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UNIVERSITY OF LOUISVILLE

OXIDATION POTENTIALS OF FERRIC AMMONIUM CITRATE

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

Of Master of Science

Department of Chemistry

By

Daniel P. Knopf

Year

1939

NAME OF STUDENT: Daniel P. Knopf

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Ammonium Citrate

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INTRODUCTION

The work done on ferric ammonium citrate was brought about through an interest in its uses as a sensitizer in the blueprint field. This compound is used to give a greenish tint to the blueprints.

The principle of the blueprint is very simple. Herschel found that certain salts of iron-the ferric salts-when exposed to light in the presence of organic matter, were reduced to ferrous salts, and thereby became powerful reducers of other metallic salts which were unaffected by the unaltered ferric salts. A paper sensitized with ferric ammonium citrate and exposed - to sunlight under a negative will be affected only where the negative is more or less transparent. The light will reach this part and reduce the ferric salt. The paper is then dipped in a potassium ferricyanide solution and the part that was exposed reacts quickly to form a deep insoluble blue pigment. The unexposed ferric salts are unaffected and can be washed away. (22)

Ferric ammonium citrate has also medicinal purposes. The ordinary soluble ferri salts precipitate proteins readily and are therefore styptic, astringent, and even corrosive. (20) This salt in contrast (ferric ammonium citrate) is a pleasant chalybeate being practically free from astringency or local irritant action. (25) It also may be applied to ulcers

where it precipitates the proteins and checks oozing and hemorrhages. Ferric ammonium citrate is also used to treat anemia. It tends to bring about an increase in the number of circulating red blood cells or an increase in their hemo-globin content. Benefits from its use in malaria, amenorrhea and consumption is probably linked up with the association of anemia with these conditions. (4)

This research is on the oxidation potentials of ferric ammonium citrate and the effect of certain conditions on these potentials. The suggestion for this type of work came when it was noticed in a blueprinting establishment that there were no controls for the various solutions and only rule of thumb methods prevailed. This was not a research in blueprinting. It was, however, a study in a field closely related to the problems of the blueprinting field.

CALIBRATION OF APPARATUS & THEORY INVOLVED

The apparatus used in this work which was more or less vital to the correctness of the results was (1) set of weights - chromium plated, class S; (2) 50 cubic centimeter burette; (3) potentiometer and saturated calomel electrode; (4) Glass Electrode.

The weights were calibrated with a one gram gold-plated weight, which had been previously calibrated by the Bureau of Standards. As the set of weights used were Class S, this set was designed for high grade analytical and assay weights, thus the tolerances were as follows:

<u>Denomination</u>	<u>Tolerance</u>	(May be either positive or negative.)
50 g.	0.3 mg.	
20 g.	0.2 mg.	
10 g.	0.15 mg.	
5 g.	0.15 mg.	
2 g.	0.10 mg.	
1 g.	0.10 mg.	
500 mg.	0.05 mg.	
200 mg.	0.05 mg.	
100 mg.	0.05 mg.	
50 mg.	0.03 mg.	
20 mg.	0.03 mg.	
10 mg.	0.02 mg.	

<u>Denomination</u> (cont'd)	<u>Tolerance</u> (con'd)
5 mg.	0.02 mg.
2 mg.	0.01 mg.
1 mg.	0.01 mg. (17)

The method used to check these weights was somewhat similar to that suggested by Richards in the Journal of American Chemical Society, vol. 22, pp. 44 (1900). Instead of a the gram weight, however, the one gram Bureau of Standard's weight was used. This method gave the following values:

<u>Denomination</u>	<u>Value</u>	<u>Deviation</u>	<u>Allowed Tolerance</u>
50 g.	50.0000 g.	0.0 mg.	0.3 mg.
20 g.	20.0001 g.	0.1 mg.	0.2 mg.
10 g.	10.0000 g.	0.0 mg.	0.15 mg.
10 g.	10.0001 g.	0.1 mg.	0.15 mg.
5 g.	4.9998 g.	0.2 mg.	0.15 mg.
2 g. (dot)	2.0000 g.	0.0 mg.	0.10 mg.
2 g.	2.0000 g.	0.0 mg.	0.10 mg.
1 g.	1.0000 g.	0.0 mg.	0.10 mg.
500 mg.	0.5000 g.	0.0 mg.	0.05 mg.
200 mg.	0.2000 g.	0.0 mg.	0.05 mg.
100 mg.	0.1000 g.	0.0 mg.	0.03 mg.
100 mg.	0.1000 g.	0.0 mg.	0.03 mg.
50 mg.	0.0500 g.	0.0 mg.	0.03 mg.

<u>Denomination</u>	<u>Value</u>	<u>Deviation</u>	<u>Allowed Tolerance</u>
20 mg.	0.0200 g.	0.0 mg.	0.03 mg.
10 mg.	0.0100 g.	0.0 mg.	0.02 mg.
10 mg.	0.0100 g.	0.0 mg.	0.02 mg.
5 mg.	0.0050 g.	0.0 mg.	0.02 mg.
2 mg.	0.0020 g.	0.0 mg.	0.01 mg.
2 mg.	0.0020 g.	0.0 mg.	0.01 mg. (17)

These weights were, therefore, with one exception within the required accuracy at read values for analytical work. Nevertheless the calibrated value was used in all work.

The burette used was calibrated against a burette approved by the Bureau of Standards. As the water was the same temperature in both the burette being calibrated and the Bureau of Standards' burette, no provisions were necessary to take care of the expansion of water caused by heat.

<u>Standard</u>		<u>Calibrated Burette</u>	
<u>First Reading</u>	<u>Second Reading</u>	<u>First Reading</u>	<u>Second Reading</u>
0 - c.c.	- 50 c.c. (50 ml.)	0.1 c.c.	- 50 c.c. (49.9 c.c.)
0 c.c.	- 40 c.c. (39.99 ml.)	10.1 c.c.	- 50 c.c. (39.9 c.c.)
0 c.c.	- 30 c.c. (29.98 ml.)	20.1 c.c.	- 50 c.c. (29.9 c.c.)
0 c.c.	- 20 c.c. (20.01 ml.)	30.0 c.c.	- 50 c.c. (20 c.c.)
0 c.c.	- 10 c.c. (10.00 ml.)	40.0 c.c.	- 50 c.c. (10 c.c.)
50 c.c.	- 39.95 c.c. (10.05 c.c.)	0 c.c.	- 10 c.c. (10 c.c.)

