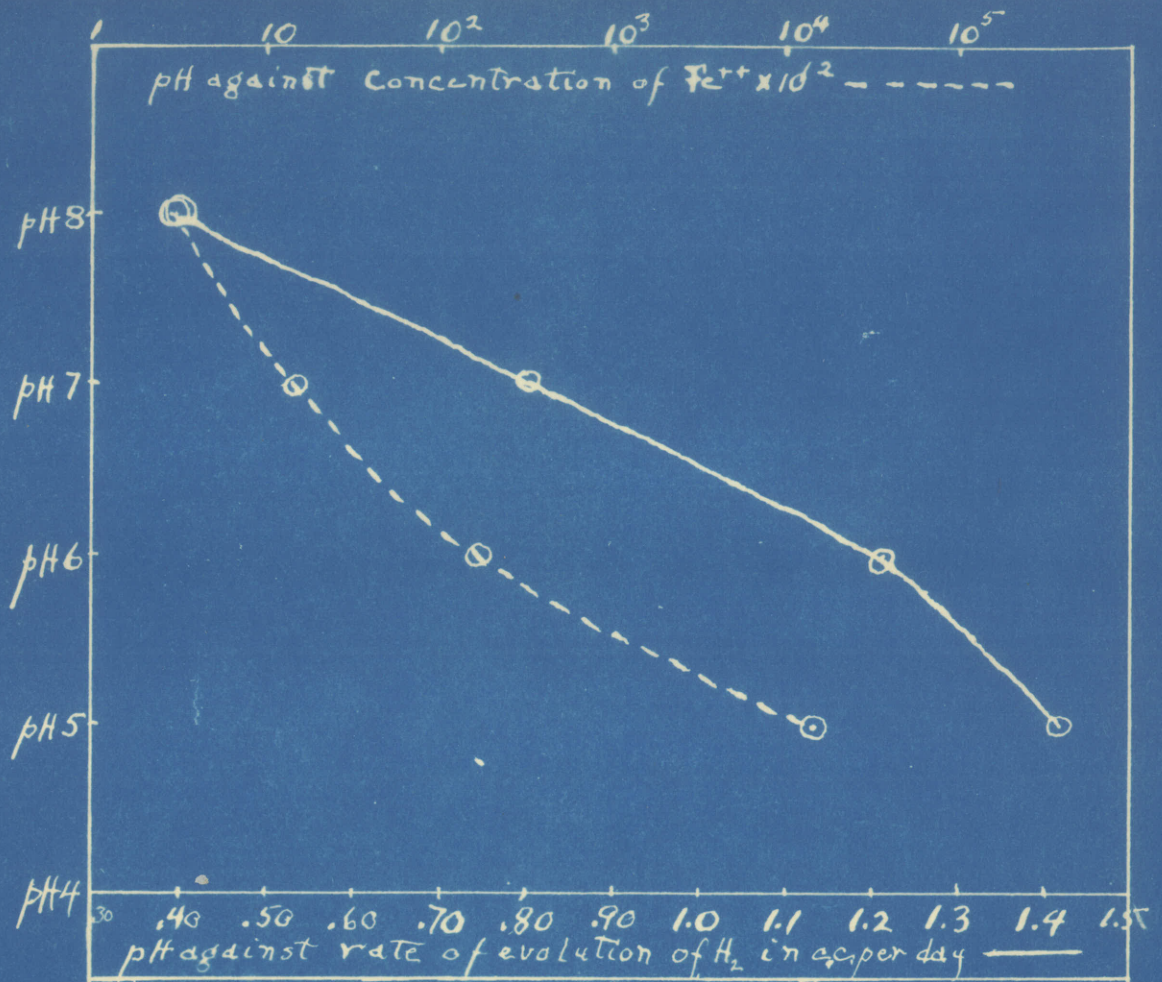
Experiment 10 was repeated.

| <u>Time</u> | <u>E. M. F.<br/>Iron Electrode</u> | <u>E. M. F.<br/>Hydrogen Electrode</u> | <u>P. H.</u> |
|-------------|------------------------------------|----------------------------------------|--------------|
| 11.29       | .546 <i>volts</i>                  | .543 <i>volts</i>                      | 5.05         |
| 11.30       | .593                               |                                        |              |
| 11.31       | .622                               |                                        |              |
| 11.32       | .634                               |                                        |              |
| 11.33       | .640                               |                                        |              |
| 11.34       | .645                               |                                        |              |
| 11.35       | .649                               |                                        |              |
| 11.36       | .652                               |                                        |              |
| 11.37       | .655                               |                                        |              |
| 11.38       | .657                               |                                        |              |
| 11.39       | .6587                              |                                        |              |
| 11.40       | .6592                              |                                        |              |
| 11.45       | .6597                              | .543                                   | 5.05         |

Experiment 12.

Experiment 11 was repeated.

| <u>Time</u>        | <u>E. M. F.<br/>Iron Electrode</u> | <u>E. M. F.<br/>Hydrogen Electrode</u> | <u>P. H.</u> |
|--------------------|------------------------------------|----------------------------------------|--------------|
| 3.06 $\frac{1}{2}$ | .651                               | .540                                   | 5.00         |
| 3.07               | .657                               |                                        |              |
| 3.08               | .660                               |                                        |              |
| 3.09               | .6610                              |                                        |              |
| 3.10               | .6618                              |                                        |              |
| 3.15               | .6637                              |                                        |              |
| 3.20               | .6650                              |                                        |              |
| 3.25               | .6658                              | .537                                   | 4.95         |



Considering these experiments, it will be seen that the Series with Sodium phosphate agree well within themselves, but the readings with potassium acid phthallate, while they agree fairly well, do not quite check with those in the sodium phosphate solution. The following table shows this:

| From titration<br>Experiment 5 |           | From titrating individual<br>solutions of sodium<br>phosphate |                              | From titrating<br>potassium acid<br>phthallate |           |
|--------------------------------|-----------|---------------------------------------------------------------|------------------------------|------------------------------------------------|-----------|
| P. H.                          | E.M.F. Fe | P. H.                                                         | E.M.F. Fe                    | PH.                                            | E.M.F. Fe |
| 7.47                           | .762      | 7.50                                                          | .764                         |                                                |           |
| 7.00 #                         | .754      | 7.00                                                          | .755                         |                                                |           |
| 6.06                           | .720      |                                                               |                              |                                                |           |
| 5.00 #                         | .693      | 5.00                                                          | .695!                        | 5.00                                           | .666 !    |
| # (Calculated)                 |           |                                                               | ! ( Mean of two experiments) |                                                |           |

From these potentials the concentration of ferrous ions may be calculated by the formula  $E = E.P._{Fe} - \frac{.058}{2} \log (Fe^{++})$ .

