COULOMETRIC-ACIDIMETRIC TITRATIONS AND RELATED STUDIES IN ACETIC ACID - ACETIC ANHYDRIDE SOLUTIONS

Thesis by

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ABSTRACT

Part I

A coulometric titration of bases is described in which the supporting electrolyte consists of a sodium perchlorate solution in acetic anhydride, containing a small amount of acetic acid. A number of inorganic bases (sodium acetate, potassium hydrogen phthalate, sodium fluoride, sodium chloride, sodium nitrate and sodium sulfate) have been titrated in this solvent with accuracies of ±0.2%. Perchloric acid is generated with 100% efficiency with a mercury anode. The end point is determined potentiometrically.

Application of this coulometric technique has been made to the determination of fluoride ion. Most anions other than perchlorate display basic character in this solvent and were titrated with the fluoride. The titration has been applied to the determination of the total base in mixtures of fluoride with sulfate, chloride and nitrate. In some instances two end points can be observed with binary mixtures, so that analysis for each component is possible. An example is a mixture of fluoride and chloride.

Part II

An investigation of reactions occurring at and around platinum electrodes, both anode and cathode, in the electrolysis of a solution of 0.1 VF sodium perchlorate in acetic anhydride, which contains a small amount of acetic acid (0.1 VF), is described. Chronopotentiometric techniques have been extensively employed in these studies.

The cathode reaction is the reduction of the small amount of acetic acid present in the acetic anhydride solution. The reduction products are hydrogen and acetate ion:

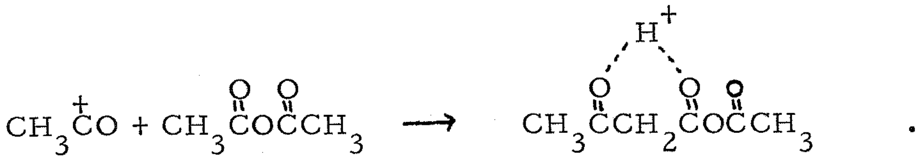
$$CH_3CO_2H + e^- = 1/2\ H_2 + CH_3CO_2^-\ .$$

The anode reaction is probably the oxidation of acetic acid or acetic anhydride to form hydrogen ions or acetylium ions:

$$2\ CH_3CO_2H \longrightarrow C_2H_6 + 2\ CO_2 + 2\ H^+ + 2\ e^-$$

$$2\ (CH_3CO)_2O \longrightarrow C_2H_6 + 2\ CO_2 + 2\ CH_3\overset{+}{C}O + 2\ e^-$$

The acetylium ions condense rapidly with the solvent to form slightly dissociated products:



$$CH_3\overset{+}{C}O + CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 \cdot H^+\ .$$

Further condensations to higher, very slightly dissociated products occur. These higher condensation products, in the protonated form, are such weak acids that they do not react with sodium acetate in the acetic anhydride solution. Thus, hydrogen ions are effectively lost from the solution. Coulometric-acidimetric titrations of bases, performed with hydrogen ions generated at a platinum anode in acetic anhydride, were unsuccessful because of this loss of hydrogen ions.

An appendix is included in which attention is drawn to the very reducing potentials attainable in acetic anhydride. From preliminary experiments it appears that sodium ion is more easily reduced than the acetic anhydride solvent.

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PART I

COULOMETRIC-ACIDIMETRIC TITRATIONS (1)

Introduction

As pointed out by Lingane (2), the extension of coulometric methods to non-aqueous solvents would greatly broaden the practical scope of this technique. Only a handful of coulometric experiments involving non-aqueous media, however, have been reported. Meyer and Boyd (3) have described a method for a coulometric Karl Fisher titration in a methanol solution. Streuli (4) and Hanselman and Streuli (5) described coulometric titrations of several amines in acetonitrile. In the latter case the supporting electrolyte was 0.05 VF*lithium perchlorate trihydrate, and the authors state that the three waters of hydration provided enough water so that its oxidation to oxygen served as the hydrogen ion-producing electrode reaction. Hanselman and Streuli (5) have also used the electro-oxidation of hydroquinone to quinone in acetonitrile to generate hydrogen ions.

The large number of volumetric-acidimetric titrations (6), which have been described in which acetic acid is used as the solvent, led to an attempt to develop a coulometric-acidimetric titration procedure for an acetic acid-acetic anhydride solvent system. The procedure which has resulted combines the advantages of both coulometric and non-aqueous acidimetric titrations. It should be applicable to the

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*VF is the symbol for "volume formal." A volume formal solution contains 1 gram formula weight of the stated compound per liter of the solution.

determination of microgram quantities of bases which are too weak to be titratable with acid in aqueous solutions.

The generation of perchloric acid in acetic acid-acetic anhydride mixtures was accomplished by anodically oxidizing a mercury electrode. The predominant electrode reaction is:

$$2\ Hg = Hg_2^{++} + 2\ e^- .$$

The mercurous ion formed at the electrode reacts with acetic acid to form mercurous acetate and hydrogen ions:

$$Hg_2^{++} + 2\ CH_3CO_2H = Hg_2(CH_3CO_2)_{2\ (s)} + 2\ H^+ .$$

Mercurous acetate is a stable, sparingly soluble salt in this solvent and accumulates during the titration.