<u>Standard (con't)</u>		<u>Calibrated Burette (con't)</u>	
First Reading	Second Reading	First Reading	Second Reading
39.95 c.c.	29.98 c.c. (9.97c.c.)	10 c.c.	20 c.c. (10 c.c.)
29.98 c.c.	19.95 c.c. (10.03 c.c.)	20. c.c.	30 c.c. (10 c.c.)
19.95 c.c.	10.00 c.c. (9.95 c.c.)	30 c.c.	40 c.c. (10 c.c.)
10.00 c.c.	0.00 c.c. (10.00 c.c.)	40. c.c.	50 c.c. (10 c.c.)

In all work with the burette that required accuracy, the known value was used rather than the face value. Thus in all titrations the known rather than that of the face value was used while in such work as making up solutions, the face value was used. There was one exception to this-in making up the ferric ammonium citrate accurate measuring was used both in regards to weight of material used and as to the amount of liquid in the solution. This was necessary for there was no practical method at hand to compute its oxidizing normality.

The potentiometer used was made by Leeds and Northrup Company. It was used in conjunction with a saturated Calomel cell. The principle of the potentiometer is reasonably simple. The method used was that of Poggendorff. (23)

POTENTIOMETER

It is probably the simplest and most accurate in cases where the cell is too easily polarized to allow taking direct readings.

This method depends upon balancing the unknown against a known electromotive force. It is illustrated in the figure on the preceeding page. AB represents a wire stretched on a meter scale, U- an approximate two volt dry cell, C- the cell to be measured, D- a galvanometer, and K a key. The two cells must be connected so as to oppose each other, though both negative poles could be connected to A. The measurement consists in finding the position on the bridge of the sliding contact D where there is no deflection of the galvanometer when the key is closed. Then if the wire is of uniform resistance throughout, the fractional part of the wire AD/AB is that part of the electromotive force of V that equals the electromotive force of C; that is - AD/AB times the electromotive force of V equals the electromotive force of C. (23)

These operations, however, are carried on by a potentiometer of more convenient design, but its functions are not as easily illustrated. The slide wire of the illustrated figure, AB is arranged as a circular coil and D remains stationary. Rotation of the coil then changes the distance AD. To extend the range of the resistance and to facilitate reading, there are two sets of coils in series. The resistance of one of the coils is equal to one division of the other and is itself divided into 1000 equal parts. By moving contacts in two coils, it is possible to pick

off part of this resistance (corresponding to AD of the figure) and balance the corresponding fall of potential against either the standard cell C' or the unknown voltage E using the galvanometer. A double-pole, double-throw switch facilitates the shifting from the standard cell to the cell which is to be measured. (7) V is not a standard cell, but only one which should remain constant during the measurement. In order to get a comparison with a standard cell, C', a new balance is found at D'. Then $AD:AD' = \text{e.m.f. of C} :: \text{e.m.f. of } c'.$ (23)

The standard cell that was used in the potentiometer used in this work was a Weston Cell which had an approximate value of 1.0183v. The equation representing the true value from zero degrees to forty degrees is $-E = 1.0183 - 0.00004075(t - 20) - 0.000000944(t - 20)^2 - 0.0000000098(t - 20)^3$ (1)

This cell consists of:

10-15% Cd amalgam	CdSO ₄ paste satd. soln. CdSO ₄	HgSO ₄ Paste satd. soln. Hg ₂ SO ₄	Hg
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The above equation shows that the temperature coefficient of the electromotive force of the Weston cell for most practical purposes is zero. For this reason and also because of its constancy, this cell is the most widely used standard in electromotive force measurements. The effects of aging are small and amount to but a few microvolts per year. (5)

In order to measure the potential difference at a metal-solution junction, it was necessary to have another metal solution junction or "half-element" of known potential difference. Such metal solution junctions are termed standard electrodes. (5) Usually either a normal or deci-normal calomel electrode is used, if one is using this type of cell. However, it was found more convenient to use the saturated potassium chloride-calomel cell. In this research, this cell seemed to be more easily duplicable and thus aided in the accuracy of the research. It was necessary to prepare an entirely new cell, as adding just saturated potassium chloride to an old already prepared cell, gives questionable accuracy. One investigator (6) noticed that the value of the cell was not appreciably changed by just adding fresh potassium chloride. He found that it was necessary to also add fresh calomel and mercury to the cell. One case was cited as an illustration: a 0.1 M calomel cell B₆ was employed in combination 6 and gave an observed value for the combination at twenty-five degrees of 0.3934 volt (theory = 0.4016 volt.) When the potassium chloride solution in the cell had been replaced by some fresh solution, the value of the combination was 0.3935 volt. The entire contents of the cell were then removed, the cell thoroughly cleaned and prepared again with all fresh materials. The resulting value of the combination was 0.4015. (6) This

would seem to indicate that whenever a new cell is prepared, an entire change of materials must be effected if accurate values are desired. These same investigators after intensive study came to the conclusion that the saturated potassium chloride-calomel cell is the best cell for use in conjunction with a saturated salt bridge, because it has a very small temperature coefficient, is easily reproducible, can safely be used at temperatures from 5 degrees to 60°, and can be relied upon for its constancy of value over long periods of time. (6) Since for this type of work it was necessary to use a saturated potassium chloride-agar bridge, the saturated potassium chloride-calomel cell was the logical one to use.

The Beckman pH meter or glass electrode was used in this work to determine the degree of acidity or alkalinity of the solution under observation. This type was used for several reasons - the first and principal one being that a glass electrode is not poisoned by a strong oxidizing solution as in the hydrogen electrode. One investigator (14) in plotting the change of electromotive force during the titration of sulfuric acid and sodium hydroxide, found that this titration followed the course of a similar titration using the hydrogen and quinhydrone electrodes even upon the addition of potassium permanganate to the sulfuric acid. This observation showed that the glass electrode responded only to changes

in the hydrogen-ion concentration and is not influenced by the powerful oxidation potential produced by the presence of potassium permanganate. (14) The second reason is that the major portion of the solution runs from a pH of 2-8. Thus the glass electrode was practical for the effects of alkaline solutions in increasing the divergence between the electromotive forces of the glass and of the H_2/Pt begins to be noticeable at about a pH of 9; i.e. at the point where the buffer action of sodium hydrogen silicate in the glass would begin to resist the action of alkaline solutions less effectively. since the apparent first dissociation constant of sulfurous acid is about 10^{-9} . (11) The rapidly increasing divergence between the two electromotive forces in the presence of sodium and lithium ions begins about at a pH 13, and the apparent second dissociation constant of H_2SiO_3 is 10^{-13} . (11) Beyond this pH it is probable that the surface of the glass is attacked with increasing rapidity as the solution becomes more alkaline. (12) The Beckman pH meter carries with it a graph (with explanation on how to use it) that one uses to calculate pH's greater than 9. Therefore, it is possible to use the glass electrode for solutions with greater alkalinity than 9. However, it is the opinion of this investigator that for alkaline, non-oxidizing solutions, the hydrogen electrode is far more efficient. Another advantage of the glass electrode is its extreme handiness and convenience of use.

