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A COMPARISON OF THE FLUORIDE COMPLEXING
OF FERRIC ION IN POLYETHYLENE AND GLASS
CELLS

by

THEODORE DAVID HUBERT

B.A. Montana State University, 1951

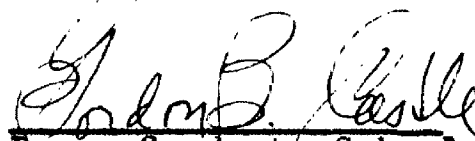
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for the degree of Master of Arts

MONTANA STATE UNIVERSITY

1954

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INTRODUCTION

The formula for the complex ion formed between the ferric ion and the fluoride ion has long been written as FeF_6^{-3} . However the work of Low and Pryde(1) in their study of the potential of the ferrous-ferric half cell as a function of the hydrogen fluoride concentration shows that this cannot be the formula in acid solution. Their data indicates the FeF^{+2} ion. Brosset and Gustaver (2) in their potentiometric measurements of the ferrous-ferric half cell have assumed the FeF^{+2} and FeF_2^+ ions. Babko and Kleiner(3) in their measurements of the decolorization of the ferric thiocyanate complexes with fluoride have assumed the ions FeF_2^+ , FeF^{+2} , FeF_3 , FeF_4^- , and FeF_5^{-2} . Dodgen and Rollefson (4) in their electrometric titration of the ferrous-ferric half cell have assumed the ions FeF^{+2} , FeF_2^+ , and FeF_3 . Following is a table showing the values of the equilibrium constants obtained by these investigators for the ferric-fluoride complex ions:

TABLE (I)

<u>Equilibria</u>				<u>Dodgen and Rollefson</u>	<u>Babko and Kleiner</u>	<u>Brosset and Gustaver</u>	
Fe^{+3}	\rightleftharpoons	FeF^{+2}	$+ \text{H}^+$	K_1	189	200	165
FeF^{+2}	\rightleftharpoons	FeF_2^+	$+ \text{H}^+$	K_2	10.4	25	11.4
FeF_2^+	\rightleftharpoons	FeF_3	$+ \text{H}^+$	K_3	.58	2	---
FeF_3	\rightleftharpoons	FeF_4^-	$+ \text{H}^+$	K_4	---	.1	---
FeF_4^-	\rightleftharpoons	FeF_5^{-2}	$+ \text{H}^+$	K_5	---	.002	---

The work of Dodgen and Rollefson was performed at 25° C.,

the other two do not indicate any specific temperature. It is evident from Table (I) that K_1 and K_2 can be used to find most of the ferric-fluoride complex ions present in an acid solution whereas K_4 and K_5 are probably negligible. K_3 should also possibly be considered.

Mr. Yates⁽¹⁰⁾ of Montana State University, in his work on the electrometric titration of the complex fluoride ions of gallium and beryllium, found that equilibrium took a long period of time to be reached. He was concerned that the fluoride ion in the acid solution would tend to react with the glass cell over this long period of time. To eliminate this possibility he used polyethylene cells. He found that these cells gave a decided difference in observed potential difference compared to the glass cells.

With this fact in mind, several titrations were performed on the ferrous-ferric half cell in glass and polyethylene containers to determine if there were any variation in the observed potential difference between the two types of cell. There was a definite variation. Dodgen and Rollefson⁽⁴⁾ had performed their electrometric titration on the ferrous-ferric half cell in glass containers. The problem of this thesis was therefore to determine the effect on the equilibrium constants K_1 , K_2 , and K_3 of using polyethylene and glass containers for the ferrous-ferric half cell. The electrometric method of titration used is similar to that of Dodgen and Rollefson⁽⁴⁾.

SOLUTIONS

Perchloric Acid 0.9991M

Sodium Fluoride 0.5000M

Sodium Perchlorate 0.5M

Stock Solution Fe^{+2} .0343M

Fe^{+3} .0358M

H^{+} .2356M

ClO_4^{-} .4124M

Ionic strength .554

Methods of Preparing Solutions

Perchloric Acid 0.9991M:

An amount of 71% C.P. perchloric acid was weighed out which would give 1M perchloric acid when diluted to one liter. The resulting solution was then titrated against three weighed samples of sodium carbonate using methyl orange as an indicator. The resulting normality was determined as 0.9991.

Sodium Fluoride 0.5M

C.P. sodium fluoride was dried at 110°C. for a period of 2½-3 hours. An accurately weighed amount was then diluted to 500 ml in a volumetric flask which gave a solution of sodium fluoride of concentration 0.5000M.

Sodium Perchlorate 0.5M

The amount of water in reagent grade hydrated sodium perchlorate was determined by weighing hydrated samples, drying, and reweighing. An amount of sodium perchlorate hydrate was then weighed out which when diluted to two liters in a volumetric flask gave a solution of 0.5M sodium perchlorate.