The values obtained are -

| P. H.  | E. M. F.<br>Fe. | (Fe <sup>++</sup> )    |                                                            |
|--------|-----------------|------------------------|------------------------------------------------------------|
| 8.00   | .769            | $4.88 \times 10^{-12}$ |                                                            |
| 7.00   | .754            | $1.61 \times 10^{-11}$ |                                                            |
| 6.00   | .720            | $2.34 \times 10^{-10}$ |                                                            |
| 5.00 { | .693            | $2.04 \times 10^{-9}$  | Na <sub>3</sub> P O <sub>4</sub> Solution                  |
| 5.00 { | .666            | $1.74 \times 10^{-8}$  | KH = C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> Solution |

These results are shown graphically on the opposite page, and compared with the rate of evolution of hydrogen from Series 1 A. No marked resemblance can be traced. A graph is also appended showing the relation of buffered P.H. to the time of evolution of 20 c.c. of hydrogen. This is in fair agreement with that obtained by McHaffie (loc. cit.)

SERIES 11.Description.

A Series was also set up to try the effect of water on iron under various conditions.

A florence flask was filled with water and boiled vigorously. A quantity of Baker's 99.8% iron wire ( 5.2316 gms.) having been introduced, the flask was boiled again to expell gas clinging to the iron. A cork with a delivery tube was then inserted and the flask again boiled. The end of the delivery tube was then dipped into some boiling conductivity water and the flask allowed to suck back; a bubble of gas still remaining being removed by boiling again with the end of the delivery tube under the surface of the water in the other vessel.

A second flask of the same size was set up, using the pure iron wire, but without removing the dissolved air.

A wrought iron wire was then secured and set up with conductivity water without removal of air. Also a steel piano wire was cut up in two-inch lengths and set up similarly. The surfaces of all these wires were determined, and the weights used (with the exception of the first flask set up) were such as to provide equal surfaces.

Results:

- (a) Pure iron - no oxygen, weight Fe = 5.2316 gm.
- (b) Pure iron - oxygen present, weight Fe. = 4.9788 gm.
- (c) Wrought iron - oxygen present, weight Fe. = 9.1965 gm.
- (d) Steel wire - oxygen present, weight Fe = 11.3967 gm.

(a) did absolutely nothing as far as could be seen.

(b) gave yellow rust inside of two hours. In a day a bluish coloration indicated the presence of ferrous ions. The ferrous rust formed at points of contact between the wires and between wire and glass, and spread from there. In eight days a black rust was falling to the bottom and exposing bright iron. Ferric rust had disappeared.

The yellow rust in this case formed in many *places* as a spiral, giving the appearance of a yellow thread wrapped around the wire.

(c) started to corrode overnight. Rust occurred mainly in patches, presenting a crater-like appearance - a dark centre and little tufts of rust in a circle around it. Presently little individual spicules of rust began to form all over the wire and also on the glass. The yellow color persisted for five months. The flask was then taken down. The wire was covered with small black patches, with a small amount of yellow rust around them. Yellow rust was on the bottom of the flask. The P H of the solution was 9.4.

(d) rusted entirely in craters at first, all having a dark spot surrounded by a circle of yellow rust tufts. Then spicules of rust appeared between the craters and also on the glass. In five months nothing was present but numerous black spots surrounded by a barely visible circle of yellow. Much yellow rust was on the bottom of the flask. The P H of the solution was 9.4. None of these gave off any gas.

After forty-two days, 3 gms. of ferrous sulphate were added to (b). No effect was observed in five days. Then 3 gms. of Ferric sulphate were added. The iron evolved quantitles of gas almost immediately, the record being -

Dec. 12th, 9 a.m. added Ferric Sulphate

12 a.m. over a test tube full of hydrogen.

6 p.m. 20 c.c. of hydrogen.

13th, 9 a.m. 21 c.c. " "

6 p.m. 12 c.c. " "

14th 6 p.m. 9 c.c. " "

At this point gas evolution ceased.

SERIES 111Description.

Calcium Sulphate and calcium carbonate are two important constituents of Winnipeg soil, and have also been identified with corrosion of iron elsewhere<sup>14</sup>. It was therefore desirable to study their action along with that of the soil.

A series of experiments was carried out using pure iron wire throughout.

- (a) A solution consisting of calcium sulphate and calcium carbonate periodically shaken with conductivity water over a period of 26 days.
- (b) A solution of soil and distilled water which had been periodically shaken during 17 days and then allowed to settle for 9 days.
- (c) Some of the residual soil and solution from (b).

These three being poured in on top of the iron and corked without removing the air.

- (d) Some residual soil and solution from (b) was heated in an autoclave at 15 lbs. and 121 °C for one hour to kill all bacteria, and then put up by means of the gas removing process of Series I, the soil being liquid enough to pump through much as would a solution.
- (e) A solution of sodium phosphate titrated to Ph 8.0 by boiled hydrochloric acid, was mixed with a quantity of barium sulphate. The barium sulphate was prepared by precipitation (using excess sulphuric acid) from cold solution, so as to keep the particles as small as possible. It was then separated and washed by centrifuging until the supernatant fluid gave no test for sulphates with barium chloride and a very minute trace test for chlorides with silver nitrate. Before being used a small amount of the barium sulphate was thoroughly stirred up with some of the sodium phosphate solution, then allowed to settle out and the supernatant solution was pipetted off and tested. Cresol red was added to equal amounts of this and of the original solution which had not been mixed with the barium sulphate. The colors in the two test tubes were indistinguishable, thus showing that the barium sulphate had no effect on the acidity of the solution. The bulk of the barium sulphate and solution were then thoroughly mixed and put up by the gas removing apparatus. The mixed barium sulphate and solution pumped quite easily.

- (f) Baker's standard sand was digested with concentrated hydrochloric acid for 24 hours and then washed carefully by decantation until the wash waters showed no chloride test with silver nitrate. It was then dried at 110 °C for four hours and placed in a flask along with the iron wire. A solution of sodium phosphate titrated to Ph 8.0 was then put in the large flask and pumped in on top of the sand and iron.

The weight of iron used was  $5.0000 \pm .0021$  gm.

Behavior:

(a) the wire showed yellow quite soon and then blackened, in three or four days no yellow remaining.

(b) did absolutely nothing that could be seen. The wire is now, after five months, as bright as when put in.

(c) gave out much water after two or three days. This was either due to swelling of the soil such as occurs with some colloids, or to gas being entangled in the soil. A flask was set up, as a check, having the same soil and solution, but no iron in it. This flask did nothing, showing that swelling was not occurring. The soil and iron turned out gas for more than a month with no sign of coloration. Thirty-eight days after setting up evolution of gas ceased, and the solution and that part of the wire which protruded above the soil, turned yellow and then red. It is probable that leakage occurred around the cork. The cork was then sealed heavily with paraffin, but no change has been observed since.