(12)

The glass electrode has been just recently introduced although its basic principle that the potential difference between two solutions separated by a glass depends on the hydrogen-ion concentrations of the solution has been known for quite some time. (10) In a cell of this type:

the potentials of the two calomel electrodes cancel one another and the electromotive force of the cells is equal to the potential difference at the glass membrane, a. Provided there is no potential in this membrane.

$$E = RT/F \ln. c_2/c_1$$

If either c_1 or c_2 is known the other can be calculated. However, owing to differences in the surface of the glass membrane, a small correction must be applied for "asymmetry potential" due to the glass. This correction can be ascertained by determining the electromotive force of the cell when the hydrogen-ion concentration of both are known or equal. (5)

THEORY

According to modern ideas, oxidation occurs, not only when oxygen is added to a substance, but also whenever electrons or negative charges ^{are} withdrawn from, its molecules, atoms or ions. Similarly, reduction consists in the addition of electrons to, or withdrawal of positive electricity from the molecules, atoms or ions of a substance. (5)

In order that a relation may be obtained between the electromotive force of oxidation-reduction cells and the tendency of the components to pass from a lower to a higher state of oxidation (oxidation), or from a higher to a lower state of oxidation (reduction) let us consider the cell,

The reaction which takes place in this cell may be represented by the equation:

the direction of the reaction depended upon the relative concentration of the reacting substances.

The equilibrium constant of the foregoing reaction is-

$$K = (\text{Fe}^{++})^2 (\text{Hg}_2^{++}) / (\text{Fe}^{+++})^2 (\text{Hg}_2)_e$$

where the subscript, e, denotes the equilibrium concentrations.

In accordance with the equation for the maximum work (a) that may

be obtained from a reversible reaction;

$$A = RT \ln K' - RT \ln (Fe^{++})^2 (Hg^{++}) / (Fe^{+++})^2 (Hg_2)$$

Further since the concentration of the mercury and the mercurous ions are constant, we may write:

$$E = RT/2F \ln K' - RT/F \ln (Fe^{++}) / (Fe^{+++})$$

where

$$K = (Fe^{++})^2 / (Fe_e^{+++}),$$

Setting $RT/2F \ln K = E_0$ we obtain:

$$E = E_0 - RT/nF \ln. (Fe^{++}) / (Fe^{+++}).$$

For any cell,

above equation may be written in the general form:

$$E_{(c^0/c')} = E_0 - RT/nF \ln. c^0/c',$$

Where $E_{(c^0/c')}$ is the electromotive force produced by the change of the ions from a higher state of oxidation (M') to a lower state of oxidation (MO); c^0 and c' are the ionic concentrations in the lower and higher state of oxidation; E^0 is the electromotive force of the cell when c^0 is equal to c' and "n" is the difference of the ions. This electromotive force E is called the oxidation potential and E_0 is termed the normal oxidation potential of the electrode $Pt \begin{smallmatrix} M' \\ MO \end{smallmatrix}$. (5)

The values of E_0 are calculated on the assumption - approximate at best - that the ratio of the concentrations of

the ferric and ferrous ions are equal to the concentrations of the respective salts. This method of obtaining data was used by Peters' (16), Carters and Clews (2), T. J. Glovers' (9), and others.

Since all oxidation potentials are expressed on the basis that the tendency of hydrogen to pass from the ionic to the atomic is zero, when in contact with a solution which is normal with respect to hydrogen ions, the electromotive force has been reduced to the hydrogen value. Thus the value representing the oxidation potential, E , is referred to that of hydrogen in contact with a normal solution of its ions at zero.

From the value of E thus obtained, the value of the normal oxidation potential E_0 , may be calculated from the equation:

$$E = E_0 - \frac{RT}{nF} \ln. \frac{c^0}{c'} \quad (5)$$

EXPERIMENTAL

This research is an attempt to find the effect of various conditions on the ferri-ferro potential of ferrous ammonium sulphate and ferric ammonium citrate with a buffer potassium oxalate. Various other experimenters (2) (13) (3) (15) have measured the effect of acid, base, temperature, and concentrations on the ferri-ferro potential itself, but with one exception in the literature, ⁽¹⁸⁾ none have attempted to measure these effects on a buffered ferri-ferro potential. In this one exception oxidation and reduction buffers were used and it was found that the potential readings varied from 0.64 - 0.10 volts. (It was found in the present set of experiments the variations in potential were from 0.5423 to 0.015.) The effects of added amounts of acid (H_2SO_4) and bases (NaOH) were likewise studied.

Fig. I
 — = Oxidation Potential, E
 1 cm block horizontally = 0.5 c.e.
 1 cm. block vertically = 0.003v

Fig II

— = Oxidation Potential, E.

1 cm. block horizontally = 0.04 pH

1 cm. block vertically = 0.03 V

EXPERIMENT NO. 1

The buffer potassium oxalate was run against the "ferro" solution to check the effect of the buffer with just one of the components of the "ferri-ferro" potential. It was found that the addition of only 3.3 milliliters of ferrous ammonium sulphate caused a loss of 0.3935 V. in the solution. After this loss of oxidation potential in the solution, there was only a loss of 0.044 v. caused by the addition of 46.7 milliliters of ferrous ammonium sulphate. This showed a rather decided break in potential as may be seen on Figure No. 1 on the preceeding page.

The potassium oxalate solution (1N.) was slightly alkaline having a pH of 8.7, however, the addition of ferrous ammonium sulphate gradually changed the pH towards the acid side. The steady downward progression of pH showed a curve similar to that of Figure No. 1.

Table No. 1

$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot \text{K}_2\text{C}_2\text{O}_4$ c.c.		E	pH
0	25.00	0.4460	8.7
0.5	25.00	0.4205	8.7
1.0	25.00	0.4054	8.6
$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot \text{K}_2\text{C}_2\text{O}_4$ c.c.		E	pH

1.5	25.00	0.3620	8.5
2.0	25.00	0.3240	8.45
2.5	25.00	0.2625	-
2.6	25.00	0.2220	-
2.7	25.00	0.1920	-
2.8	25.00	0.1485	-
2.9	25.00	0.1240	-
3.0	25.00	0.1170	8.40
3.1	25.00	0.0750	-
3.2	25.00	0.0610	-
3.3	25.00	0.0525	-
3.4	25.00	0.0410	-
3.5	25.00	0.0410	8.36
4.0	25.00	0.0360	8.29
4.5	25.00	0.0315	8.28
5.0	25.00	0.0315	8.28
6.0	25.00	0.0265	8.12
7.0	25.00	0.0230	8.10
8.0	25.00	0.0185	8.05
10.0	25.00	0.0163	8.00
12.0	25.00	0.0163	-
(Fe(NH ₄)(SO ₄)) (K ₂ C ₂ O ₄) c.c.		E	pH
15.0	25.00	0.0116	7.55
20.0	25.00	0.0085	6.89
25.0	25.00	0.0085	6.60

30.0	25.00	0.0085	6.41
35.0	25.00	0.0085	6.10
40.0	25.00	0.0085	6.10
45.0	25.00	0.0085	5.90
50.0	25.00	0.0085	5.80

Fig. III

— = Oxidation Potential, E

1 cm. block horizontally = 0.002 v.