Stock Solution

0.1 mole of ferrous sulfate hydrate was dissolved in 300 ml of water. The ferrous ion was then precipitated with 6N ammonium hydroxide, centrifuged, washed with water, dissolved in 3N perchloric acid, precipitated again with ammonium hydroxide, and washed with water. The precipitate was then dissolved in enough standard perchloric acid to make an excess of .25M perchloric acid when the solution was diluted to one liter. The ferrous ion was then titrated for with standard potassium permanganate. The amount of hydrogen peroxide which would be required to oxidize one-half of the ferrous ion to ferric ion was then calculated and added to the solution. The total iron was then determined by the Zimmerman-Reinhard method.⁽⁵⁾ The ferrous ion was again titrated for and the difference between the total iron and ferrous ion was determined as the ferric ion. The hydrogen ion was then determined by the method of Schumb, Scherrill, and Sweetser.⁽⁶⁾ The perchlorate

ion was then calculated to be the sum of:

$$(H^+) + 2(Fe^{+2}) + 3(Fe^{+3}).$$

The resulting concentrations were found to be:

$$Fe^{+2} \quad .0343M$$

$$Fe^{+3} \quad .0358M$$

$$H^+ \quad .2356M$$

$$ClO_4^- \quad .4124M$$

The ionic strength was then calculated as:

$$\frac{1}{2}(4 \times .0343 + 9 \times .0358 + .2365 + .4124) = .554$$

CELLS

Two types of cells were used in this comparison. The first consisted of a pyrex glass container fitted with a ground glass cap with holes for the admission of the stirrer, carbon dioxide, salt bridge, and sodium fluoride solution. This cell is similar to that used by Dodgen and Rollefson⁽⁴⁾. A 1.6M sodium perchlorate salt bridge was used. The amount of agar used to hold the salt in the bridge was varied with the temperature. For the 50° C. salt bridge, the amount of agar added made the sodium perchlorate solution so viscous that a vacuum was required to draw the salt solution into the bridge.

The other cell was made by cutting the top from a four ounce polyethylene bottle and fitting the same cap as used for the glass cell to it. The same salt bridge was used for each type of cell.

Polyethylene stirring rods were made by melting polyethylene and drawing the liquid into glass tubing of the proper diameter. The liquid was allowed to solidify and the glass tube was broken leaving the rod of polyethylene. The rod was then cut to the proper length and the stirring end shaped in an open flame.

To eliminate air in the cell, carbon dioxide was continually passed through it. This was accomplished by allowing several pieces of dry ice in a 500 ml flask wrapped

with a towel to sublime slowly. The gas was then passed through 0.5M sodium perchlorate solution at the temperature of the water bath in which the cells were immersed and then into the cells.

The cell electrodes consisted of platinum which had been gold plated in a 1N hydrochloric acid solution of auric chloride. The plating was performed by using the platinum electrodes as cathodes in the auric chloride solution and passing a low current through the solution for a period of $1\frac{1}{2}$ -2 hours. A platinum anode was used in this plating process.

To measure the potential between the two cell containers, a Leeds and Northrup type K-2 potentiometer and a Leeds and Northrup galvanometer no. # 2430 were used. An Eplab standard cell rated at 1.0184V and a Willard wet cell were also used.

For the addition of the fluoride, a 5 ml micro-burette was fitted with a special tip for ease in getting under the stirrer motors. After each addition of fluoride, the tip of the burette was touched to the cell solution to be sure all of the fluoride was in the cell.

THE PROCEDURE FOR THE TITRATION

Titrations were carried out at three temperatures; 15° , 25° , and 50° C. Two titrations with the glass cell and two titrations with the polyethylene cell were made at each temperature. In order to detect any slight variation in potential that would have been due to the glass or the polyethylene, all the other conditions in the two types of cells were made as consistent as possible. With this in mind the same exact amounts of sodium perchlorate, perchloric acid, distilled water, and stock solution were added to each cell namely:

90.0 ml 0.5M sodium perchlorate
5.0 ml 0.9991M perchloric acid
5.0 ml distilled water
1.0 ml stock solution
101.0 ml total

This would make the ionic strength of the cell 0.5 and the initial hydrogen ion concentration $H_0^+ = .0518M$.

The cells were then placed in a water bath regulated at $\pm .02^\circ$ of the proper temperature. The stirrers were left on throughout the entire titration. After the small initial potential (usually .1 to .4 millivolt) had remained constant for $\frac{1}{2}$ hour, the addition of fluoride was begun. In order to obtain the comparison as accurately as possible, the same amounts of fluoride were added in each titration and the corresponding potential difference was recorded.

Example:

<u>Ml of NaF</u>	<u>Potential difference</u>
0.1	.01784
0.2	.03252
0.4	.05407
0.8	.07919
1.2	.09714
2.0	.12566
3.0	.15271
4.0	.1761
5.0	.1976

The small initial potential was then added or subtracted from the observed potential to give the true potential difference.

Up to 1.2 ml of added fluoride, the potential showed no sign of drifting and an equilibrium potential reading could be obtained within a period of 5-10 minutes. However with additions of fluoride of 2.0 ml and up the potential of the polyethylene cell showed a decided upward drift requiring up to three hours to come to a permanent equilibrium point. The glass cell on the other hand showed a consistent potential inside of 20-30 minutes. This would seem to indicate a reaction between hydrogen fluoride and the glass of the glass cell. Since there was no chance for reaction of hydrogen fluoride and glass in the polyethylene cell, we may assume that the true equilibrium time was around three hours. Therefore the apparent equilibrium time of $\frac{1}{2}$ hour in the glass cell must have been due to a factor which tended to decrease the potential difference. This could easily be ascribed to a reaction between hydrogen fluoride and glass.