(d) did nothing for some time, then started to evolve gas and been doing it ever since at a remarkably regular rate. The wire, where showing through the soil, is blue-green, as is also the soil around it, where protruding into the solution above the soil, it is still bright and shows no sign of any corrosion.

(e) evolved gas very rapidly for a short time and then ceased completely. This behavior resembled that of the members of Series 1 B., and hence it was repeated, using nearly saturated sodium phosphate solution and taking particular precautions to dry the flask.

(f) evolved gas slowly and continuously.

(g) is the experiment repeating (e). The gas evolution was very rapid at first, but the rate has dropped to approximately that of (d) and is showing no signs of further slackening.

The P. H.s of the various solutions concerned are (a) - 7.8- Cresol Red, (b) 8.3 - Thymol Blue alkaline checked with cresol red. (c) (the solution above the soil) - 8.0 phenol red. (d) ~~for~~ (e), (f) and (g) were made 8.0 to correspond to (c) as already described.

#### Electrical Measurements.

The soil solution was also examined electrometrically.

The Bovie enclosed electrode was used as described previously, hydrogen being bubbled through the soil solution after setting up for about twenty minutes before beginning the titration. The iron electrode was then inserted and read against time. The hydrogen electrode could not be used as, owing to the presence of sulphates, it is untrustworthy. 14

#### Experiment 13

An attempt was made to find the effect of the stirring due to bubbling of hydrogen. The set up was the same as that described for other iron electrode work. The iron was inserted and read against time with the hydrogen supply cut off at first. It had been previously determined that the bubbling of hydrogen had no effect on the Ph. of the soil solution.

| <u>Time</u> | <u>E.M.F. Fe</u> | <u>Time</u> | <u>E.M.F. Fe</u> |
|-------------|------------------|-------------|------------------|
| 3.25        | .445 volts       | 3.32        | .621 volts       |
| 3.26        | .501             | 3.33        | .625             |
| 3.27        | .555             | 3.34        | .629             |
| 3.28        | .581             | 3.35        | .6326            |
| 3.29        | .597             | 3.36        | .6354            |
| 3.30        | .607             | 3.37        | .6378            |
| 3.31        | .615             | 3.38        | .6399            |

| <u>Time</u> | <u>E.M.F. Fe</u>           | <u>Time</u>                    | <u>E.M.F. Fe</u> |
|-------------|----------------------------|--------------------------------|------------------|
| 3.39        | .6416 volts                | 4.27                           | .548 volts       |
| 3.40        | .6436                      | 4.28                           | .537             |
| 3.41        | .6453                      | 4.29                           | .526             |
| 3.42        | .6468                      | 4.30                           | .540             |
| 3.43        | .6482                      | 4.31                           | .553             |
| 3.44        | .6493                      | 4.32                           | .562             |
| 3.45        | .6502                      | 4.33                           | .569             |
| 3.46        | .6514                      | 4.34                           | .560             |
| 3.47        | .6528                      | 4.35                           | .569             |
| 3.48        | .6538                      | 4.40                           | .630             |
| 3.49        | .6548                      | 4.45                           | .696             |
| 3.50        | .6560                      | 4.47                           | .702             |
| 3.55        | .6606                      | 4.49                           | .707             |
| 4.05        | .6692                      | Flushed in about 1 c.c of KCl. |                  |
| 4.15        | .6773                      | 4.51                           | .702             |
| 4.25        | .6867                      | 4.53                           | .707             |
| 4.26        | Started Hydrogen bubbling. | 4.55                           | .710             |
|             |                            | 4.57                           | .713             |
|             |                            | 5.00                           | .716             |
|             |                            | 5.05                           | .722             |
|             |                            | 5.10                           | .725             |

The experiment was discontinued at this point on account of the U arm of the calomel cell needing flushing, while flushing apparently varied the potential of the iron electrode.

It was seen from this experiment that stirring was necessary and that it apparently only hastened the attainment of equilibrium. Therefore, in all subsequent experiments, hydrogen was bubbled through while the readings were taken.

Experiment 14

An iron electrode was inserted in the soil solution and read while hydrogen was bubbled through:

| <u>Time</u> | <u>EMF Fe.</u>    | <u>Time</u> | <u>EMF Fe.</u>    |
|-------------|-------------------|-------------|-------------------|
| 3.27        | .495 <i>volts</i> | 3.46        | .704 <i>volts</i> |
| 3.28        | .510              | 3.47        | .707              |
| 3.29        | .521              | 3.48        | .709              |
| 3.30        | .532              | 3.49        | .712              |
| 3.31        | .541              | 3.50        | .714              |
| 3.32        | .551              | 3.55        | .722              |
| 3.33        | .561              | 4.00        | .727              |
| 3.34        | .572              | 4.05        | .731              |
| 3.35        | .590              | 4.10        | .735              |
| 3.36        | .608              | 4.15        | .739              |
| 3.37        | .633              | 4.20        | .7420             |
| 3.38        | .651              | 4.25        | .7446             |
| 3.39        | .664              | 4.30        | .7469             |
| 3.40        | .674              | 4.35        | .7491             |
| 3.41        | .682              | 4.40        | .7508             |
| 3.42        | .688              | 4.45        | .7520             |
| 3.43        | .693              | 4.50        | .7535             |
| 3.44        | .698              | 5.02        | .7563             |
| 3.45        | .700              |             |                   |

The U arm needing flushing, the experiment again had to be stopped.

The need for flushing the U arm was overcome in subsequent experiments by taking readings every five minutes, rather than every minute, and turning off the stopcock in the U arm between readings.

Experiment 15.

Experiment 14 was repeated, turning off the stopcock in the U arm as indicated above:

| <u>Time</u> | <u>E.M.F. Fe</u> | <u>Time</u> | <u>E.M.F. Fe.</u> |
|-------------|------------------|-------------|-------------------|
| 3.20        | .448 volts       | 3.55        | .728 volts        |
| 3.21        | .462             | 4.00        | .739              |
| 3.22        | .475             | 4.05        | .747              |
| 3.23        | .490             | 4.10        | .756              |
| 3.24        | .503             | 4.15        | .759              |
| 3.25        | .514             | 4.20        | .761              |
| 3.26        | .522             | 4.25        | .7627             |
| 3.27        | .533             | 4.30        | .7641             |
| 3.28        | .543             | 4.35        | .7654             |
| 3.29        | .552             | 4.40        | .7664             |
| 3.30        | .562             | 4.50        | .7680             |
| 3.35        | .613             | 5.00        | .7689             |
| 3.40        | .664             | 5.10        | .7691             |
| 3.45        | .695             | 5.20        | .7688             |
| 3.50        | .714             | 5.30        | .7689             |

Experiment 16.