1 cm. block vertically = 0.2 g/l. $K_2C_2O_4$

Fig. IV

— = Oxidation Potential, E

1 cm. block horizontally = 0.60 V.

1 cm. block vertically = 0.02 pH.

Fig. V
 — Oxidation Potential, E
 1 cm. block horizontally = 0.002 V.
 1 cm. block vertically = 0.2 e.c.

Fig. VI

— Oxidation Potential, E

1 cm. block horizontally
= 0.002 V

1 cm. block vertically
= 0.02 pH

EXPERIMENT NOS. 2 & 3

The next step in the problem was to find the effect on the buffer upon the other member of the "ferri-ferro" potential. 30 milliliters of potassium oxalate was gradually added to 25 milliliters of ferric ammonium citrate and a reading was taken approximately every cubic centimeter. There was no rapid drop in the oxidation potential and also there was no tapering off, just a steady drop in the potential throughout the whole run.

The addition of 3 milliliters of dilute sulfuric acid and then again the addition of potassium oxalate raised the oxidation potential approximately 0.05 v., but affected little the change in potential upon the addition of potassium oxalate.

The loss in potential in Experiment No. 2 was 0.1438 and the loss in Experiment No. 3 was 0.1385 caused by the addition of 30 cubic centimeters of the buffer potassium oxalate. This was a great deal less than the buffer affected the ferro solution, indicating that the ferric ion is less activated by the buffer.

A curve was then drawn plotting the pH of the aforementioned runs against the oxidation potentials. The first run potassium oxalate against ferric ammonium citrate showed almost a straight line of increasing alkalinity.

The addition of the acid, however, ruined the steady progression toward alkalinity and graph No. 6 did not show as steady a line as the first.

TABLE NO. 2

$(K_2C_2O_4)$	$(-Fe(NH_4)_3 (C_6H_5O_7)_3 -)$		
c.c.	c.c.	E	pH
0.0	25.00	0.6573	4.55
0.5	25.00	0.6532	-
$(K_2C_2O_4)$	$(-Fe(NH_4)_3 (C_6H_5O_7)_3 -)$		
c.c.	c.c.	E	pH
1.0	25.00	0.6385	5.0
1.5	25.00	0.6326	-
2.0	25.00	0.6261	5.2
3.0	25.00	0.6131	-
4.0	25.00	0.6064	5.6
5.0	25.00	0.5985	-
6.0	25.00	0.5895	5.8
7.0	25.00	0.5829	-
8.0	25.00	0.5786	6.01
9.0	25.00	0.5725	-
10.0	25.00	0.5676	6.29
11.0	25.00	0.5630	-
12.0	25.00	0.5615	6.30
13.0	25.00	0.5570	-
14.0	25.00	0.5536	6.50
15.0	25.00	0.5510	-
16.0	25.00	0.5480	6.69
18.0	25.00	0.5415	-
20.0	25.00	0.5363	6.85
25.0	25.00	0.5240	7.10
30.0	25.00	0.5135	7.35

TABLE NO. 3
(3 c.c.'s of H_2SO_4)

$(\text{K}_2\text{C}_2\text{O}_4)$ c.c.	$(-\text{Fe}(\text{NH}_4)_3(\text{C}_6\text{H}_5\text{O}_7) -)$ c.c.	E	pH
0.0	25.00	0.7175	2.6
0.5	25.00	0.7175	-
1.0	25.00	0.7175	-
2.0	25.00	0.7126	3.8
2.5	25.00	0.7110	-
3.0	25.00	0.7029	3.91
4.0	25.00	0.6990	-
5.0	25.00	0.6937	3.88
6.0	25.00	0.6891	-
7.0	25.00	0.6830	4.10
8.0	25.00	0.6735	-
9.0	25.00	0.6655	4.30
10.0	25.00	0.6566	-
11.0	25.00	0.6465	4.58
12.0	25.00	0.6480	-
13.0	25.00	0.6395	5.18
14.0	25.00	0.6336	-
15.0	25.00	0.6240	5.15
16.0	25.00	0.6201	-
17.0	25.00	0.6190	5.30
18.0	25.00	0.6151	-
19.0	25.00	0.6083	5.45
20.0	25.00	0.6048	-

$(K_2C_2O_4)$	$(Fe(NH_4)_3(C_6H_5O_7)_3)$	E	pH.
c.c.	c.c.		
21.0	25.00	0.6048	-
22.0	25.00	0.6012	5.71
23.0	25.00	0.5953	-
24.0	25.00	0.5922	-
25.0	25.00	0.5902	5.81
27.0	25.00	0.5860	5.90
30.0	25.00	0.5790	6.15

EXPERIMENT NO. 4

In this run an attempt was made to find the effect of pH upon the oxidation potential of ferric ammonium citrate. It can be seen from graph No. 7 that as the pH increased the potential decreased in this compound. This seemed to indicate that alkalinity tends to decrease the oxidizing power of these compounds.