Experimental

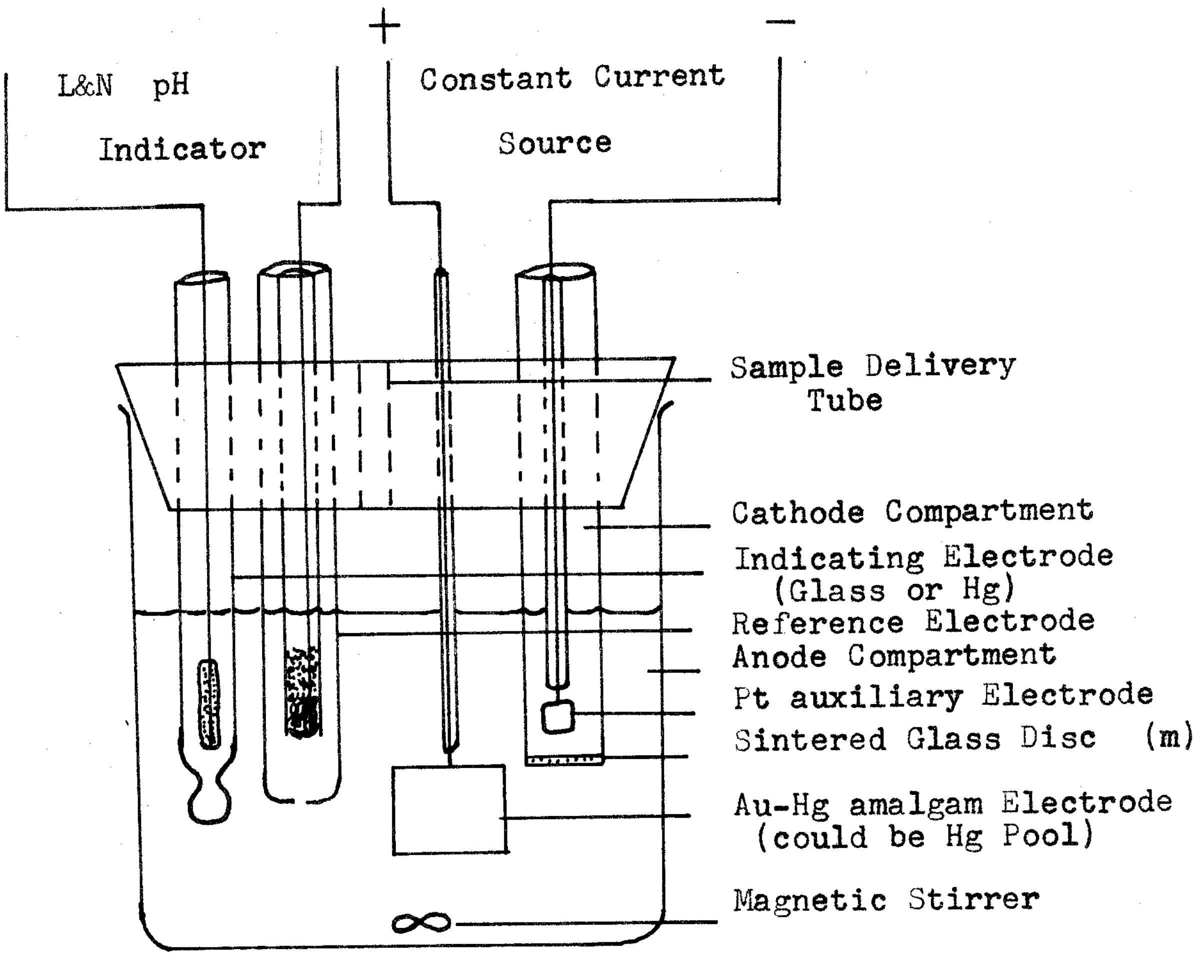
Except for the sodium perchlorate all chemicals were commercial products of highest purity and were used without further purification.

All batches of sodium perchlorate, which were tested, contained significant amounts of basic impurities which had deleterious effects on the sharpness of the potentiometric end point of the coulometric titration. After one recrystallization from boiling acetic acid, the impurities were reduced to an acceptably low level and the end point sharpness was substantially improved.

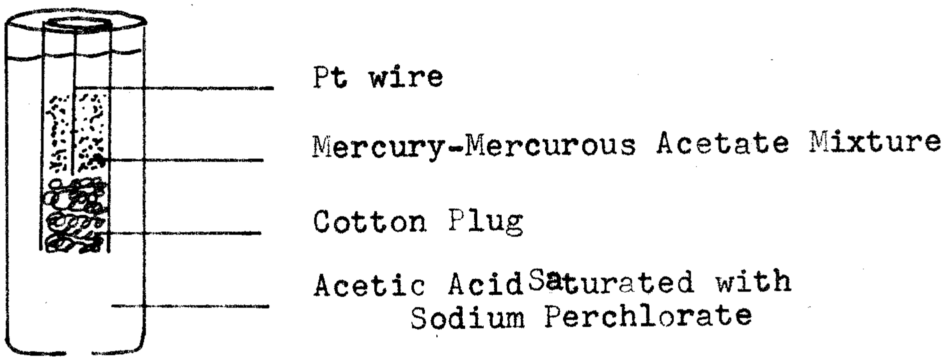
Perchloric acid was generated in a supporting electrolyte of 0.1 VF sodium perchlorate in a solvent consisting of 90-95 mole % acetic anhydride and 5-10 mole % acetic acid.

Standard solutions of base were prepared by dissolving dried, weighed quantities of sodium carbonate or potassium hydrogen phthalate in measured volumes of acetic acid.

The titration cell was a 150 ml beaker fitted with a rubber stopper (Fig. I-1). Although the solvent gradually attacked the rubber stopper, no impurities appeared to be introduced into the solution during the time required for a titration (up to 45 min.). The mercury generating anode employed was either a 5 cm^2 amalgamated gold foil electrode or a mercury pool electrode of approximately 20 cm^2 area. Both electrodes functioned well, but the pool electrode was more suitable for titrations of large amounts of base, because the resulting mercurous acetate did not insulate this electrode from the solution as rapidly. The auxiliary cathode consisted of a small platinum foil separated from the body of the solution by a sintered glass tube. The cathode compartment was filled with the same supporting electrolyte as the anode compartment. Hydrogen gas and sodium acetate were formed at the cathode. No diffusion of cathodic reaction products into



COULOMETRIC CELL



REFERENCE ELECTRODE

FIG.I-1

the main body of the solution was observed during the time required for a titration.

The coulometric titration was followed potentiometrically by means of either a glass electrode or an amalgamated gold wire and a specially constructed mercury-mercurous acetate reference electrode. The glass electrode was stored in acetic acid, when not in use, to maintain its sensitivity; storage in water or acetic anhydride caused the reproducibility and sensitivity of the electrode to decrease markedly.