Experiment 15 was repeated.

| <u>Time</u> | <u>E.M.F. Fe</u> | <u>Time</u> | <u>E.M.F. Fe.</u> |
|-------------|------------------|-------------|-------------------|
| 3.24        | .384             | 4.05        | .723              |
| 3.25        | .399             | 4.10        | .734              |
| 3.26        | .414             | 4.15        | .743              |
| 3.27        | .426             | 4.20        | .748              |
| 3.28        | .437             | 4.25        | .753              |
| 3.29        | .447             | 4.30        | .757              |
| 3.30        | .458             | 4.40        | .7628             |
| 3.35        | .502             | 4.50        | .7643             |
| 3.40        | .563             | 5.00        | .7651             |
| 3.45        | .620             | 5.10        | .7659             |
| 3.50        | .674             | 5.20        | .7661             |
| 3.55        | .698             | 5.30        | .7660             |
| 4.00        | .714             |             |                   |

A second soil solution had been previously prepared by shaking periodically during about one month, and then allowing it to settle out. Some of this was used in the same way.

### Experiment 17.

Experiment 16 was repeated, using soil solution No. 2.

| <u>Time</u> | <u>E.M.F. Fe</u> | <u>Time</u> | <u>E.M.F. Fe.</u> |
|-------------|------------------|-------------|-------------------|
| 8.45        | .324 volts       | 9.50        | .606 volts        |
| 8.46        | .358             | 10.00       | .666              |
| 8.47        | .379             | 10.11       | .713              |
| 8.48        | .395             | 10.20       | .720              |
| 8.49        | .409             | 10.30       | .725              |
| 8.50        | .421             | 10.40       | .735              |
| 8.55        | .471             | 10.50       | .740              |
| 9.00        | .503             | 11.00       | .746              |
| 9.10        | .535             | 11.10       | .7469             |
| 9.20        | .531             | 11.20       | .7477             |
| 9.30        | .566             | 11.30       | .7479             |
| 9.41        | .587             |             |                   |

### Experiment 18

Experiment 17 was repeated.

| <u>Time</u> | <u>E.M.F. Fe</u> | <u>Time</u> | <u>E.M.F. Fe</u> |
|-------------|------------------|-------------|------------------|
| 3.23        | .440             | 4.00        | .740             |
| 3.24        | .458             | 4.10        | .7484            |
| 3.25        | .470             | 4.20        | .7447            |
| 3.26        | .479             | 4.30        | .7578            |
| 3.27        | .470             | 4.40        | .7618            |
| 3.28        | .477             | 4.51        | .7644            |
| 3.29        | .485             | 4.55        | .7642            |
| 3.30        | .495             | 5.03        | .7678            |
| 3.40        | .582             | 5.05        | .7647            |
| 3.50        | .719             |             |                  |

Experiment 19.

Experiment 18 was repeated.

| <u>Time</u> | <u>E.M.F.</u> | <u>Fe</u> | <u>Time</u> | <u>E.M.F.</u> | <u>Fe</u> |
|-------------|---------------|-----------|-------------|---------------|-----------|
| 3.30        | .542          | volts     | 4.10        | .747          | volts     |
| 3.31        | .560          |           | 4.22        | .753          |           |
| 3.33        | .556          |           | 4.47        | .760          |           |
| 3.34        | .558          |           | 4.55        | .7631         |           |
| 3.35        | .559          |           | 5.00        | .7650         |           |
| 3.40        | .591          |           | 5.05        | .7660         |           |
| 3.50        | .710          |           | 5.10        | .7661         |           |
| 4.00        | .737          |           | 5.15        | .7662         |           |

The Ph. of soil solution No. 1 (after gas had been removed) was 8.0. The iron electrode potential in a solution of Ph 8.04 (Exp. 5) was .769 volts, and the iron electrode potential in soil solution No. 1 was .767 volts (mean of Exp. 15 and 16). Also the measured Ph. of soil solution No. 2, using phenol red, was 7.6. The iron electrode potential in a solution of Ph. 7.6, was .764, while in Soil solution No. 2 it was .765 (mean of Exp. 18 and 19). It is thus seen that the iron has no undue potential in soil solutions and indeed may be used as a rough measure of hydrogen ion concentration in solutions where the presence of sulphates renders the hydrogen electrode useless.

The following experiments were carried out to determine the potential of iron in a clay suspension.

Experiment 20

The apparatus and procedure was the same as that of Exp. 19, etc., except that a soil suspension in its solution (Soil No.1 sterilized and degassed) was used in place of soil solution.

Experiment 20. (Cont'd)

| <u>Time</u> | <u>E.M.F. Fe</u> | <u>Time</u> | <u>E.M.F. Fe</u> |
|-------------|------------------|-------------|------------------|
| 3.19        | .473 volts       | 3.35        | .710 volts       |
| 3.20        | .566             | 3.45        | .740             |
| 3.21        | .600             | 4.00        | .749             |
| 3.22        | .625             | 4.15        | .7546            |
| 3.23        | .643             | 4.25        | .7555            |
| 3.24        | .654             | 4.39        | .7561            |
| 3.25        | .662             | 4.55        | .7561            |
| 3.30        | .697             | 5.10        | .7558            |

Experiment 21

Experiment 20 repeated.

| <u>Time</u> | <u>E. M. F. fe</u> | <u>Time</u> | <u>E.M.F. Fe</u> |
|-------------|--------------------|-------------|------------------|
| 8.11        | .510               | 8.40        | .729             |
| 8.12        | .572               | 8.50        | .737             |
| 8.13        | .609               | 9.00        | .740             |
| 8.14        | .629               | 9.10        | .744             |
| 8.15        | .639               | 9.21        | .7467            |
| 8.16        | .651               | 9.30        | .7485            |
| 8.17        | .664               | 9.45        | .7509            |
| 8.18        | .675               | 10.00       | .7519            |
| 8.19        | .681               | 10.15       | .7530            |
| 8.20        | .699               | 10.30       | .7539            |
| 8.25        | .709               | 10.45       | .7535            |
| 8.30        | .720               | 11.00       | .7540            |

These results indicate a slightly lower voltage than would be expected, using a substance of Ph. 8.0. In fact, they correspond with the potential obtained from a solution of Ph. 7.0. (See Exp. 5.). This indicates that the equilibrium voltage corresponds to more iron in solution when soil is present than in the soil solution

with no solid clay present.