TABLE OF RUN
(acid)

$\text{H}_2\text{SO}_4(\text{dil.})$ c.c.	$(\text{Fe}(\text{NH}_4)_3(\text{C}_6\text{H}_5\text{O}_7)_3)$ c.c.	E	pH
0.0	25.00	0.6750	5.2
0.5	25.00	0.6937	4.65
1.5	25.00	0.7670	3.89
2.0	25.00	0.7741	3.22
2.5	25.00	0.7825	3.05
3.0	25.00	0.7865	2.91
4.0	25.00	0.7950	2.71
5.0	25.00	0.8020	2.61
7.0	25.00	0.8090	2.45
10.0	25.00	0.8140	2.31
13.0	25.00	0.8205	2.18
16.0	25.00	0.8205	2.05
21.0	25.00	0.8240	1.90
31.0	25.00	0.8352	1.79

TABLE OF RUN
(basic)

0.9708 N. NaOH c.c.	(Fe(NH ₄) ₃ (C ₆ H ₅ O ₇) ₃) c.c.	E	pH
0.0	24.85	0.6715	4.7
0.5	24.85	0.6715	4.63
1.0	24.85	0.6666	4.7
1.5	24.85	0.6586	4.8
2.0	24.85	0.6465	4.9
2.5	24.85	0.6412	5.0
3.0	24.85	0.6340	5.1
4.0	24.85	0.6210	5.34
5.0	24.85	0.5947	5.6
6.0	24.85	0.5780	5.9
7.0	24.85	0.5548	6.2
8.0	24.85	0.5174	6.5
9.0	24.85	0.4949	6.8
9.5	24.85	0.4795	6.91
9.9	24.85	0.4571	7.10
11.0	24.85	0.4275	7.40
13.0	24.85	0.3715	8.0
15.0	24.85	0.2890	8.39
17.0	24.85	0.2310	8.60
21.0	24.85	0.1877	8.78
25.0	24.85	0.1354	9.10
30.0	24.85	0.1180	-

EXPERIMENT NO. 5

After obtaining a curve upon the effect of pH on the oxidation potentials of ferric ammonium citrate, naturally, the next logical step was to find the effect of pH on the "ferro" potential. In order to obtain an idea as to how it would effect the buffered (oxidation buffer) "ferri-ferro" potential, this solution was also buffered.

As can be seen from the graph, there were two separate "breaks" and two leveling off places. From a pH of 5.8 to one of 7.3, there was little or no change of potential, however, an increase in pH from 7.35 to 9.35 caused a fall in potential of 0.2 v. This happens again as an increase of pH from 9.3 to 13.6 only causes a drop in potential of 0.042v., while an increase of pH from 13.3 to 13.8 caused a drop of 0.072 v. This curve also bore out relationships ascribed in previous runs.

TABLE NO. 5.
(25 c.c. $K_2C_2O_4$)

0.9708 N. NaOH		$Fe(NH_4)_2(SO_4)_2$	
c.c.		c.c.	
			E pH
0.0		50.00	0.0095 5.8
0.5		50.00	0.0093 6.91
1.0		50.00	0.0093 7.35
2.5		50.00	0.0050 7.60
0.9708 N. NaOH		$Fe(NH_4)_2(SO_4)_2$	
c.c.		c.c.	E. pH

3.0	50.00	-0.0250	7.70
3.5	50.00	-0.0370	7.90
4.0	50.00	-0.0830	8.29
4.5	50.00	-0.1120	8.75
5.0	50.00	-0.1540	8.91
5.5	50.00	-0.1890	9.35
6.0	50.00	-0.2080	10.20
6.5	50.00	-0.2255	13.10
7.0	50.00	-0.2255	13.30
7.5	50.00	-0.2475	13.60
10.0	50.00	-0.3051	13.80

Fig. 1

1sm. block horizontally = 2001r

1sm. block vertically = 0.40% Fe^{+++}

EXPERIMENT NO. 6

In this graph the potentials of ferric ammonium citrate were plotted against those of ferrous ammonium sulphate. From the graph an approximate mean of 0.7235 v. was derived. This was off a bit from the potential given in the critical table which is 0.7477. However, as the definite mean of this electrode has not been ascertained and as this research was not with identical ions, this was not considered too far off.

TABLE NO. 6

Ratio $\text{Fe}^{+++} : \text{Fe}^{++}$ in %	Observed e.m.f. E	Absolute p.d. of the Pt. Fe^{+++} Fe^{++} Electrode	Normal Oxidation Potential Referred to the normal Calomel Electrode as Zero E_0
100:0.0	0.7240	1.2506	
5.19:94.81	0.7290	1.2556	0.8035
9.81:90.19	0.7290	1.2556	0.7859
24.61:75.39	0.7230	1.2496	0.7517
35.23:64.77	0.7230	1.2496	0.7386
37.44:62.56	0.7190	1.2456	0.7258
60.36:39.64	0.7190	1.2456	0.7100

Fig. X

— = Oxidation Potential, E

--- = Normal Oxidation Potential, E₀

1 sm. block horizontally = 1.0 % Zn

1 sm. block vertically = 0.002 V

Fig. XI

— = Normal Oxidation Potential, E_o

1 cm. block horizontally = 0.05 pH

1 cm. block vertically = 0.002 V

EXPERIMENT NO. 7

This was the first run in the final form. One milliliters - of N. Potassium oxalate was used as an oxidation buffer. A decided break at the proportion of 73.11 % ferri to 26.89 % ferro was noticed which would seem to indicate that the oxidation buffer was ineffectual at this concentration.

Another explanation that might fit this phenomena is that of T. J. Glover. Since the ratio $f^0/\text{oxidant}/f^r$ reductant is not equal to the ratio $(\text{Fe}^{+++}/\text{Fe}^{++})$ ferric ions divided by ferrous work. The E values thus obtained have been termed "apparent" to distinguish them from the true value as defined by the thermodynamic method. The theory advanced ~~was~~ that the ferric and ferrous ions combine with other ions or undisassociated substances to form complex ferric and ferrous ions, thus forming a new oxidation-reduction system in which the complex ferric ion and the complex ferrous ion form the oxidant and reductant respectively. This system may displace the original ferric-ferrous ion system either partially or (if the complexes formed dissociate to such a slight extent that only a relatively small proportion of ferrous-ferric ion is present) wholly. The amount or composition of these complex ions may vary with the condition of the system, and so the oxidation-reduction potential of the ferrous-ferric mixtures will vary accordingly. (9)

The mean oxidation potential (normal) derived by approximation was 0.4840v. The plot of the ferri potential against those of the ferro potentials showed a similar curve to that of run No. 5.

TABLE NO. 7

Ratio $\text{Fe}^{+++}:\text{Fe}^{++}$ in %	Observed E.M.F. E.	Absolute p.d. of the $\text{Pt} \text{Fe}^{+++}$ $ \text{Fe}^{++}$ Electrode	Normal Oxidation Referred to the Normal Calomel Electrode as Zero, E_0	pH
100.0:0.0	0.5800	1.1066		5.1
84.47 :15.53	0.4490	0.9756	0.4056	4.3
73.11 :26.89	0.3485	0.8751	0.3229	3.7
64.46 :35.54	0.4180	0.9446	0.4027	3.2
57.62 :42.38	0.4431	0.9697	0.4352	2.91
52.11 :47.89	0.4715	0.9981	0.4709	2.70
47.54 :52.46	0.5005	1.0271	0.5025	2.59
43.71 :56.29	0.5260	1.0526	0.5325	2.48
40.465:59.535	0.5422	1.0688	0.5521	2.40
37.68 :62.32	0.5536	1.0802	0.5665	2.30
35.23 :64.47	0.5590	1.0856	0.5752	2.25

EXPERIMENT NO. 8

In this run the strength of the buffer was increased to 10 milliliters of N. potassium oxalate. This increase in the buffer lowered the oxidation potential on an average of about 0.4v., per reading. This increased buffer action caused the change in charge to fall back to approximately even concentration before the potential increased. The mean value of the normal oxidation potential was estimated from the graph to be 0.0920v.