An ordinary calomel reference electrode could not be employed not only because chloride ion, which diffuses into the main body of the solution, is titrated as a base, but also because the sodium perchlorate supporting electrolyte causes potassium perchlorate to precipitate at the junction of the calomel reference cell with the non-aqueous solution and spurious potential readings result. The mercury-mercurous acetate reference electrode (Fig. I-1) was prepared by adding excesses of solid mercurous acetate and mercury metal to anhydrous acetic acid, which was saturated with sodium perchlorate. All potentials in this thesis refer to this reference electrode (ref.).

The potential of the glass (or amalgamated gold wire)-reference electrode pair was measured with the millivolt scale of a Leeds and Northrup pH Indicator. The potentials measured were not assumed to have any absolute significance but were used empirically to detect the end point of the titration.

The constant current source was modeled after that described by Lingane (7). A servomechanism was employed to regulate automatically a series resistance in the coulometric cell circuit to compensate for changes in the supply voltage and cell impedance. Even though the resistance of the supporting electrolyte was from 2000 to 6000 ohms, currents from 1-25 ma were maintained constant to ±0.05%.

The Titration

Generation of perchloric acid

The oxidation of a mercury electrode in acetic acid-acetic anhydride solvent is a very satisfactory means of generating hydrogen ions (perchloric acid) with 100% efficiency. This is true because the predominant electrode reaction (a), as well as the most likely side reactions (b), (c) and (d), result in the generation of one hydrogen ion or its equivalent (removal of base) for each electron:

$$2\,Hg = Hg_2^{++} + 2\,e^- \qquad (a)$$

$$2\,CH_3CO_2H = (CH_3CO)_2O + 1/2\,O_2 + 2\,H^+ + 2\,e^- \qquad (b)$$

$$2\,CH_3CO_2H = C_2H_6 + 2\,CO_2 + 2\,H^+ + 2\,e^- \qquad (c)$$

$$2\,CH_3CO_2^- = C_2H_6 + 2\,CO_2 + 2\,e^- \qquad (d)\ .$$

The mercurous ions formed in reaction (a) undergo any of the following reactions to form hydrogen ions or to remove base from the solution:

$$Hg_2^{++} + 2\,CH_3CO_2H = Hg_2(CH_3CO_2)_{2\,(s)} + 2\,H^+$$

$$Hg_2^{++} + 2\,CH_3CO_2^- = Hg_2(CH_3CO_2)_{2\,(s)}$$

$$Hg_2^{++} + 2\,X^- = Hg_2X_{2\,(s)}$$

where X^- represents the anion of an insoluble mercurous salt, e.g. chloride.

In fact it is not possible to write a reasonable anodic reaction for a mercury electrode in a sodium perchlorate-acetic acid-acetic anhydride electrolyte which does not result in 100% current efficiency for the generation of perchloric acid (or its equivalent). In accordance with this, no difficulty was observed in generating perchloric acid with 100% efficiency, with the mercury anode, at current densities from 0.2 to 2.0 ma/cm^2 in the titration of a number of bases.

Detection of the end point

After soaking in acetic acid for several hours, the glass electrode responded readily to changes in hydrogen ion concentration in the acetic acid-acetic anhydride solvent. A typical titration curve for the titration of ca. 0.015 mmoles of sodium fluoride in a volume of 90 ml is shown in Fig. I-2, curve 2. The potential of the glass electrode vs. the reference electrode (ref.) is plotted as a function of the generating time. The end point was taken as the point of