Results:

The gas record of the solutions which evolved gas is -

| <u>System</u> | <u>Days of Evolution</u> | <u>C.C. Evolved</u> | <u>C.C. per Day</u> | <u>Mean</u> |
|---------------|--------------------------|---------------------|---------------------|-------------|
| C.            | 11                       | 16                  | 1.45                | 1.59        |
|               | 11                       | 19                  | 1.73                |             |
| D.            | 22                       | 20                  | 0.91                | 1.59        |
|               | 8                        | 18.5                | 2.56                |             |
|               | 13                       | 18.5                | 1.42                |             |
|               | 11                       | 20.0                | 1.80                |             |
|               | 13                       | 19.5                | 1.50                |             |
|               | 11                       | 19.0                | 1.73                |             |
|               | 13                       | 20.1                | 1.55                |             |
|               | 13                       | 19.6                | 1.51                |             |
|               | 15                       | 19.8                | 1.32                |             |
| E.            | 4                        | 19.4                | 5                   |             |
| F.            | 27                       | 17.6                | 0.65                |             |
| G.            | 2½                       | 20.3                | 8.12                |             |
|               | 11                       | 19.8                | 1.80                |             |

It is a rather striking fact that C and D should both have the same mean rate of evolution of gas.

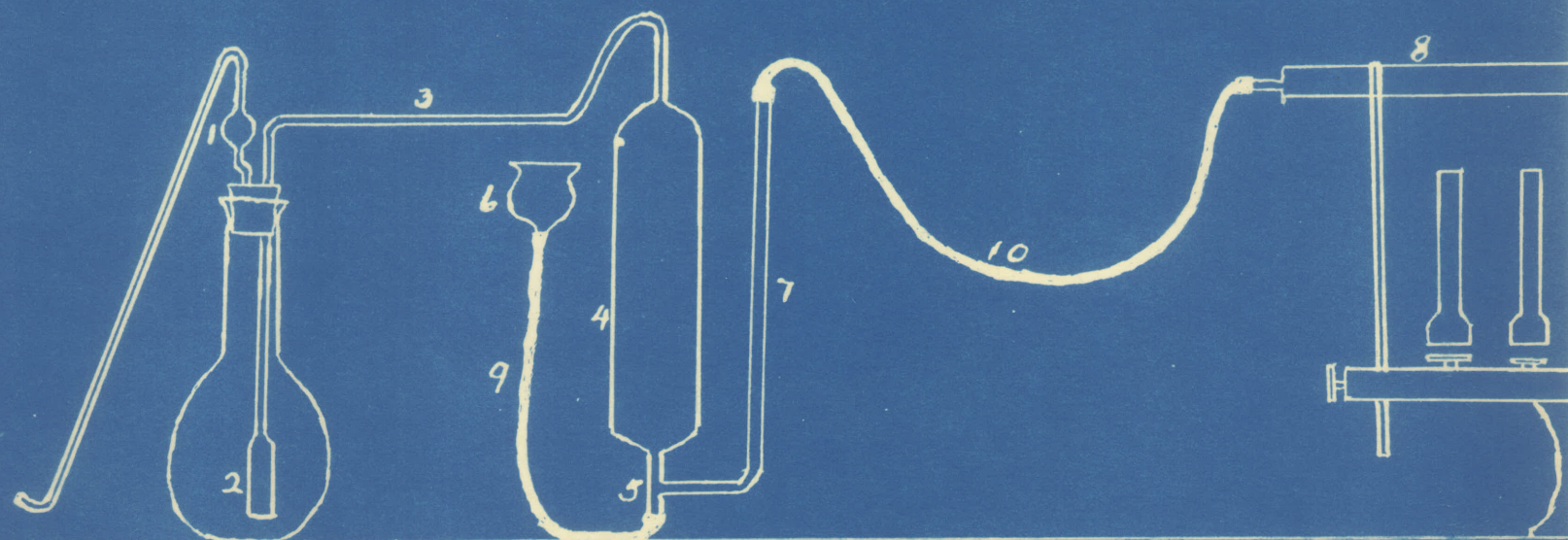
Experiments were carried out to determine any buffer actions in the various substances used in this Series. The hydrogen electrode, as mentioned before, cannot be used owing to the presence of sulphates. Colorimetric means, however, can be used.

Titration of the soil solutions, both Nos. 1 and 2, showed that any buffer action present was inappreciable, two or three drops of .01 N. acid or base being sufficient to alter their Ph. about 6 units, much as is the case with distilled water.

Titration of the soil suspension was effected as follows. A quantity of Soil No. 1 and of soil solution No. 1 was put up in a large test tube. The volumes of each, when the soil had settled out, were about equal. To this a small quantity of acid was added. The whole was then shaken vigorously for about five minutes and allowed to settle out for twenty-four hours. Some of the clear solution could then be pipetted off and its Ph. measured. A further quantity of acid was added to the test tube and shaken up, and the next day its effect could be determined. By this somewhat tedious method a titration of the soil suspension was carried out and a distinct buffer action was shown. 11 c.c. of .01N acid added in this manner produced a change in Ph. of .5 units, while addition of 28.4 c.c. of .01N base was necessary to bring this sample to Ph. 9.4.

This is a behavior altogether different from that of distilled water on addition of either acid or base, and is much more similar to that of a solution of sodium phosphate. In other words, it indicates a buffer action. There was approximately 30 c.c. of soil and solution. Now, in 11 c.c. of .01N Hydrochloric acid we have approximately .00365 gms. of hydrogen ions. This in 40 c.c. (soil plus soil solution plus acid) represents a hydrogen ion concentration of  $3.65 \times 10^{-3}$  which would be about Ph. 2.5. Thus we have added sufficient hydrogen ions to change the hydrogen ion concentration from Ph. 8.0 to Ph. 2.5 in water solution and the actual change produced has been from Ph. 8.0 to Ph. 7.5. Similar calculations can be made for the addition of base, and it is clear that the suspended soil definitely buffers the Ph. of the surrounding liquid.

FIGURE IV



#### SERIES IV

It has been shown (loc. cit.) that Calcium Sulphate has an important effect on the corrosion of iron in soils. Also the effect of carbon dioxide solution on iron, alone, and in conjunction with Calcium sulphate and calcium carbonate, is of importance from the fact that the system  $\text{CaSO}_4 - \text{CaCO}_3 - \text{CO}_2 - \text{H}_2\text{O}$  is known to have a strong buffer action at Ph. 5.1 (Shipley and McHaffie, loc. cit.). This is within the hydrogen ion concentration range of Series I, and if corrosion obtained be due solely to the buffer action of the solution, the rate of evolution of gas ought to check with that of Ph. 5.0, Series I. If, however, the corrosion be greater it will be seen that some peculiar action must be ascribed to the  $\text{CaSO}_4 - \text{CaCO}_3 - \text{CO}_2$  system apart from that due to its buffer value.

#### Description:

A diagram of the apparatus used is shown in Figure IV.

1. Bulb on delivery tube
2. Small tube sealed to a large tube
3. Glass seal
4. 50 c.c. pipette used as reservoir
5. T join
6. Mercury levelling bulb
7. Glass tube to allow the introduction of Carbon dioxide.
8. Combustion tube full of copper
- 9, 10. Rubber tubes.