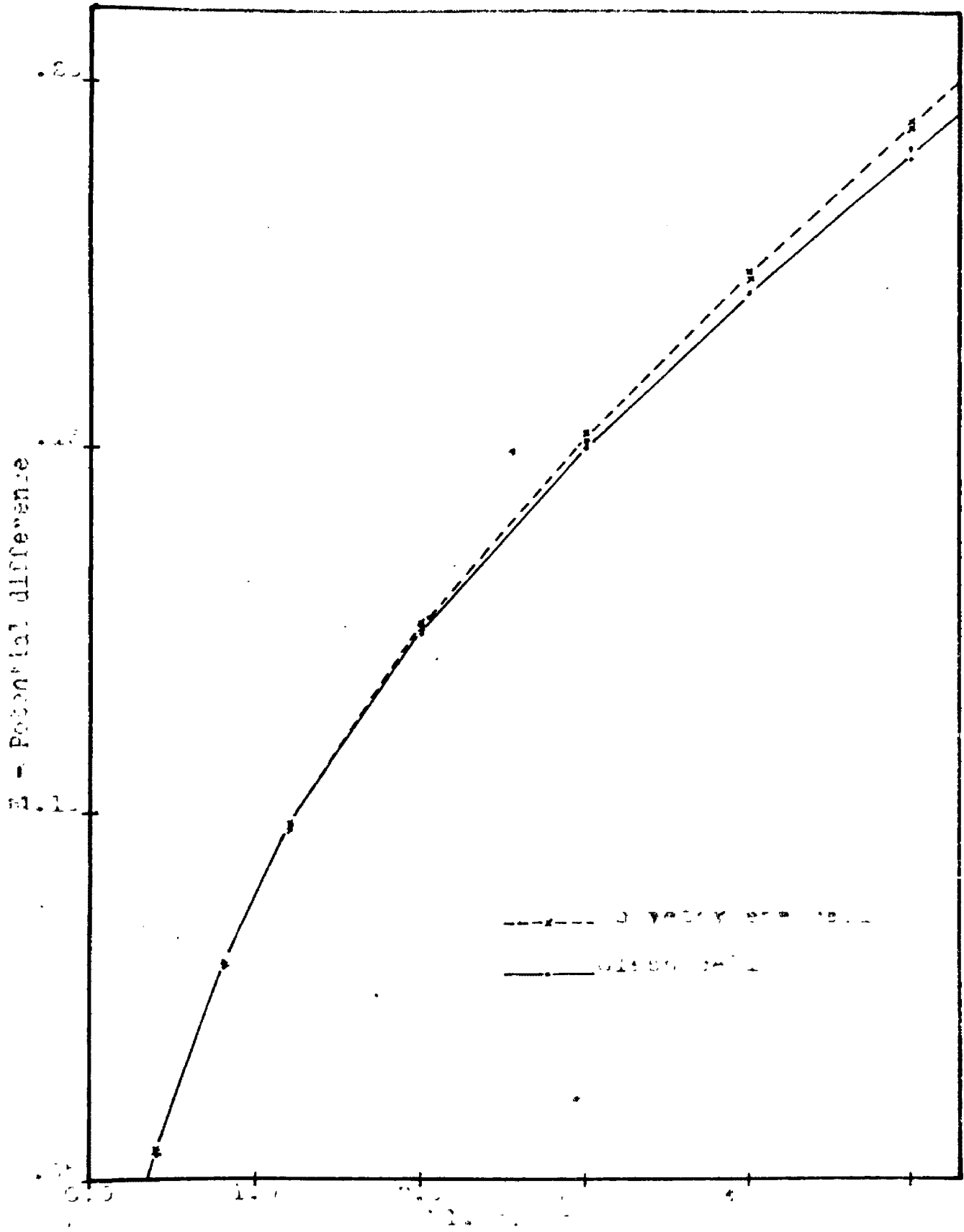
OBSERVED DATA

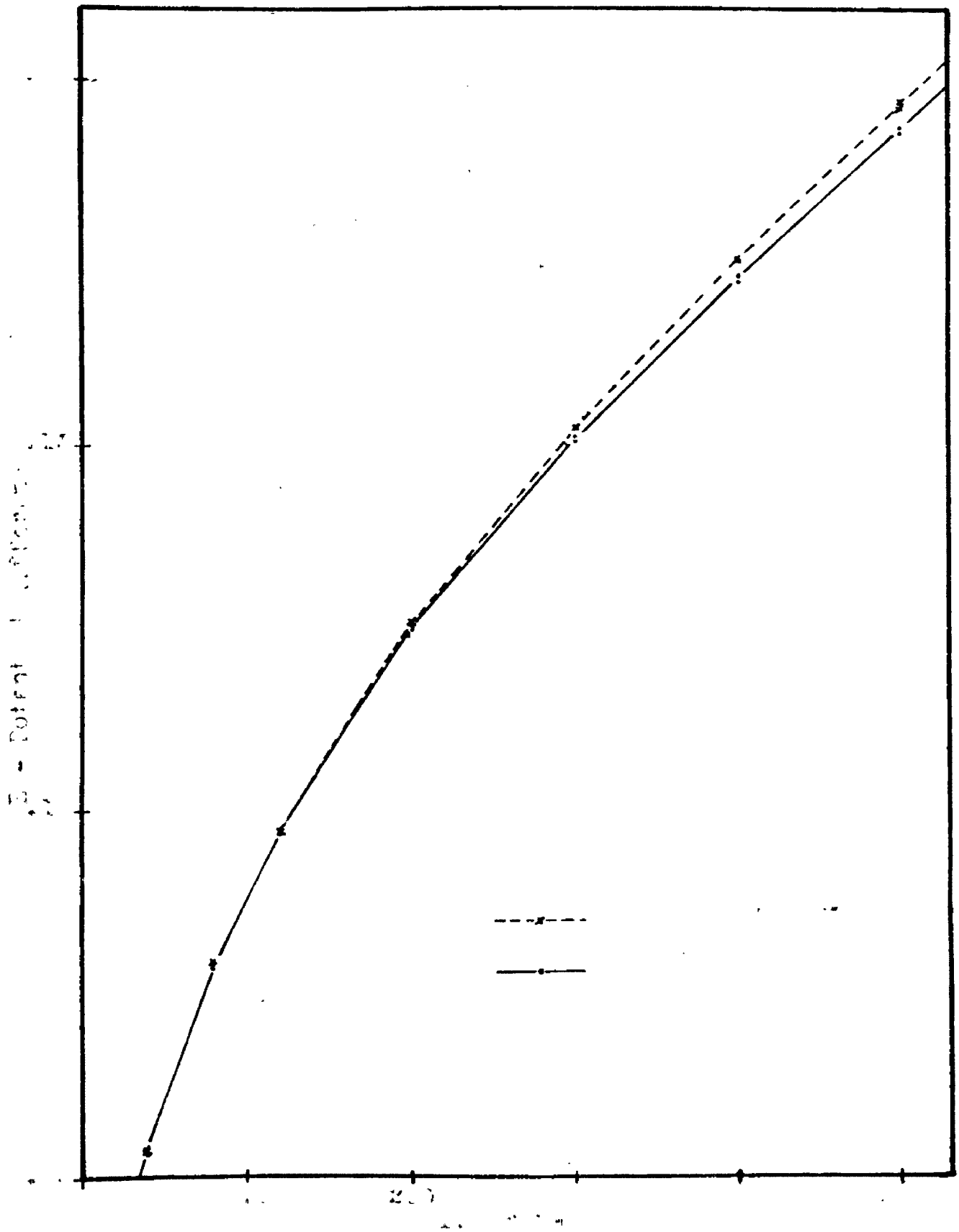
TABLE (II)