POTENTIOMETRIC TITRATION CURVE FOR FLUORIDE IN ACETIC ANHYDRIDE

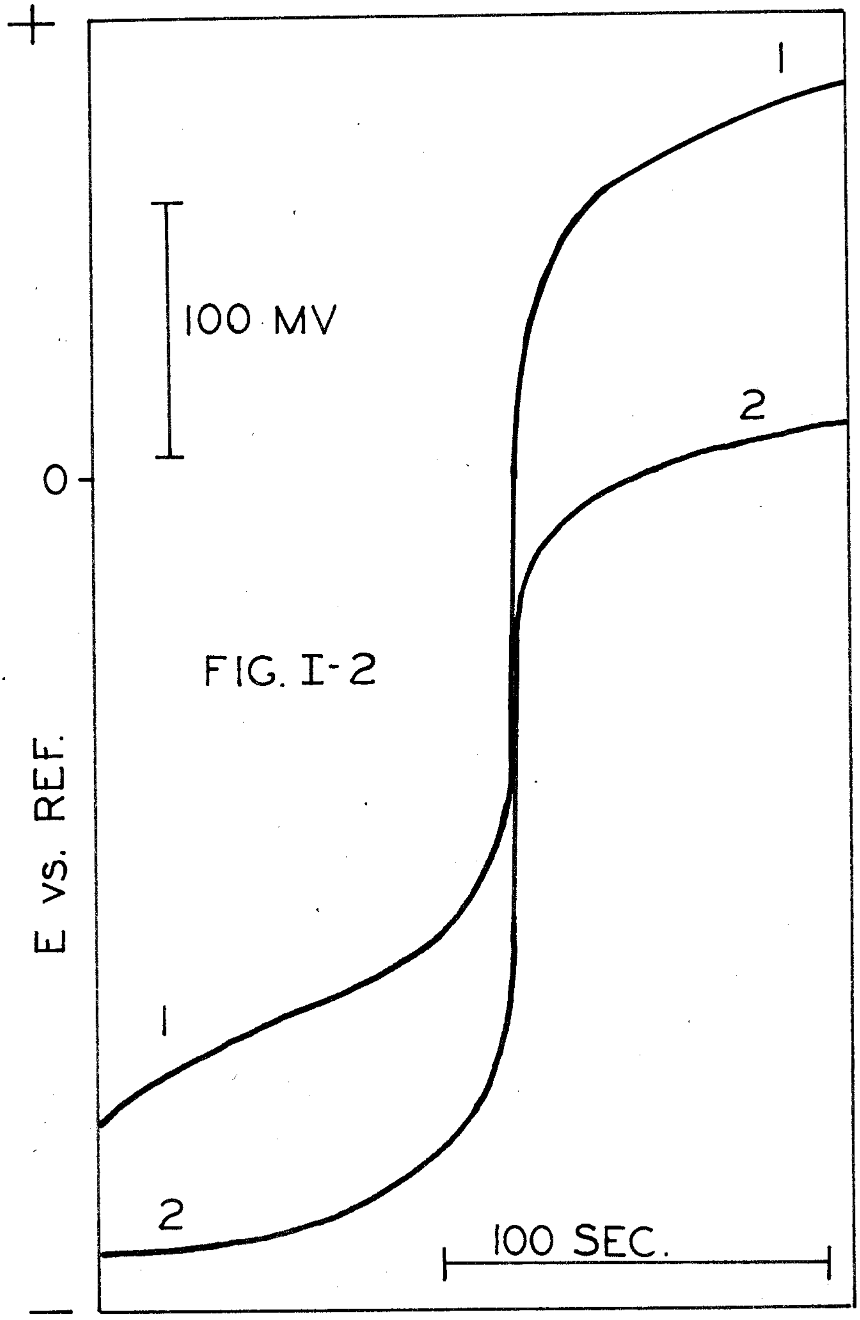


FIG. I-2

GENERATING TIME

Curve 1: Mercury indicating electrode

Curve 2: Glass indicating electrode

Generating current 15.62 ma.

maximum slope of this curve.

A mercury indicating electrode (an amalgamated gold wire) may be substituted for the glass electrode. This electrode responded readily to changes in mercurous ion concentration in this solvent. A typical titration curve for the titration of sodium fluoride is shown in Fig. I-2, curve 1. The potential of the mercury indicating electrode vs. the reference electrode (ref.) is plotted as a function of the generating time. The electrode functions as a mercury-mercurous acetate electrode which responds to the concentration of acetate ion and, hence to the concentration of fluoride ion and perchloric acid.

For the titration of solutions of a single base this mercury indicating electrode offers no advantages over the glass electrode, but it has usefulness for analyses of mixtures of anions in which one or more of the anions form mercurous salts which are less soluble than mercurous acetate.

Mixtures of chloride and fluoride (or acetate) display only a single potential inflection when a glass electrode is used to detect the end point of the coulometric titration (Fig. I-3, curve 2); if the mercury indicating electrode is substituted for the glass electrode, however, two distinct potential inflections are observed corresponding to the chloride and fluoride ions present (Fig. I-3, curve 1). Up to the first potential inflection the indicating electrode functions as

POTENTIOMETRIC TITRATION CURVE FOR A FLUORIDE- CHLORIDE MIXTURE

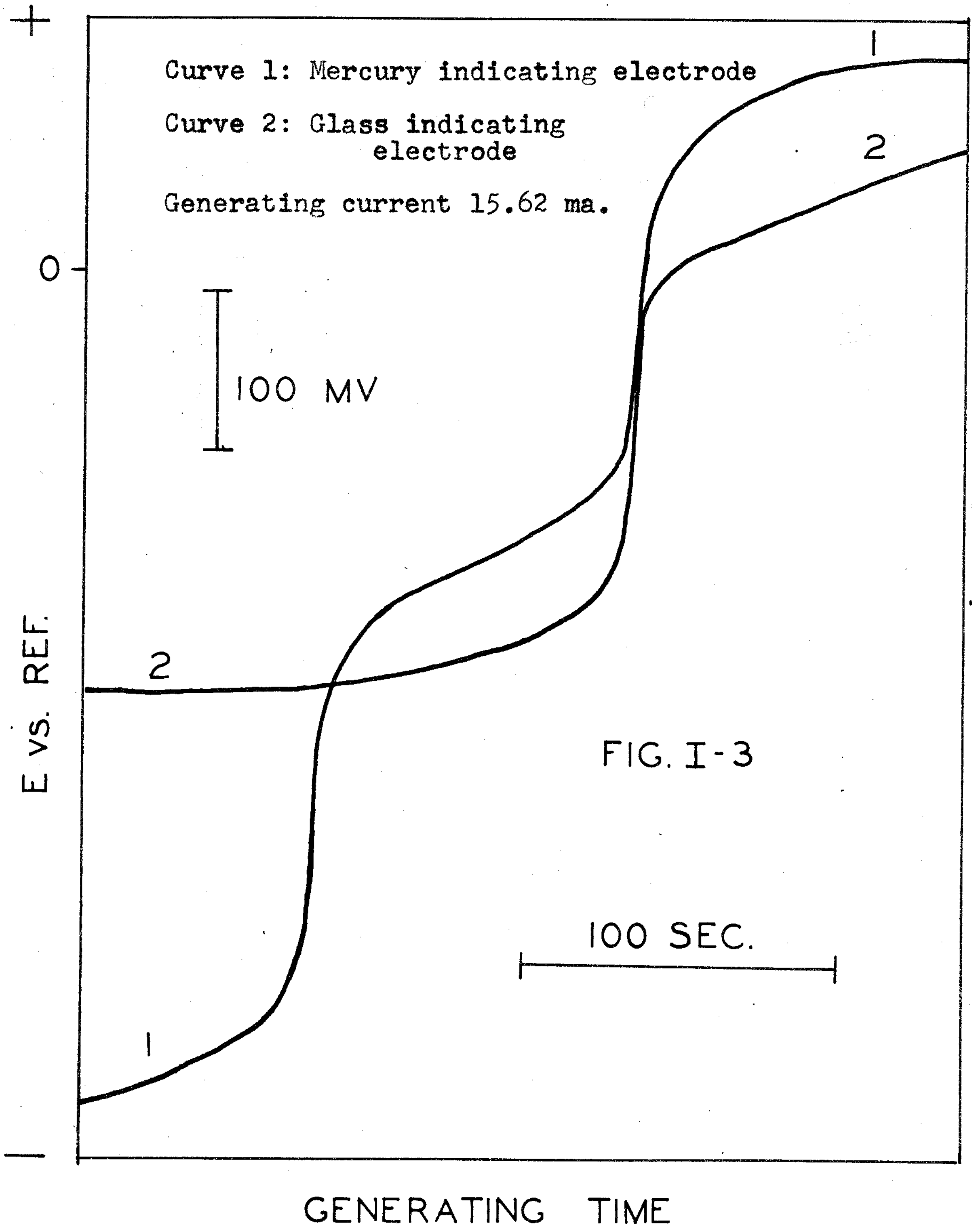


FIG. I-3

a mercury-mercurous chloride electrode that responds to the concentration of chloride ion. Subsequently, the electrode functions as a mercury-mercurous acetate electrode that responds to the concentration of acetate ion (and, therefore, to the concentration of fluoride ion).