It was again noticed that the curve derived from plotting the pH against the normal oxidation potentials followed approximately the same outline as the preceeding runs.

In order to show how a typical experiment was carried out, the method used is described in detail at this point.

The electrode was platinized in the usual fashion.

The next step was to balance the resistances of the potentiometer against the Weston cell until the galvanometer read zero - then the switch was thrown over to the dry cell.

The ferric ammonium citrate was added by the calibrated burette into a 250 milliliters beaker, as was the N. potassium oxalate. The burette was then thoroughly cleaned and filled with ferrous ammonium sulphate. The beaker containing the ferric ammonium citrate and N. potassium oxalate was connected to the calomel cell and the potentiometer by means of an agar-agar bridge. This bridge was made by bending a piece of

at both ends and filling the tubing with agar-agar which had been saturated with potassium chloride.

The number of milliliters of ferrous ammonium sulphate that was desired was run in through the burette. The key of the potentiometer was then closed and a reading made. As a saturated potassium chloride-calomel cell was used 0.246 v. was added to each reading. A pipette would then remove about three milliliters of the solution and put it into the glass electrode for a pH reading. The solution was returned to the original solution after the pH reading.

This method with certain omissions or additions related in the experiment described was used throughout the research.

TABLE NO. 8

Ratio $\text{Fe}^{+++} ; \text{Fe}^{++}$ in %	Observed E.M.F. E	Absolute p.d. of the Pt $\left \begin{array}{l} \text{Fe}^{+++} \\ \text{Fe}^{++} \end{array} \right.$ Electrode	Normal Oxidation referred to the Normal Calomel Electrode as Zero, E_0	pH
100.00:0.0	0.3995	0.9261	.	6.51
84.47:15.53	0.3766	0.9032	0.3332	6.51
73.11:26.89	0.2469	0.7735	0.2213	6.30
64.46:35.54	0.1436	0.6702	0.1283	5.09
57.62:42.38	0.1033	0.6299	0.0954	5.90
52.11:47.89	0.1014	0.6280	0.1008	5.68
51.12:48.88	0.0909	0.6175	0.903	
47.54:52.46	0.1025	0.6291	0.1045	5.61
43.71:56.29	0.1131	0.6397	0.1196	5.30

Ratio Fe : Fe in %	Observed E.M.F. E	Absolute p.d. of the Pt Fe Electrode	Normal oxidation Referred to the Normal Calomel Electrode as Zero, E_o	pH
40.465:59.535	0.1194	0.6460	0.1293	5.11
37.68:62.32	0.1440	0.6706	0.1569	4.79
35.23:64.77	0.1537	0.6803	0.1699	4.70

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EXPERIMENT NO. 9

In this run the oxidation buffer was again increased, this time to 25 milliliters of N. potassium oxalate. The oxidation potential fell again, this time but slightly - the average difference per reading only varying between 0.08-0.10v. The difference in the mean reading was 0.0760v. (10c.c. mean = 0.0920; 25c.c. mean = 0.0160v.)

This constant and a more or less steady loss in potential may have been due to a loss in the ability of the iron solution to hold hydrogen. This was the theory advanced by the two French investigators who stated that: "The potentials of iron depend on the hydrogen it can hold." (24) Thus the addition of the potassium oxalate increased the alkalinity and thus decreased the potential.

The curve derived from plotting pH against normal oxidation potentials followed the same outline as that of the one plotting the percentage of ferric ions against the normal oxidation potentials.

TABLE NO. 9

Ratio $\text{Fe}^{+++}:\text{Fe}^{++}$ in %	Observed E.M.F. E	Absolute p.d. of the $\text{Pt} / \text{Fe}^{+++}$ Fe^{++} Electrode	Normal Oxidation Potential Referred to the Normal Calomel Electrode as Zero, E_0	pH
100.00:0.00	0.3310	0.8576	-	8.1
84.47:15.53	0.2590	0.7856	0.2156	7.8
73.11:26.89	0.1672	0.6938	0.1416	7.58
64.46:35.54	0.0545	0.5811	0.0392	7.42
57.62:42.38	0.0239	0.5505	0.0160	7.29
52.11:47.89	0.0150	0.5416	0.0144	7.29
51.12:48.88	0.0145	0.5411	0.0139	
47.54:52.46	0.0265	0.5531	0.0285	7.10
43.71:56.29	0.0292	0.5558	0.0357	7.10
40.465:59.535	0.0350	0.5616	0.0449	6.89
37.68:62.32	0.0351	0.5617	0.0480	6.70
35.23:64.27	0.0381	0.5647	0.0543	6.58

Fig. XVII

— = Normal Oxidation Potential E_o

1 cm. block horizontally = 0.04 pH

1 cm. block vertically = 0.001 V

EXPERIMENT NO. 10

In the next three runs to be described, 10 milliliters of buffer (potassium oxalate) solution were used with varying amounts of acid.

In experiment 10, 3 milliliters of 0.9642 N. citric acid was used. The curve described from plotting the percentage of ferric against the oxidation potentials closely resembled the curve found in that experiment where only one milliliter of buffer was used in the solution. The only difference was that the potentials in this experiment were considerably below those of the one referred to. The normal oxidation mean of this run computed approximately from the graph was 0.1330 as compared to 0.4840v, of the run where one milliliter of buffer was used. The curve derived from plotting pH against the normal oxidation potential does not follow a similar pattern as the curve plotting oxidation potential against percentage of ferric ions in solution. Instead it showed a "break" toward the alkaline side at the point where according to the potential readings, there was a decided change in the oxidation potentials.