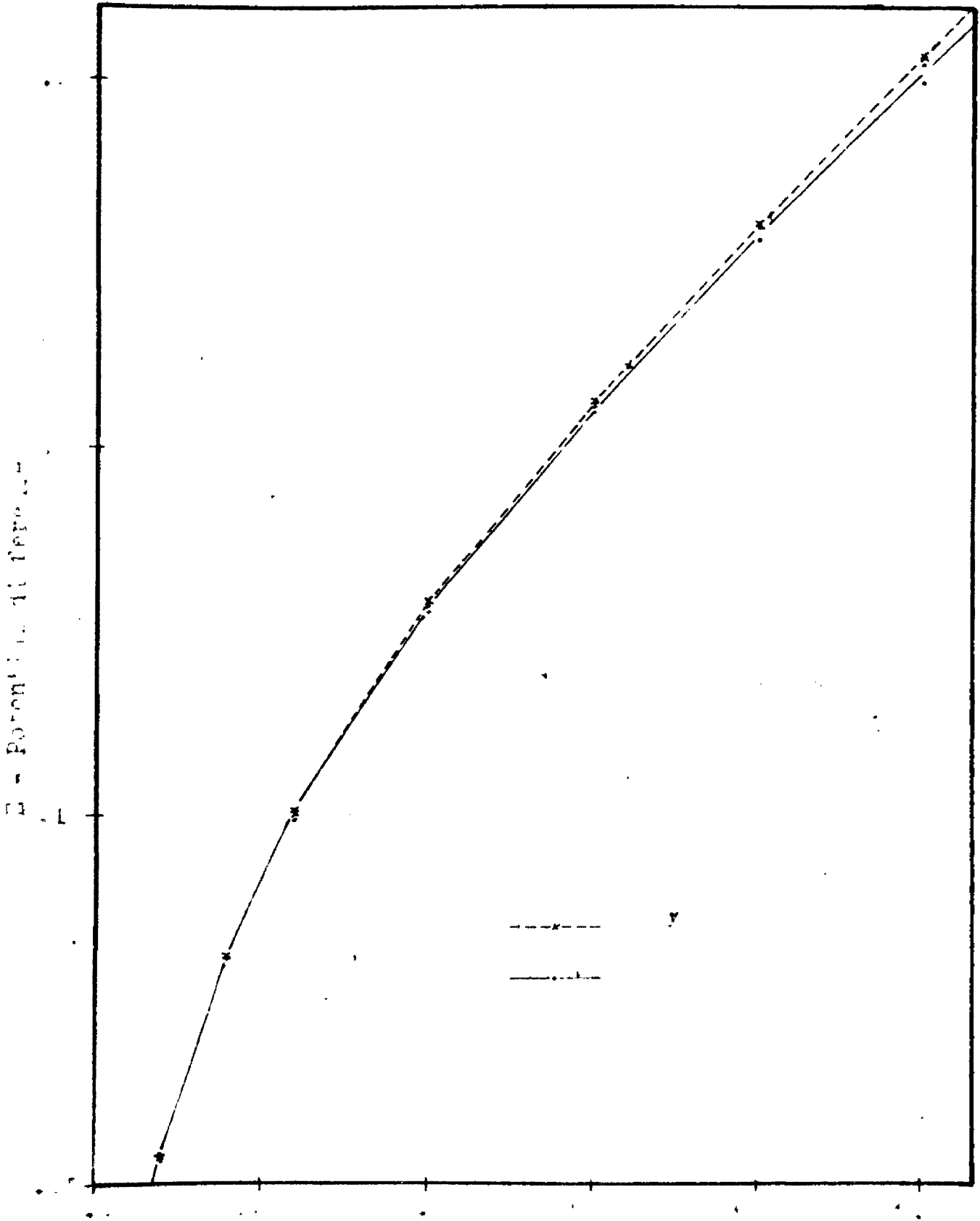
<u>Temperature</u>	<u>Ml NaF</u>	E			
		<u>Glass</u>		<u>Polyethylene</u>	
15°C.	0.1	.01896	.01936	.01809	.01837
	0.2	.03378	.03426	.03340	.03317
	0.4	.05427	.05477	.05418	.05363
	0.8	.07989	.08036	.08011	.07927
	1.2	.09829	.09838	.09866	.09785
	2.0	.12505	.12460	.1260	.1252
	3.0	.15067	.14993	.1522	.1511
	4.0	.1715	.1715	.1745	.1737
	5.0	.1900	.1915	.1952	.1944
	25°C	0.1	.01791	.01725	.01760
0.2		.03199	.03293	.03226	.03243
0.4		.05399	.05324	.05337	.05398
0.8		.07870	.07900	.07993	.07910
1.2		.09731	.09697	.09724	.09732
2.0		.12516	.12481	.12661	.12557
3.0		.15134	.15079	.15285	.15262
4.0		.1734	.1728	.1759	.1760
5.0		.1938	.1931	.1964	.1975
50°C		0.1	.01818	.01820	.01857
	0.2	.03246	.03281	.03288	.03268
	0.4	.05330	.05428	.05388	.05363
	0.8	.08050	.08119	.08092	.08112
	1.2	.09944	.10047	.10025	.10056
	2.0	.12771	.12894	.1288	.12909
	3.0	.1550	.1564	.1613	.1567
	4.0	.1787	.1803	.1807	.1809
	5.0	.2000	.2027	.2032	.2037

Figures 1,2, and 3 are graphs of the observed potential difference plotted against the milliliters of fluoride. They show the polyethylene cell to give a slightly higher e.m.f. than the glass cell after 1.2-2.0 ml of fluoride had been added.

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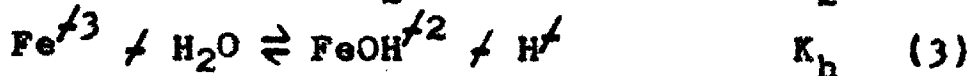