When quantities of base greater than about 10 microequivalents were titrated, it was observed in the vicinity of the end point that the potential of the glass electrode did not achieve a steady value for several minutes after the generation of mercurous ions had ceased. For such cases it was necessary to generate about 95% of the equivalent amount of perchloric acid, to wait 5 min., and then to generate in small increments with a 2-3 minute pause after each increment, until the potential of the glass electrode was stable. Failure to wait for final potential equilibrium caused consistently high results.

The reasons for the slow approach to equilibrium may include a slow reaction between mercurous ions and acetic acid. There is some evidence for this. The potential of the glass electrode vs. ref., near the end point, increases to its equilibrium value following each generation increment, while the potential of the mercury indicating electrode vs. ref. decreases to its equilibrium value. The glass electrode responds to the concentration of hydrogen ions and the mercury electrode to the concentration of mercurous ions. After each generation increment an excess of mercurous ions is observed to decrease slowly to the equilibrium value. At the same time the hydrogen ion concentration increases from its former value slowly to the equilibrium value for the reaction:

$$Hg_2^{++} + 2\,CH_3CO_2H = Hg_2(CH_3CO_2)_{2\,(s)} + 2\,H^+ .$$

The slow establishment of this equilibrium would account for the observed indicating electrode potential behavior. Other factors influencing the slow approach to equilibrium may include the response of the indicating electrodes and generally slower reactions in this solvent system.

Solvent system

The supporting electrolyte used for the coulometric titrations consisted of a mixture of 90-95 mole % acetic anhydride and 5-10 mole % acetic acid. This mixture was 0.1 VF in sodium perchlorate. The large amount of acetic anhydride was advantageous for several reasons. First, as pointed out by Streuli (8), many substances display stronger basic properties in acetic anhydride solvent than in acetic acid. Experiments confirmed this for potassium hydrogen phthalate, sodium acetate, and sodium fluoride. Much sharper end points were obtained in the mixed solvent than in acetic acid alone. The end points became less sharp as the concentration of acetic acid was increased; therefore, the aliquots of the acetic acid solutions of bases were restricted to a few milliliters in 90 ml of supporting electrolyte.

A second advantage of the acetic anhydride is its dielectric constant ($\epsilon = 20.5$) which is over three times that of acetic acid ($\epsilon = 6.1$). As a result the sodium perchlorate is more ionized in the mixed solvent and the conductivity of a 0.1 VF sodium perchlorate solution in acetic anhydride is greater than the conductivity of a saturated (ca. 0.6 VF) solution of sodium perchlorate in glacial acetic acid. This greater conductivity makes it simpler to maintain a constant generating current in the mixed solvent than in glacial acetic acid solvent. Some acetic acid is needed to react with the mercurous ions generated at the electrode.

It was found that the addition of sodium perchlorate to acetic acid solutions of weak bases caused such a large depression in the potential inflection at the end point that the precision with which a titration could be performed was seriously reduced. This is due to the weakly acidic nature of sodium perchlorate in acetic acid:

$$Na^+ClO_4^- + CH_3CO_2H = Na^+(CH_3CO_2)^- + H^+ClO_4^- .$$

Perchloric acid is more dissociated than is sodium acetate in acetic acid (9). In the mixed solvent, however, this undesirable effect is much less pronounced and precise titrations result.

Finally, the presence of even small amounts of water in glacial acetic acid solvent causes the end point in an acidimetric titration to be much more poorly defined. The presence of the large excess of acetic anhydride in the mixed solvent ensures that the solvent remains virtually anhydrous.

Titration procedure

Ninety milliliters of supporting electrolyte were introduced into the coulometric cell and an aliquot of the sample of base in acetic acid was added. Perchloric acid was generated until a potential inflection was observed. The amount of base present was calculated from Faraday's Law after correcting for basic impurities in the electrolyte solution.

The supporting electrolyte used for the generation of perchloric acid contained small amounts of basic impurities (ca. $2x10^{-5}$ meq. per ml). The amount of these impurities was determined for a particular batch of electrolyte solution and corrections were made in the calculations of results of coulometric-acidimetric titrations of bases.

Results

Table I-1 summarizes the results obtained for titrations of standard solutions of potassium hydrogen phthalate and sodium acetate.

Table I-1

Results of coulometric-acidimetric titrations of standard solutions of potassium hydrogen phthalate and sodium acetate.

Base taken µeq.	Number of titrations	Base found µeq. and av. dev.	% error
Potassium Hydrogen phthalate - amalgam electrode			
18.73	7	18.72 ± 0.01	-0.06
37.08	4	37.08 ± 0.02	0.00
92.91	3	92.88 ± 0.03	-0.03
Sodium acetate - amalgam electrode			
0.316	4	0.312 ± 0.008	-1.3
0.627	3	0.634 ± 0.005	+1.1
2.81	4	2.81 ± 0.00	0.00
5.57	3	5.57 ± 0.01	0.00
13.94	3	13.94 ± 0.02	0.00
48.00	2	48.00 ± 0.02	0.00
Sodium acetate - mercury pool electrode			
48.00	3	47.98 ± 0.04	-0.04
94.95	4	94.91 ± 0.05	-0.04
237.9	3	237.9 ± 0.1	0.00
332.9	1	332.6	-0.09

The sodium acetate was prepared by dissolving sodium carbonate in acetic acid.

The maximum quantity of base that could be titrated was fixed by the fact that with quantities of base greater than about 0.3 meq. in 90 ml solvent, the time required for the titration became prohibitively long. The lower limit of the titration is about $3\text{x}10^{-4}$ meq. of base, because for smaller quantities the potential inflection at the end point became too gradual for precise determinations to be made.