TABLE NO. 10

Ratio $\text{Fe}^{++}:\text{Fe}^{+}$ in%	Observed E.M.F. E	Absolute p.d. of the $\text{Pt} / \text{Fe}^{++}$ Electrode	Normal Oxidation Potentials Referred to the Normal Calomel Electrode as Zero, E_0	pH
100.00:0.00	0.4210	0.9476		5.48
84.47:15.53	0.2907	0.8473	0.2473	5.40
73.11:26.89	0.1260	0.6526	0.1004	5.09
64.46:35.54	0.1164	0.6430	0.1011	4.65
62.95:37.05	0.1160	0.6426	0.1055	
61.54:38.46	0.1160	0.6426	0.1066	4.51
60.14:39.86	0.1184	0.6450	0.1095	4.90
58.87:41.13	0.1211	0.6466	0.1116	4.89
57.62:42.38	0.1220	0.6486	0.1151	4.89
52.11:47.89	0.1315	0.6581	0.1309	4.70
47.54:52.46	0.1433	0.6699	0.1453	4.41
43.71:56.29	0.1600	0.6866	0.1665	4.21
40.465:59.535	0.1824	0.7090	0.1923	3.75
37.23:64.72	0.2366	0.7632	0.2428	2.68

EXPERIMENT NO. 11

In this run, the amount of acid was increased to 10 milliliters of 0.9642 N. citric acid, the amount of buffer used being constant.

It can be seen that in this graph an almost straight line~~was~~ formed by plotting the normal oxidation potential against the percentage of ferric ions present, while plotting the oxidation potentials against the percentage of ferric ions present form~~a~~ a curve.

The mean oxidation potential increased as compared to the first acid run of this series. It increased from 0.1330v. to 0.2295 v., an increase of 0.0965 v.

The pH curve again described a similar one to the one using 3 milliliters of the acid and~~was~~ totally dissililar to the oxidation potential curve.

TABLE NO. 11

Ratio $\text{Fe}^{+++} : \text{Fe}^{++}$ in %	Observed E.M.F. E	Absolute p.d. of the $\text{Pt} \mid \text{Fe}^{+++} / \text{Fe}^{++}$ Electrode	Normal Oxidation Potentials Referred to the Normal Calomel Electrode as Zero, E_0	pH
100.00: 0.00	0.2219	0.7485		4.00
84.47:15.53	0.2050	0.7316	0.1616	3.55
73.11:26.89	0.1973	0.7239	0.1717	3.25
64.46:35.54	0.2003	0.7269	0.1850	3.45
57.62:42.38	0.2114	0.7380	0.2035	3.25
52.11:47.89	0.2244	0.7510	0.2238	3.11
47.54:52.46	0.2360	0.7626	0.2380	
43.71:56.29	0.2474	0.7740	0.2539	2.41
40.465:59.535	0.2586	0.7852	0.2685	2.30
37.68:62.32	0.2753	0.8019	0.2882	2.25
35.23:64.77	0.2880	0.8146	0.3042	2.88

Fig. XXI

— = Normal Oxidation Potential, E_0
 1 cm. block horizontally = 0.01 P.H.
 1 cm. block vertically = 0.002 v.

EXPERIMENT NO. 12

In this run 22 milliliters of 0.9642 N. citric acid were used with 10 milliliters of the buffer. Again the mean oxidation potential was computed and found to have been raised, this time to 0.2790v. This gave us an increase in potential of about 0.0495 v. for the additional 12 milliliters of acid. Thus it seemed to indicate that the higher the acidity of the solution tended to increase the oxidation potentials. This was indicated in the earlier runs when it was pointed out that the potentials of both ferrous ammonium sulphate and ferric ammonium citrate increased with a fall in pH and decreased with a rise in pH. Also the French investigators mentioned earlier found that the potentials of an iron solution increased with a fall in pH and fell with a rise in pH. (24) However, other investigators working without buffers found that the oxidation potentials fell with increasing concentration of acid, and on plotting, the values of the potentials were seen to decrease linearly with the normality of the hydrochloric acid for concentration between 1.0N. and 10.0N. The total change involved was considerable. However, it was found that there was a definite variation of effect by acid on different compounds.(2) Through the finding from this work it could be said that when a buffer was used with ferric ammonium citrate, increased acidity, increased the oxidation potentials of the compound.

The graph of the curve of the normal oxidation potential against the pH showed practically the same type of curve that the two previous figures show.

TABLE NO. 12

Ratio Fe :Fe in %	Observed E.M.F. E.	Absolute p.d. of the Pt Fe Fe Electrode	Normal Oxidation Potential Referred to the Normal Calomel Electrode as Zero, E_o	pH
100.00:0.00	0.5423	1.0689		3.55
84.47:15.53	0.4555	0.9821	0.4121	3.55
81.93:18.07	0.4129	0.9395	0.3742	3.51
79.53:20.47	0.3252	0.8918	0.2910	3.50
77.25:22.75	0.2895	0.8157	0.2582	3.49
75.15:24.85	0.2690	0.7956	0.2417	3.42
73.11:26.89	0.2610	0.7855	0.2351	3.42
71.20:28.80	0.2589	0.7855	0.2351	3.39
69.39:30.61	0.2589	0.7855	0.2379	3.30
67.69:32.31	0.2589	0.7855	0.2399	3.30
66.03:33.97	0.2591	0.7857	0.2421	3.20
64.46:35.54	0.2602	0.7868	0.2449	3.30
57.62:42.38	0.2671	0.7937	0.2592	3.11
52.11:47.89	0.2756	0.8022	0.2750	2.95
47.54:52.46	0.2836	0.8102	0.2856	3.02
43.71:56.29	0.2925	0.8191	0.2990	3.08
40.465:59.535	0.3016	0.8282	0.3115	3.00
37.68:62.32	0.3113	0.8379	0.3242	2.95
35.23:64.77	0.3210	0.8476	0.3372	2.82

Fig. XXII

EXPERIMENTS NOS. 13-14-15

The next series of runs were made to determine the effects of temperature on various concentrations of the "ferrous-ferri" electrode.

The first concentration run was 84.47% ferri: 15.53% ferro. The potentials in this run fell through out except during the portion where the temperature of the solution was between 30° and 40° when the potentials rose slightly.

The second concentration run was 73.11% ferri: 26.89% ferro. The potentials of this solution upon heating rose abruptly until a temperature of 45° was reached, the potentials thereafter gradually fell upon increased rise in temperature.

The third and last concentration run was 64.46% ferri: 35.54% ferro. The potentials of this solution fell constantly as heat was applied.