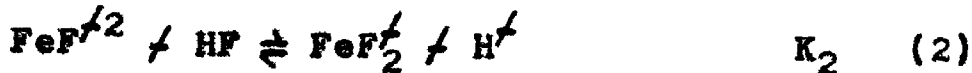




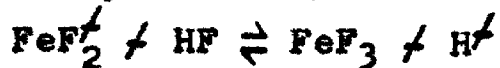


CALCULATION OF K_1 , K_2 , and K_3

Assuming the equilibria:



as did Dodgen and Rollefson⁽⁴⁾, K_1 and K_2 may be estimated as well as K_3 where K_3 represents the equilibria:



K_h^0 has been determined by Bray and Hershey⁽⁷⁾ at 25° and 35° C. Extrapolation of the negative logarithms of these values and substitution in the equation:

$$\log K_h = \log K_h^0 + 4 \log \gamma \quad (\text{where } \gamma \text{ is mean activity coefficient of hydrochloric acid at ionic strength 0.5})$$

gives values of $K_h(15^\circ) = .000969$

$$K_h(25^\circ) = .00197$$

$$K_h(50^\circ) = .0089$$

The values of γ are from Harned and Owen⁽⁸⁾ for hydrochloric acid at ionic strength of 0.5 and are:

$$\gamma(15^\circ) = .7658$$

$$\gamma(25^\circ) = .7571$$

$$\gamma(50^\circ) = .7344$$

Broehne and DeVries⁽⁹⁾ give values of K_4^0 at 15°, 25°, and 50°

and 35° C. Extrapolating to obtain the 50° value and dividing all the K_4^0 values by γ^2 gives values of $K_4(15^\circ) = .00135$, $K_4(25^\circ) = .00117$, and $K_4(50^\circ) = .000848$. Broehne and DeVries⁽⁹⁾ also give a value to $K_5 = 4$ which is comparatively independent of the temperature.