Determination of fluoride

A coulometric-acidimetric titration of fluoride has been accomplished with this coulometric technique and the details of the titration are described in the following publication.

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Coulometric-Acidimetric Titration of Fluoride in Acetic Anhydride

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▶ A coulometric titration of fluoride ion has been developed in which the supporting electrolyte consists of a sodium perchlorate solution in acetic anhydride containing a small amount of acetic acid. The fluoride is titrated as a base in this solvent with an accuracy of 2 to 3 parts per thousand. Perchloric acid is generated with 100% titration efficiency at a mercury anode. The end point is detected potentiometrically. Most anions other than perchlorate display basic character in the solvent employed and are therefore titrated with the fluoride. The titration has been applied to the determination of the total base in mixtures of fluoride with sulfate, chloride, nitrate, and carbonate. In some instances two end points can be observed with binary mixtures so that analysis for each component is possible. An example is a mixture of fluoride and chloride.

A VOLUMETRIC TITRATION of fluoride ion with perchloric acid in anhydrous acetic acid has been described by Pifer and Wollish (*4*). The procedure is simple and accurate and the titration is not so sensitive to solution conditions as are the standard methods for the determination of fluoride in aqueous solutions (*2*). Recently, the authors described a procedure for the coulometric generation of perchloric acid in an acetic acid–acetic anhydride solvent (*3*). The present paper describes the application of this procedure to a coulometric titration of fluoride. This procedure offers the advantages of both coulometric and nonaqueous titrations in that no standard solutions are required, microgram to milligram quantities of fluoride can be determined accurately, and the relative basic behavior of fluoride is greatly accentuated in the solvent used so that sharp end points are obtained.

The generation of perchloric acid was accomplished, as described previously (*3*), by the electro-oxidation of a mercury electrode according to the reaction:

$$2Hg + 2CH_3COOH = Hg_2(OOCCH_3)_{2(s)} + 2H^+ + 2e \quad (1)$$

This reaction proceeds with 100% current efficiency in a supporting electrolyte consisting of sodium perchlorate dissolved in an acetic acid–acetic anhydride mixture (*3*). The mercurous acetate formed is a stable, insoluble precipitate that accumulates during the titration. The end points of the fluoride titrations were determined potentiometrically with either a glass- or mercury-indicating electrode and a mercury–mercurous acetate reference electrode (*3*). Plots of millivolts *vs.* generation time produced sharp potential inflections (Figure 1) in which the point of maximum slope was taken as the end point.

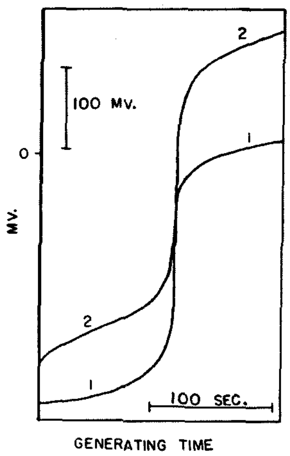

Figure 1. Potentiometric titration curve for fluoride in acetic anhydride

Curve 1: Glass-indicating electrode
Curve 2: Mercury-indicating electrode; generating current, 15.62 ma.

EXPERIMENTAL

Reagents. All chemicals were reagent grade and were used without purification except for the sodium perchlorate. The basic impurities, which were present in all batches of sodium perchlorate, were decreased to an acceptably low level by recrystallization from hot acetic acid.

The supporting electrolyte was prepared by adding 0.1 formula weight of recrystallized sodium perchlorate to 1 liter of acetic anhydride. The acetic acid for the generation of perchloric acid according to Equation 1 was introduced into the supporting electrolyte when aliquots were added of a solution prepared by dissolving sodium fluoride in acetic acid. The end points became less sharp as the concentration of acetic acid was increased; therefore, the aliquots of the acetic acid solution of sodium fluoride were restricted to a few milliliters in 90 ml. of supporting electrolyte.

Sodium fluoride solutions in acetic acid were prepared by dissolving the salt in boiling acetic acid in a Teflon beaker. The cool solution was transferred to a volumetric flask and diluted to volume. At room temperature such fluoride solutions could be stored in borosilicate glassware for several days with no loss of fluoride; but, for longer storage periods, it was necessary to store the fluoride solutions in polyethylene. Sodium fluoride solutions in acetic acid cannot be heated in borosilicate glassware without loss of fluoride.

The sodium fluoride solutions were standardized volumetrically by titration with a standard perchloric acid solution in anhydrous acetic acid. Methyl violet was used as indicator (*1*). Additional potentiometric standardizations of the fluoride solutions agreed within 2 parts per thousand with the value obtained using methyl violet as indicator.

Sodium fluoride solutions in water were also prepared. Dilute aqueous solutions of sodium fluoride could be heated for 1 to 2 hours in borosilicate glassware without loss of fluoride, but upon evaporation to dryness, reaction with the borosilicate glass beaker produced significant loss. Removal of water prior to analysis was achieved without loss of fluoride by evaporation of the solution in a Teflon beaker. The removal of the water was facilitated by the addition of a small amount of acetic acid, which caused the Teflon beaker to be wet by the solution and resulted in a more even evaporation.

Solutions of sodium chloride, sodium sulfate, and sodium nitrate in acetic acid were prepared by dissolving the salts in hot acetic acid.

Apparatus. The constant current source has been described previously as have the cell and the arrangement for potentiometric determination of the end point (*3*). The glass electrode did not appear to suffer from exposure to millimolar fluoride solution for periods of up to 6 hours. Unless otherwise indicated, a 5-sq. cm. gold foil amalgamated with mercury was used as the generating electrode.

For determination of chloride, in fluoride-chloride mixtures, a gold wire amalgamated with mercury was substituted for the glass electrode. The potential of the indicator electrode was measured with a high-impedance pH meter.