The pH of the three solutions were respectively 4.3, 3.7, and 3.2. As can be seen either from the graph or from the chart, the potentials fell upon heating and the lower the pH the higher the potential. One investigator working with unbuffered solutions found exactly the opposite upon heating. These men found: (1) an increment in potential with increase in temperature; (2) increment diminishes with increasing acid concentration; (3) mixtures containing a much larger proportion of ferric than ferrous (chloride) have potentials raised by temperature at all acid concentrations; (4) in mixtures containing high proportions of ferrous chloride the effect of temperature was to raise potential in low acid concentration and depress at high. (3)

TABLE NO. 13

Ratio $\text{Fe}^{+++}:\text{Fe}^{++}$ in %	Observed E.M.F. E.	Absolute p.d. of the Pt Fe^{+++} Fe^{++} Electrode	Normal Oxidation Potential Referred to the Normal Calomel Electrode as Zero, E_0	Temp.
84.47:15.53	0.3940	0.9206	0.3506	22.5°
84.47:15.53	0.3010	0.8276	0.2576	30.0°
84.47:15.53	0.3096	0.8362	0.2662	40.0°
84.47:15.53	0.2960	0.8266	0.2526	50.0°
84.47:15.53	0.2735	0.8001	0.2301	60.0°
84.47:15.53	0.2735	0.8001	0.2301	70.0°
84.47:15.53	0.2681	0.7947	0.2247	80.0°
84.47:15.53	0.2461	0.7726	0.2026	90.0°
84.47:15.53	0.2329	0.7595	0.1895	100.0°

TABLE NO. 14

73.11:26.89	0.1110	0.6376	0.0854	23.0°
73.11:26.89	0.2900	0.8166	0.2644	36.0°
73.11:26.89	0.3130	0.8396	0.2874	45.0°
73.11:26.89	0.3013	0.8279	0.2757	60.0°
73.11:26.89	0.2945	0.8211	0.2689	70.0°
73.11:26.89	0.2878	0.8144	0.2622	80.0°
73.11:26.89	0.2828	0.8094	0.2572	90.0°
73.11:26.89	0.2773	0.8039	0.2517	100.0°

TABLE NO. 15

Ratio $\text{Fe}^{+++}:\text{Fe}^{++}$ in %	Observed E.M.F. E	Absolute p.d. of the Pt. $\left\{ \begin{array}{l} \text{Fe}^{+++} \\ \text{Fe}^{++} \end{array} \right.$ Electrode	Normal Oxidation Potential Referred to the Normal Calomel Electrode as Zero, E_0	Temp.
64.46:35.54	0.4335	0.9601	0.4182	24.0°
64.46:35.54	0.4149	0.9415	0.3996	30.0°
64.46:35.54	0.4100	0.9366	0.3947	40.0°
64.46:35.54	0.4012	0.9278	0.3859	50.0°
64.46:35.54	0.3936	0.9102	0.3783	60.0°
64.46:35.54	0.3846	0.9012	0.3693	70.0°
64.46:35.54	0.3735	0.8991	0.3582	80.0°
64.46:35.54	0.3665	0.8921	0.3512	90.0°
64.46:35.54	0.3536	0.8802	0.3393	100.0°

EXPERIMENTS NOS. 16 & 17

These runs were made for qualitative purposes. There was no attempt made to standardize the light source used. The type of light source used was a mercury-vapor one. This lamp is put out by the General Electric Company and goes under the name General Electric Arc. The light source was derived from the mercury which was ionized under pressure and electricity shot through it.

We notice from a glance at the graphs that the solution containing the citric acid started "breaking" a bit before the other one. Both solutions contained 5 milliliters of ferric ammonium citrate and 10 milliliters of potassium oxalate. The solutions turned a dark brown after the break in potential.

TABLE NO. 16

5 c.c. 's of $\text{Fe}(\text{NH}_4)_3(\text{C}_6\text{H}_5\text{O}_7)_3$
 10 c.c. 's of $\text{K}_2\text{C}_2\text{O}_4$
 General Electric Arc

Time (minutes)	E	pH
0	0.5815	5.5
5	0.5260	
30	0.3922	5.3
40	0.3271	5.98
45	0.3144	6.1
50	0.2899	6.3
55	0.1919	6.38
60	0.0731	6.30
65	0.0665	6.12

TABLE NO. 16 (con't)

Time (minutes)	E	pH
70	0.0636	6.25
75	0.0585	5.92
80	0.0440	5.68
85	0.0434	4.68
90	0.0575	5.35
95	0.0505	5.25
100	0.0492	5.95
105	0.0491	5.89
115	0.0445	6.10
125	0.0365	6.10
135	0.0321	4.38
155	0.0280	3.34
185	0.0150	4.26
200	0.0176	5.10
215	0.0226	5.52
275	0.0144	6.21

TABLE NO. 17

5 c.c. 's of $\text{Fe}(\text{NH}_4)_3(\text{C}_6\text{H}_5\text{O}_7)_3$
 10 c.c. 's of $\text{K}_2\text{C}_2\text{O}_4$
 10 c.c. 's of $\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3$

Time (minutes)	E	pH
0	0.5848	0.90
10	0.5490	
20	0.4210	
30	0.3270	
40	0.1346	

TABLE NO. 17 (con't)

Time (minutes)	E	pH
50	0.1110	
60	0.1027	4.00
70	0.0964	
75	0.0924	
80	0.0904	
85	0.0873	
90	0.0850	
95	0.0835	
100	0.0818	
105	0.0786	
115	0.0731	
120	0.0691	
130	0.0680	
135	0.0630	
160	0.0580	
165	0.0470	
180	0.0424	
190	0.0419	3.30
195	0.0384	
210	0.0350	
220	0.0344	
230	0.0341	
240	0.0341	
250	0.0305	
260	0.0305	
270	0.0301	

TABLE NO. 17 (cn't)

Time (minutes)	E	pH
280	0.0258	
290	0.0258	4.9

SUMMATION

It can be seen from a comparison of experiments 6 and 8 that the oxidation buffer had a definite effect on the potentials of the potentials of the ferri-ferro electrode. Without the oxidation buffer, the potential steadily as increased amounts of ferrous ions were added, but with the oxidation buffer the fall in potential was arrested at a certain point, depending on conditions affecting the solution being tested and the potentials rose thereafter with increased amounts of the ferrous ions.

The effect of acid on the buffered ferri-ferro electrode was to increase the potential of the electrode at all times under any given conditions. This was directly opposed to the findings of investigators (2) who worked with unbuffered solutions. Thus an increase of the hydrogen-ion concentration seemed to cause an attack on the buffer rather than an attack on the ferrous or ferric ions directly.

Temperature effect on this electrode (ferri-ferro) was one of constant drop in potential regardless of concentration of ferrous or ferric ions. The difference in potential of the three solutions tested seemed to be effected more by the hydrogen-ion concentration than the proportions of ferric to ferrous ions.

The effect of light upon the compound in question was studied only qualitatively. From this study it was noticed that (1) after an initial sharp fall in potential, the fall practically levelled out and with but one exception

the potential never rose after the rays of this lamp struck the solution; (2) the falling of potential continued neither as long, nor did the potential decrease as much in the solution that contained the acid.

Thus it may be concluded from these studies that the hydrogen-ion concentration was of primary importance in the buffered ferri-ferro electrode. It may be seen that with solutions under the same given conditions, the one with the higher hydrogen-ion concentration also had the higher potential.

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