One flask was filled as follows: A small amount of ~~solid~~ calcium sulphate and calcium carbonate was placed in the flask and the iron wire placed on top of this layer. A saturated solution of calcium sulphate and calcium carbonate was then poured in and, having closed with a pinchcock, tubes 9 and 10, to prevent tube 2 from filling with solution, the rubber stopper was then inserted. The solution rose to

Bulb 1. The stopper was wired and paraffined. Then carbon dioxide, freed from oxygen by means of the combustion tube, 8, was bubbled through the solution for  $1\frac{1}{2}$  hours. The mercury having been brought up a trifle past 5 by means of the levelling bulb 6, the rubber tube 10 was disconnected. The iron was thus in contact with dissolved oxygen for a time.

The method of filling was then modified to permit of filling the flask with no oxygen present. A flask was set up having in it calcium sulphate, calcium carbonate and a saturated solution of these salts. The cork was perforated and three tubes inserted, two reaching to the bottom of the flask, through one of which the carbon dioxide was bubbled into the solution, while through the other the solution could be pumped by the carbon dioxide pressure. The third tube was a short one used to allow escape of carbon dioxide when desired. The solution exit tube was stopped while the short tube was opened, and carbon dioxide freed from oxygen was bubbled through for about five hours. The iron wire having been put in its flask the stopper to this flask was inserted. The carbon dioxide stream was then diverted (by means of a three-way stopcock) from the calcium sulphate calcium carbonate solution to the system containing the iron, and was passed through it for about half an hour to sweep out the air. The solution exit tube on the flask containing the solution was then unstopped and the short tube stopped. The stopper having been slipped a little way out of the flask containing the iron, the carbon dioxide pressure was turned on to the solution, pumping it through the solution exit tube which had been arranged so as to fill the flask containing the iron. Also, on account of the stirring by the carbon dioxide bubbling through the solution, a certain amount of solid calcium sulphate and calcium carbonate was pumped over. The stopper in the "iron" flask was wired and paraffined and a mercury seal established as in the first system set up.

A third system was set up by the method of the second system, using conductivity water only. The water had been well boiled and had had carbon dioxide passed through it as it cooled and for about half an hour after complete cooling. This water was then pumped into a flask exactly as was the calcium sulphate, calcium carbonate solution in the second system.

The three systems were:

- A. Calcium Sulphate, - Calcium carbonate - and saturated solution, saturated with carbon dioxide, oxygen originally present.  
Weight Fe = 5.0008 gms.
- B. Calcium sulphate - calcium carbonate - and saturated solution, saturated with carbon dioxide, no oxygen present.  
Weight Fe = 5.0005 gms.
- C. Conductivity water saturated with carbon dioxide, no oxygen present.  
Weight of Fe = 4.9992 gms.

It was soon found that it would be necessary to refill the pipettes with carbon dioxide as the 50 c.c. was absorbed in about one to two weeks. Carbon dioxide was passed through the combustion tube and the rubber tube 10 (in diagram) was placed over a short length of glass tube. The carbon dioxide was then adjusted to bubble through water at a rate of about one to two bubbles per second. The delivery tube having been stopped with a plugged rubber tube which was wired on and then heavily paraffined (it is necessary that this seal be absolutely gastight) the levelling bulb was raised until tube 7 was full of mercury. The rubber tube through which the carbon dioxide was passing was then pinched firmly where it left the glass tube, rapidly slipped off that piece and on to tube 7 as far as where it was pinched. Thus no oxygen was introduced by the transfer. Tube 10 having been unpinched and the levelling bulb lowered until the mercury level was at the T join 5, carbon dioxide bubbled into the reservoir, the displaced mercury being poured out of the levelling bulb from time to time. Then the reservoir was full of

Carbon Dioxide the levelling bulb was raised sufficiently to seal at 5 and the rubber tube 10 was removed from the glass tube 7. The seal on the delivery tube was then broken and the apparatus was ready for use once more. This process can be carried out readily and without admission of oxygen, if care be taken to seal the end of the delivery tube securely, and if, (if a cylinder be the source of carbon dioxide, as was the case in this experiment) care be taken to make the transfer of the carbon dioxide bearing rubber tube to the apparatus, subsequent unpinching of the tube and lowering of the levelling bulb as rapid as possible.

Each volume of gas evolved was allowed to stand over a potassium hydroxide solution for some time. Since carbon dioxide was swept out of solution by the evolved hydrogen.

#### Results:

A absorbed about 30 c.c. of carbon dioxide and stood for six days before evolution of gas started. B. and C. started to evolve gas and absorb carbon dioxide almost as soon as set up.

Gas Record: System A.

| <u>Days of Evolution</u> | <u>C.C. Evolved</u> | <u>C.C. Per Day</u> |
|--------------------------|---------------------|---------------------|
| 13                       | 13                  | 1.00                |
| 4                        | 15                  | 3.75                |
| 7                        | 16                  | 2.29                |
| 9                        | 15                  | 1.66                |
| 12                       | 15                  | 1.25                |
| 13                       | 15                  | 1.15                |
| 14                       | 16.7                | 1.19                |
| 8                        | 12.0                | 1.50                |
| 9                        | 13.5                | 1.50                |
| 7                        | 11.2                | 1.60                |
| 8                        | 14.0                | 1.75                |
| 6                        | 12.5                | 2.08                |
| 14                       | 10.9                | 0.78                |
| Total 124                | Total 179.8         | Mean 1.65           |

| <u>System</u> | <u>Days of Evolution</u> | <u>C.C. Evolved</u> | <u>C.C. Per Day</u> |
|---------------|--------------------------|---------------------|---------------------|
| B.            | 11                       | 21                  | 1.91                |
|               | 2                        | 14                  | 7.00                |
|               | 4                        | 16                  | 4.00                |
|               | 2                        | 11                  | 5.50                |
|               | 4                        | 13.5                | 3.37                |
|               | 4                        | 13.0                | 3.25                |
|               | 6                        | 16.                 | 2.66                |
|               | 9                        | 14.                 | 1.55                |
|               | 7                        | 15.5                | 2.21                |
|               | 12                       | 14.5                | 1.21                |
|               | 23                       | 16.0                | 0.70                |
|               | 14                       | 13.8                | .99                 |
|               | 14                       | 12.5                | .89                 |
|               | <u>3</u>                 | <u>17.0</u>         | <u>5.67</u>         |
| Total         | 115                      | Total 207.8         | Mean 2.92           |
| System C.     | 3                        | 7.                  | 2.3                 |
|               | 5                        | 10.5                | 2.10                |
|               | 9                        | 9.5                 | 1.06                |
|               | 11                       | 15.                 | 1.36                |
|               | 12                       | 17.                 | 1.42                |
|               | 14                       | 13.5                | 0.96                |
|               | 12                       | 13.5                | 1.12                |
|               | 6                        | 11.0                | 1.83                |
|               | 12                       | 14.0                | 1.17                |
|               | <u>16</u>                | <u>13.0</u>         | <u>0.81</u>         |
| Total         | 100                      | Total 124.          | Mean 1.42           |

This shows; that carbon dioxide and water will corrode iron at quite an appreciable rate, that the presence of calcium sulphate and calcium carbonate will enhance this rate of corrosion, that the presence of a small amount of oxygen, supplied at the outset, actually retards the subsequent rate of corrosion, probably by forming a more impervious coating of oxide.