Titration of Fluoride. Ninety milliliters of supporting electrolyte were introduced into the cell and an aliquot of the fluoride sample in acetic acid was added. Perchloric acid was generated until a potential inflection was observed. The amount of fluoride present was calculated from Faraday's law after correcting for basic impurities in the electrolyte solution. Instead of the pretitration previously recommended (*3*), it has been found more convenient to determine the blank correction for the electrolyte solution in a separate titration.

In accordance with our experience in the titration of acetate and hydrogen phthalate (3), the potential of the glass electrode did not achieve a steady value in the vicinity of the end point for several minutes after the generation of perchloric acid. In the titration of a fluoride sample, it was found necessary to generate 95% of the equivalent amount of perchloric acid, to wait 5 to 10 minutes, and then to generate in small increments with a 2-minute pause after each increment to allow for the establishment of potential equilibrium. Failure to wait for final potential equilibrium caused consistently high results.

Table I. Titration of Sodium Fluoride with Electrogenerated Perchloric Acid

Fluoride Taken, μeq.	No. of Titrations	Fluoride Found, μeq., and Av. Dev.	Error, %
	Amalgamated Gold Generating Electrode		
8.895	4	8.892 ± 0.011	−0.04
17.62	5	17.63 ± 0.01	+0.06
44.10	4	44.09 ± 0.01	−0.03
88.32	3	88.17 ± 0.03	−0.17
	Mercury Pool Generating Electrode		
44.10	5	44.11 ± 0.08	+0.03
88.32	3	88.47 ± 0.02	+0.17

Table II. Assay of Reagent Grade Sodium Fluoride

Solution	Sample Taken, Mg.	No. of Titrations	Sodium Fluoride Found, Mg., and Av. Dev.	NaF, %
1	1.651	5	1.631 ± 0.002	98.79
2	2.436	5	2.420 ± 0.002	99.34
3	2.759	5	2.746 ± 0.002	99.52
4	2.835	4	2.812 ± 0.002	99.18
5	1.300	3	1.283 ± 0.000	98.69
6	2.109	5	2.091 ± 0.003	99.14
7	1.279	4	1.266 ± 0.001	98.98
8	1.655	4	1.642 ± 0.000	99.21
9	1.618	4	1.602 ± 0.000	99.01
				99.10 ± 0.20

Table III. Analyses of Aqueous Fluoride Solutions

Sodium Fluoride Taken, Mg.	No. of Titrations	Sodium Fluoride Found, Mg., and Av. Dev.	Error, %
1.425	4	1.428 ± 0.001	+0.21
1.402	5	1.402 ± 0.003	0.0
1.442	4	1.445 ± 0.002	+0.21
1.508	4	1.511 ± 0.003	+0.20

RESULTS

Table I shows the results obtained in the titration of aliquots of a standard sodium fluoride solution in acetic acid.

The quantities of fluoride in Table I are representative of typical titrations but do not indicate the entire concentration range over which the coulometric titration is applicable. Experiments have shown that as little as 0.3 μeq. or as much as 0.3 meq. of base can be titrated with no significant decrease in accuracy.

Several solutions were prepared by dissolving weighed amounts of dried reagent grade sodium fluoride (4 hours at 130°C.) in acetic acid in a Teflon beaker and diluting to a known volume with acetic acid. Aliquots of such solutions were analyzed coulometrically for fluoride. The percentages of titratable base (reported as sodium fluoride) determined for several such solutions are shown in Table II.

Analysis of Aqueous Fluoride Solutions. In order to establish the possible usefulness of this titration for the analysis of aqueous fluoride solutions, experiments were performed to determine how readily aqueous solutions of fluoride could be converted to acetic anhydride solutions. Aliquots of standard aqueous solutions of sodium fluoride having pH values between 6 and 7 were evaporated to dryness in Teflon beakers. The solid residue was dissolved in 1 to 2 ml. of acetic acid, electrolyte solution was added, and perchloric acid was generated to the potentiometric end point. The results of these analyses are shown in Table III.

Determination of Fluoride in Excess Carbonate. The possibility of extending this titration to the determination of fluoride in organic *fluorine-containing compounds* such as fluorocarbons, led us to investigate the feasibility of determining fluoride in solutions, such as would result from the fusion of a fluorocarbon with sodium peroxide. The dissolution of the sodium peroxide melt in water would produce a solution containing large amounts of sodium hydroxide and sodium carbonate, some unreacted peroxide, and sodium fluoride. In order to determine the fluoride, it is necessary to exchange perchlorate for all the other anions and then to remove the water.

Experiments with mixtures of sodium carbonate and sodium fluoride have shown that the following procedure accomplishes the complete removal of up to two hundred times as much carbonate without significant loss of fluoride:

> The solid mixture corresponding to a fusion melt was dissolved in the minimum quantity of water, usually about 5 ml. The solution was carefully acidified with 1*F* $HClO_4$ until the pH reached 4.3 to 4.0. The acid solution was heated to about 80° C. on a hot plate and swirled for 4 to 5 minutes to remove carbon dioxide. After cooling, the solution was neutralized to pH 7.2 to 7.7 with carbonate-free sodium hydroxide. This solution was evaporated to dryness and the residue was dissolved by adding 1 to 2 ml. of acetic acid and heating. The resulting solution was analyzed for fluoride by the coulometric procedure. Analyses of samples of known fluoride content according to this procedure were accurate to 4 to 5 parts per thousand.

Table IV. Analyses of Fluoride-Chloride Mixtures

Taken, μeq.			No. of Titrations	Base Found, μeq., and Av. Dev.			Error, %		
Chloride	Fluoride	Total		Chloride	Fluoride	Total	Chloride	Fluoride	Total
15.89	9.95	25.84	3	15.94 ± 0.00	9.90	25.84 ± 0.12	+0.31	−0.5	0
23.89	9.95	33.84	2	23.88 ± 0.07	9.88	33.76 ± 0.01	−0.05	−0.7	−0.24
39.77	9.95	49.72	3	39.87 ± 0.04	9.78	49.65 ± 0.02	+0.25	−1.1	−0.14
23.89	19.82	43.71	2	24.03 ± 0.00	19.72	43.75 ± 0.04	+0.59	−0.5	+0.01
39.77	19.82	59.59	2	39.99 ± 0.04	19.57	59.56 ± 0.06	+0.55	−1.3	−0.06
15.89	49.60	65.49	1	16.47	48.67	65.14	+3.66	−1.9	−0.53

It is important to carry out the evaporation of the aqueous fluoride solution in a Teflon (or equally nonreactive) vessel. Evaporation in borosilicate glass beakers leads to consistently low results, which are surprisingly reproducible.