In the titration, two quantities were observed; F_t^- the total concentration of fluoride ion and E the potential difference of the cell. The initial hydrogen ion concentration H_0^+ and the total ferric ion concentration Fe_t^{+3} are also known.

Assuming the activity coefficients of the ferrous and ferric ions to be constant the $\log \frac{(Fe_t^{+3})}{(Fe_0^{+3})}$ can be found by the equation: $\log \frac{(Fe_t^{+3})}{(Fe_0^{+3})} = \frac{-F \times E}{2.303RT}$ where F is the faraday constant, E is the measured potential difference between the reference cell and the reaction cell, R is the gas constant, T is the temperature, and 2.303 is the conversion factor from natural logarithms to logarithms to the base 10.

By considering equilibrium (3) (Fe_0^{+3}) may be found:

$$(Fe_0^{+3}) = \frac{(Fe_t^{+3})}{1 + \frac{K_h}{(H_0^+)}}$$

By the above two expressions Fe_t^{+3} the concentration of ferric ions can be calculated.

The ferric ion complexed by fluoride, Fe_c^{+3} , is evidently equal to $(Fe_t^{+3}) - (Fe_0^{+3}) - (FeOH^{+2})$. But from equilibria

(3), (FeOH^{+2}) is equal to $(\text{Fe}^{+3}) \cdot \frac{K_h}{(\text{H}^+)}$. Therefore:

$$\begin{aligned} (\text{Fe}^{+3}_c) &= (\text{Fe}^{+3}_t) - (\text{Fe}^{+3}) - (\text{Fe}^{+3}) \cdot \frac{K_h}{(\text{H}^+)} \\ &= (\text{Fe}^{+3}_t) - (\text{Fe}^{+3}) \cdot \left(1 + \frac{K_h}{(\text{H}^+)}\right) \end{aligned}$$

Since $1 + \frac{K_h}{(\text{H}^+)}$ is very nearly equal to $1 + \frac{K_h}{(\text{H}^+_0)}$ for the

concentrations used here, we may say:

$$(\text{Fe}^{+3}_c) = (\text{Fe}^{+3}_t) - \frac{(\text{Fe}^{+3})}{(\text{Fe}^{+3}_0)} \cdot \frac{(\text{Fe}^{+3}_t)}{1 + \frac{K_h}{(\text{H}^+_0)}} \cdot \left(1 + \frac{K_h}{(\text{H}^+_0)}\right)$$

Hence $(\text{Fe}^{+3}_c) = (\text{Fe}^{+3}_t) \left(1 - \frac{(\text{Fe}^{+3})}{(\text{Fe}^{+3}_0)}\right)$

The first approximation of (HF) was given by $(\text{F}^-) - (\text{Fe}^{+3}_t)$.

The first approximation of (H^+) was given by $(\text{H}^+_0) - (\text{HF})$.

The ratio $\frac{(\text{HF})}{(\text{H}^+)}$ was then determined.

The second approximation of (H^+) was determined from the equation: $(\text{HF})_a = (\text{F}^-) - (\text{Fe}^{+3}_c) \left[\frac{1 + \frac{2K_2(\text{HF})}{(\text{H}^+)}}{1 + \frac{K_2(\text{HF})}{(\text{H}^+)}} \right]$ which was

derived from equilibria (2), (4), (5), and the stoichiometric relationship for fluoride. K_2 may be estimated from the first approximation for $\frac{(\text{HF})}{(\text{H}^+)}$. The quantity a is given by the equation: $1 + \frac{K_4}{(\text{H}^+)} + 2K_4K_5 \frac{(\text{HF})}{(\text{H}^+)}$.

The second approximation of (H^+) was determined from the equation: $(H^+)a = (H^+_0)a - (HF)a$. The $HF\bar{2}$ term was considered negligible in this equation.

The ratio: $\frac{(HF)a}{(H^+)a}$ was then calculated. A third approximation could have been made for $\frac{(HF)}{(H^+)}$ but it was found that this third approximation was very nearly the same as the second so only the two approximations were made.

We now assume that the total ferric ion present as fluoride complexes must be present as $(FeF^+2) + (FeF^+2)$.

From equilibria (1) $(FeF^+2) = \frac{K_1(Fe^{+3})(HF)}{(H^+)}$

From equilibria (2) $(FeF^+1) = \frac{K_2(FeF^+2)(HF)}{(H^+)}$

Substituting in the equation $(Fe^{+3})_c = (FeF^+2) + (FeF^+2)$ and dividing through by (Fe^{+3}) and $\frac{(HF)}{(H^+)}$ we get:

$$\frac{(Fe^{+3})_c}{(Fe^{+3})} \cdot \frac{(H^+)}{(HF)} = K_1 + K_1K_2 \frac{(HF)}{(H^+)}$$

By plotting $\frac{(HF)}{(H^+)}$ against $\frac{(Fe^{+3})_c}{(Fe^{+3})} \cdot \frac{(H^+)}{(HF)}$, K_1 can be determined as the intercept and the product K_1K_2 as the slope of the line. Having found values for K_1 and K_2 , a value for K_3 can be found in a similar fashion. The equation for this calculation of K_3 would evidently be:

$$\frac{\frac{(Fe^{+3})_c}{(Fe^{+3})} \cdot \frac{(H^+)}{(HF)} - \left[K_1 + K_1K_2 \frac{(HF)}{(H^+)} \right]}{\frac{(HF)}{(H^+)}} = K_1K_2K_3 \frac{(HF)}{(H^+)}$$

The slope of this line is $K_1 K_2 K_3$ and since values of K_1 and K_2 have previously been determined, K_3 is readily calculated.