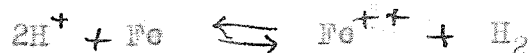
The hydrogen ion concentrations of these three solutions, when the apparatus was opened up again, were the same, i.e.  $\text{Ph}6.4$ . None were showing signs of stopping their corrosion.

A research of Bauer and Wetzol,<sup>15</sup> is of interest, and a table of their results is appended. They exposed cast iron bars to various corroding media, contained in glass, for a period of 15 months.

| <u>Condition of Experiment</u>                                  | <u>Loss of weight<br/>in grammes</u> | <u>Relative<br/>Corrosion</u> |
|-----------------------------------------------------------------|--------------------------------------|-------------------------------|
| Distilled water                                                 | 6.23                                 | 100                           |
| Tap water enriched with $\text{CaSO}_4$                         | 7.61                                 | 122                           |
| Clay saturated with distilled water                             | 10.38                                | 167                           |
| Clay saturated with tap water enriched<br>with calcium sulphate | 10.20                                | 164                           |
| Sand saturated with distilled water                             | 5.62                                 | 190                           |
| Sand saturated with tap water enriched<br>with calcium sulphate | 6.36                                 | 102                           |

From the free energy for iron( $\text{Fe}$ ,  $\text{Fe}^{++}$ ) a Ph can be calculated at which corrosion should cease.

Consider the reaction



the equilibrium constant is

$$K = \frac{(\text{Fe}^{++})(\text{H}_2)}{(\text{H}^+)^2 (\text{Fe})} = \frac{(\text{Fe}^{++})}{(\text{H}^+)^2}$$

since  $(\text{Fe})$  and  $(\text{H}_2)$  are constant.

$$\text{Now } \Delta F = -RT \ln K = -RT \ln \frac{(\text{Fe}^{++})}{(\text{H}^+)^2}$$

$$= -2 \times 293 \times 2.303 \log \frac{(\text{Fe}^{++})}{(\text{H}^+)^2} = -1360 \log \frac{(\text{Fe}^{++})}{(\text{H}^+)^2}$$

and  $\Delta F$  ( $\text{Fe}$ ,  $\text{Fe}^{++}$ ) is given from electrode potential measurements, <sup>16</sup> as  $-20,350$ .

$$\therefore -20,350 = -1,360 \log \frac{(\text{Fe}^{++})}{(\text{H}^+)^2}$$

$$\frac{(\text{Fe}^{++})}{(\text{H}^+)^2} = 9.2 \times 10^{14}$$

From the ionic product for water we have

$$(\text{H}^+) (\text{OH}^-) = 10^{-14}$$

and since there are two  $\text{OH}^-$  ions for every  $\text{Fe}^{++}$  ion and one for every  $\text{H}^+$  ion we have

$$2 (\text{Fe}^{++}) + (\text{H}^+) = (\text{OH}^-)$$

put  $a = (\text{Fe}^{++})$ ,  $b = (\text{H}^+)$ , and  $c = (\text{OH}^-)$ .

$$\text{we have } \begin{aligned} 2a + b &= c \\ bc &= 10^{-14} \end{aligned} \quad \begin{matrix} (1) \\ (2) \end{matrix}$$

$$\frac{a}{b^2} = 9.2 \times 10^{14} \quad (3)$$

$$\text{from (3)} \quad a = 9.2 \times 10^{14} b^2$$

$$\text{substituting in (1)} \quad 2 \times 9.2 \times 10^{14} b^2 + b = c \quad (4)$$

from (2)

$$b = \frac{10^{-14}}{c}$$

substituting in  
(4)

$$2 \times 9.2 \times 10^{14} \times \frac{10^{-28}}{c^2} + \frac{10^{-14}}{c} = c \quad (5)$$

multiplying by  
 $c^2$

$$2 \times 9.2 \times 10^{14} \times 10^{-28} + 10^{-14}c = c^3$$

$$c^3 - 10^{-14}c - 2 \times 9.2 \times 10^{-14} = 0$$

this is of the form  $x^3 + q x + r = 0$ . and Cardan's solution may be applied.

$$c = \left\{ 9.2 \times 10^{-14} + \sqrt{\frac{4 \times (9.2)^2 \times 10^{-28}}{4} - \frac{10^{-42}}{27}} \right\}^{\frac{1}{3}} + K$$

$$\text{Where } K = \left\{ 9.2 \times 10^{-14} - \frac{4 \times (9.2)^2 \times 10^{-28}}{4} - \frac{10^{-42}}{27} \right\}^{\frac{1}{3}}$$

neglecting the term  $\frac{10^{-42}}{27}$

$$c = \left\{ 9.2 \times 10^{-14} + 9.2 \times 10^{-14} \right\}^{\frac{1}{3}} + \left\{ 9.2 \times 10^{-14} - 9.2 \times 10^{-14} \right\}^{\frac{1}{3}}$$

$$= \left\{ 2 \times 9.2 \times 10^{-14} \right\}^{\frac{1}{3}} = 5.69 \times 10^{-5}$$

$$\text{Hence from (2)} \quad b = \frac{10^{-14}}{c} = \frac{10^{-14}}{5.69 \times 10^{-5}} = 1.76 \times 10^{-10} = (H^+)$$

and since  $Ph = \log \left( \frac{1}{H^+} \right)$

$$\therefore \log \frac{1}{1.76 \times 10^{-10}} = 9.76$$

thus at Ph 9.76 iron ought to cease corroding. This is in fair agreement with the value found, i.e. Ph 9.4.

DISCUSSION.

From the behavior of the Series some conclusions may be drawn as to the processes of corrosion in clay soils.