As an example, the quantities used to calculate K_1 , K_2 , and K_3 , for a polyethylene cell at 50° C., are shown in Table (III). Figure (4) shows an example of the graph used to calculate K_1 , K_2 , and K_3 . The actual values of K_1 , K_2 , and K_3 were obtained from a larger graph since the small size of figure (4) does not give enough accuracy. One-half inch on the large graph represented 25 units of $\frac{(\text{Fe}^{3+})(\text{H}^+)}{(\text{Fe}^{2+})(\text{HF})}$ and .025 units of $\frac{(\text{HF})}{(\text{H}^+)}$.

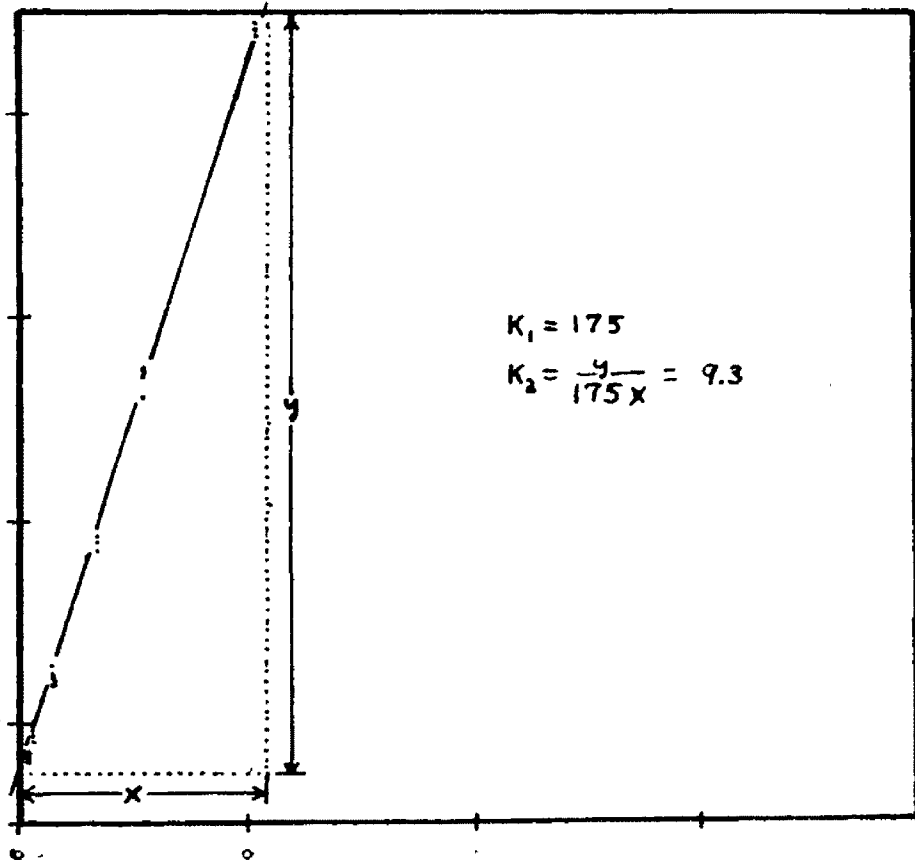
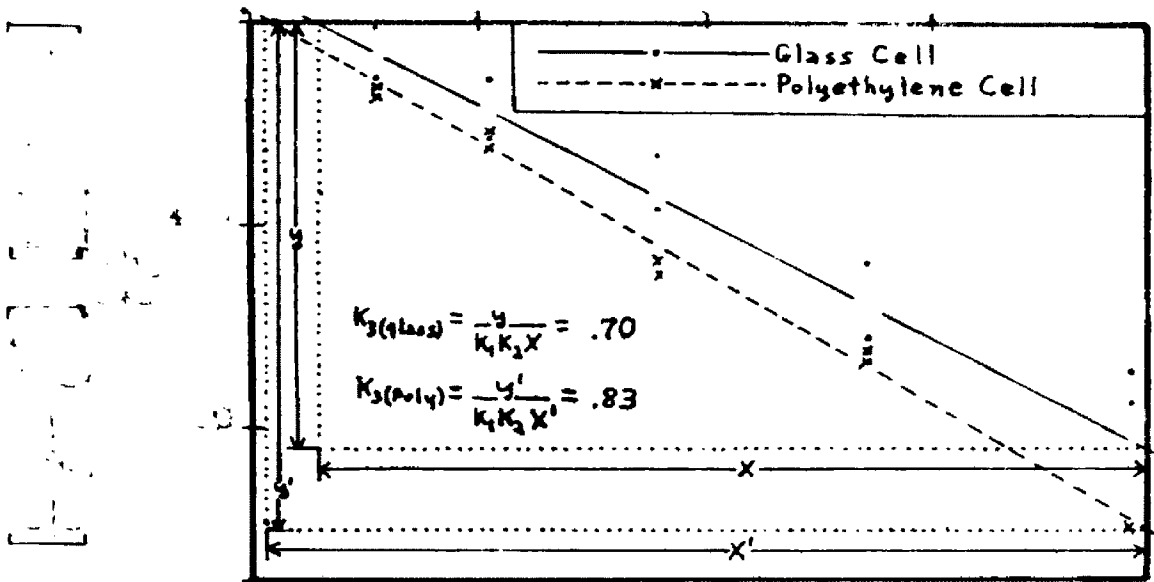
On plotting (X) against (Y) from Table (III) on a graph like Figure (4), the intercept was found to be 175 which is K_1 . The slope was measured to be 1636. Therefore K_2 is $\frac{1636}{175}$ or 9.3. On plotting (X) against (Z), the slope was measured to be 1350. Therefore $K_3 = \frac{1350}{1636} = 0.83$.