Pure iron, wrought iron and steel in a limited supply of water, go into solution sufficiently to bring the water to a Ph of 9.4. Solution of the iron then ceases. In a solution of some salt which buffers the hydrogen ion concentration at a higher value than this, the same tendency exists, and iron goes into solution continuously, and at a rate proportional to the Ph of the solution until either the entire solution, or if there be little or no stirring, that part of the solution adjacent to the iron, has reached a Ph of 9.4, when corrosion will cease. Iron does not corrode in distilled water or any solution not having a buffer action if the supply be limited and not stirred since the amount of iron required to raise such a solution to Ph 9.4 is very small. If the solution have a buffer action so great that the Hydroxyl ion concentration of a saturated solution of ferrous hydroxide be not enough to raise the Ph of the whole solution to 9.4 then two things may happen. If no stirring take place a layer of solution of Ph 9.4 may be built up around the iron and thus prevent further corrosion. If, however, the solution be stirred, the whole body will reach a Ph representing a displacement of Ph from the original, corresponding with that given by the original Ph plus the hydroxyl ion concentration of a saturated solution of ferrous hydroxide plus the buffer action of the salts present. If this Ph be lower than 9.4 then iron will go continuously into solution as ferrous ions and precipitate out at the same rate as solid ferrous hydroxide. An unlimited supply of oxygen free distilled water ought to corrode iron at the same rate as a solution buffered to Ph. 7. For, if a continuous stream of water flow past

the iron, iron will go steadily into solution, since the equilibrium Ph of 9.4 cannot be reached.

The rate of corrosion is not only proportional to the surface of the iron but is affected by the state of the solution in contact with it. Thus a suspension of clay in a soil solution corroded iron vigorously, whilst the soil solution did not. The fact that corrosion occurred at all argued a buffer action, and this was born out by titration, which showed that the soil solution had not a buffer action, while the same solution with soil present had a pronounced one. Thus the soil and solution may be considered as a buffered solution of Ph 8.0.

A comparison of the rate of corrosion in this mixture with that in a solution of sodium phosphate of Ph 8.0 shows that there is a marked difference. The soil and its solution corroded iron about four times as fast as did the phosphate solution. The explanation of this seems to lie in the fact that in the soil, the iron was exposed to innumerable thin films of solution, whereas in the sodium phosphate solution the iron was in contact with one large body of liquid. It is a well known fact that in many instances the surface of a solution offers a different concentration of solute than does the main body. Therefore it seems quite probable that the solution throughout the soil might not be at all the same as that above the soil, which is, unfortunately, all that measurements can be applied to.

This view, that the enhancement of corrosion of iron in direct contact with the soil is due to the splitting up of the solution by the soil, is born out by the experiments conducted with barium sulphate and also with sand. Iron in contact with finely divided barium sulphate, (which, being precipitated out of cold solution, was nearly colloidal) and a solution of sodium phosphate

*of* Ph 8.0 is corroding at a rate quite comparable to that of the iron in the soil and much faster than a similar solution with no barium sulphate present. Iron in contact with sand, which is much coarser than is the soil or the barium sulphate, is corroding at a much slower rate than that in the barium sulphate, but still faster than that in the clear solution.

These views are corroborated by the results of Bauer and Wetzel (Page 38), and they explain these results in quite a simple manner. Moreover, it has often been noted <sup>15,17,</sup> that where iron pipes pass through both gravel and clay that the corrosion is confined almost entirely to the parts embedded in the clay. This is very simply explained by the foregoing ideas. Iron embedded in gravel would be in contact with relatively large bodies of solution and therefore would tend to corrode more slowly. Also, such solution is removed from immediate contact with much of its undissolved solute and its buffer action would be limited to that provided by the stirring. Therefore, two agencies are present to mitigate corrosion when the iron is surrounded by gravel and both of these have been shown to have a profound influence on corrosion.

Much has been said regarding the effect of gypsum and calcium carbonate on corrosion. These two substances, in the presence of carbon dioxide, have the greatest corrosion rate of any combination studied in these experiments. Their solution, with very little solid present, corroded iron at a greater rate than did ~~the~~ soil with practically all the iron embedded in it. The effect of gypsum and calcium carbonate with carbon dioxide on pipes, where the iron would be in contact with this same solution plus the effect of fine division, would be very marked. The soil experiment evolved hydrogen about four times as fast as did the buffered solution of the same Ph. If a similar increase in rate attended the addition of finely divided

solid to a solution of calcium sulphate, calcium carbonate and carbon dioxide, then hydrogen would be evolved at about 11.7 c.c. per day from system B in Series IV. The rate of evolution from the soil system was 1.59 c.c. per day. Thus a system comprising any finely divided solid plus the calcium sulphate, calcium carbonate and carbon dioxide solution would corrode about seven times as fast as would ordinary soil.

If, however, the solid present were calcium sulphate and calcium carbonate, a probably much greater rate of corrosion would be obtained. The Ph of the systems A, B and C. Series IV was 6.4 when they were taken down. This probably represents such an equilibrium Ph as was mentioned on Page 41. Now, if a large body of calcium sulphate and calcium carbonate were present, the buffer action at Ph 5.1 (Shipley and McHaffie, loc.cit.) would probably be strengthened and the equilibrium Ph reached with the iron would be lowered. Since rate of corrosion is proportional to buffered Ph, this lowering of such Ph would still further augment the rate of corrosion.

Thus the calcium sulphate, calcium carbonate carbon dioxide system is highly corrosive, and while a pipe surrounded by gravel would be protected from the effect of fine division, still such a solution has a high rate of corrosion even in large bodies. The action of the gravel would, however, reduce the rate of corrosion to about one-seventh of its value without gravel present, and hence, even if such reduced rate is high, the gravel has still improved the situation.

### SUMMARY

- (1) Iron in a limited supply of deoxygenated solution having no buffer action, goes into solution until a Ph of 9.4 is reached, either around the iron or throughout the solution.
- (2) Iron in deoxygenated, buffered solution, goes into solution at a rate proportional to the hydrogen ion concentration of the solution until either :-
  - (a) The solution around the iron is Ph 9.4.
  - (b) The entire solution is Ph. 9.4
  - (c) A hydrogen ion concentration be reached representing an equilibrium between a saturated solution of ferrous hydroxide and the buffer action solution. If this value be higher than  $10^{-9.4}$  iron will continue to go into solution at a rate proportional to this equilibrium hydrogen ion concentration.
- (3) A Hydrogen ion concentration at which iron ought to cease corroding has been calculated from the free energy of iron (Fe, Fe ) and is in fair agreement with the value found by experiment.
- (4) A limited supply of calcium sulphate, calcium carbonate solution does not corrode iron in the absence of oxygen.
- (5) A deoxygenated solution of calcium sulphate, calcium carbonate supplied with carbon dioxide corrodes iron rapidly.
- (6) Solid soil is essential to corrosion of iron by soil solution in the absence of oxygen. This is due to division of the solution, and to buffer action caused by the solid, and has been imitated by other finely divided solids in buffer solutions. The presence of such solids enhance the rate of corrosion of iron.
- (7) An explanation has been given as to the non-corrosion of iron in gravel as compared with iron in clay.

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