TABLE (III)

<u>ml of NaF</u>	<u>delta E</u>	<u>$-\log \frac{Fe^{+3}}{Fe_0^{+3}}$</u>	<u>$\frac{Fe^{+3}}{Fe_0^{+3}}$</u>	<u>Fe^{+3}</u>
0.1	.01794	.2799	.5249	.0001606
0.2	.03268	.5098	.3092	.00009462
0.4	.05363	.8366	.1457	.00004458
0.8	.08112	1.2655	.05426	.00001660
1.2	.10056	1.5687	.02700	.000008262
2.0	.12909	2.0138	.009687	.000002964
3.0	.1567	2.4445	.003593	.0000009946
4.0	.1809	2.8220	.001507	.0000004611
5.0	.2037	3.1777	.0006642	.0000002032

<u>Fe_0^{+3}</u>	<u>HF</u>	<u>H⁺</u>	<u>$\frac{HF}{H^+}$</u>	<u>HF alpha</u>
.0001701	.0003249	.05143	.006317	.0003162
.0002473	.0007407	.05096	.01453	.0007136
.0003058	.001666	.04993	.03336	.001599
.0003386	.003590	.04780	.07510	.003458
.0003483	.005523	.04567	.1209	.005346
.0003545	.009354	.04145	.2257	.009120
.0003567	.01407	.03624	.3882	.01379
.0003578	.01869	.03114	.6001	.01839
.0003578	.02323	.02613	.8890	.02291

<u>H⁺alpha</u>	(X) <u>$\frac{HFalpha}{H^+alpha}$</u>	(Y) <u>$\frac{Fe_0^{+3}}{Fe^{+3}}$</u>	(Z) <u>$\frac{Fe_0^{+3}}{Fe^{+3}} \cdot \frac{H^+}{HF} - \left[K_1 K_2 \frac{HF}{H^+} \right]$</u>
.05278	.00599	176.7	---
.05238	.01362	192	---
.05139	.0311	221	---
.04942	.0700	291	14
.04743	.1127	374	133
.04346	.2098	570	248
.03858	.3574	1003	680
.03393	.5419	1432	683
.02946	.7776	2264	1051.



CONCLUSION

The equilibrium constants calculated for glass and polyethylene cells at the various temperatures are given in Table (IV).

TABLE (IV)

	<u>GLASS</u>	<u>POLYETHYLENE</u>
15° C.	K ₁ = 198 K ₂ = 11.2 K ₃ = .82	K ₁ = 198 K ₂ = 11.2 K ₃ = 1.10
25° C.	K ₁ = 180 K ₂ = 10.3 K ₃ = .84	180 10.3 .997
50° C.	K ₁ = 175 K ₂ = 9.3 K ₃ = .70	175 9.3 .83

In Figures (1), (2), and (3) it was shown that the polyethylene cell gave a slight but decidedly higher potential difference than the glass cell upon additions over 1.2-2.0 ml. of fluoride. The effect of this difference on K₁ and K₂ was not apparent in their calculation. The effect on K₃ however was apparent; the glass cell giving consistently lower values of K₃ as shown in Table (IV). If we assume that the polyethylene cell gives the correct value of K₃, the % error involved in using glass cells at the three temperatures would be:

$$15^{\circ} \text{ C. } \frac{(1.1 - .82) \times 100}{1.1} = 25\%$$

$$25^{\circ} \text{ C. } \frac{(.997-.84)}{.997} \times 100 = 16\%$$

$$50^{\circ} \text{ C. } \frac{(.83-.70)}{.83} \times 100 = 16\%$$

The reason for this discrepancy in results was ascribed to the assumption that the hydrogen fluoride in the glass cell reacted with the glass of the cell.

SUMMARY

Two electrometric titrations were performed on the ferrous-ferric half cell using glass containers and two electrometric titrations were performed on the ferrous-ferric half cell using polyethylene containers at the temperatures 15° , 25° , and 50° .

The time for equilibrium to be reached was found to be longer in the polyethylene than the glass cell.

The equilibrium constants K_1 , K_2 and K_3 for the ferric-fluoride complex ions in glass and polyethylene cells at the various temperatures were calculated and compared.

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