In an actual analysis of a fusion melt, in which large amounts of hydroxide or peroxide would be present, the entire treatment of the fusion melt must be carried out in a nonreactive vessel or else the introduction of silicate into the solution causes large positive errors.

INTERFERENCES

Because almost every anion except perchlorate displays some basic character in acetic acid–acetic anhydride solutions, most anions interfere in the titration and either must be removed or exchanged for perchlorate. In some cases more than one end point can be observed with fluoride solutions containing another basic anion. This is true, for example, with mixtures of chloride and fluoride.

Mixtures of chloride and fluoride display only a single, potential inflection when a glass electrode is used to detect the end point (Figure 2, curve 2); however, if a mercury indicating electrode is substituted for the glass electrode, two distinct potential inflections are obtained corresponding to the chloride and fluoride present as shown in Figure 2, curve 1. Up to the first potential inflection the indicating electrode is functioning as a Hg-Hg_2Cl_2 electrode that responds to the concentration of chloride ion. Subsequently, the electrode functions as a Hg-$Hg_2(CH_3COO)_2$ electrode that responds to the concentration of acetate ion and, therefore, to the concentrations of fluoride ion and perchloric acid. For the titration of pure fluoride solutions this electrode offers no advantages over the glass electrode, but it has obvious usefulness for analyses of mixtures of anions in which one or more of the anions form mercurous salts that are less soluble than mercurous acetate.

The results of determinations of various mixtures of sodium chloride and sodium fluoride are given in Table IV.

The error in the determination of the mixture increases as the fluoride concentration increases; the error in the total base remains relatively constant and small (Table IV). The cause of the dependence of the errors on fluoride concentration is due to the small difference in the solubility products of mercurous chloride and mercurous acetate in acetic anhydride. As the fluoride (and therefore the acetate) concentration is increased, the two potential inflections overlap. This effect is similar to the effect that is observed when aqueous solutions of bromide and iodide are titrating potentiometrically with silver ion and a silver-indicating electrode.

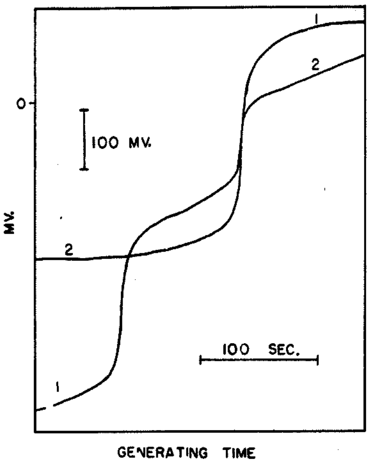

Figure 2. Potentiometric titration curve for a fluoride-chloride mixture

Curve 1: Mercury-indicating electrode
Curve 2: Glass-indicating electrode; generating current, 15.62 ma.

For roughly equivalent concentrations of chloride and fluoride in a mixture, both components may be accurately determined with the use of the mercury-indicating electrode. The end point corresponding to total base can be observed with either the glass- or mercury-indicating electrode as demonstrated in Figure 2.

In most instances only the sum of anions present in a sample can be determined. This is especially true when the solubility products of the mercurous salts formed are relatively close together; thus, the sum of fluoride and nitrate and fluoride and sulfate in binary mixtures can be determined with an accuracy of 2 to 3 parts per thousand by following the procedure designed for fluoride. These experiments indicate that coulometric-acidimetric titrations for nitrate and for sulfate could be carried out with accuracies as good as those achieved for fluoride.

In the case of sulfate, 2 faradays are required for the titration of each mole of sulfate, and it is likely that the titration reaction is

$$Hg_2^{+2} + SO_4^{-2} = Hg_2SO_{4(s)}$$

Coulometric-acidimetric titrations in acetic acid–acetic anhydride solvents should facilitate the analysis of small amounts of weak bases. The present procedure would be somewhat more convenient if the generation of acid could be accomplished with 100% titration efficiency at a platinum electrode by the oxidation of acetic acid or some other suitable substance. Current efficiencies of up to 95% have been obtained for the generation of perchloric acid by anodic generation at a platinum electrode in acetic anhydride–acetic acid solution. The reactions that take place at a platinum anode are at present being studied in an effort to account for this lower current efficiency and improve it.

ACKNOWLEDGMENT

Appreciation is expressed to the National Science Foundation for a fellowship held by W. B. M.

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Extensions of the titration

In principle, the method of coulometric generation of perchloric acid should be applicable to the determination of many of the basic substances which are titratable volumetrically in acetic acid. Examples investigated, namely, sodium acetate, potassium hydrogen phthalate, sodium fluoride, sodium chloride, sodium nitrate, and sodium sulfate have shown this statement to be true. Organic bases, too, can be determined by this technique. Exceptions would include those substances, [illegible], which would react with acetic anhydride to form non-basic products. This technique should be applicable to the determination of some amides which are relatively strong bases in acetic anhydride (7).

The coulometric generation of perchloric acid in acetic acid-acetic anhydride mixtures would be more convenient and more straightforward if the mercury anode could be replaced by a platinum generating anode. The oxidation of acetic acid at a platinum anode would provide a means for generating hydrogen ions with 100% current efficiency if the reaction were (b) or (c). (See page 7.) In the coulometric titration of samples of inorganic bases with the products of electrolyte oxidation, less than 100% efficiency for the generation of perchloric acid was observed.

The side reactions responsible for this apparent loss of perchloric acid have been studied. This study is the subject of part II of this thesis.

PART II

STUDIES AT A PLATINUM ELECTRODE IN ACETIC ACID-ACETIC ANHYDRIDE SOLUTIONS

Introduction

As mentioned in part I of this thesis, early attempts to generate perchloric acid at a platinum electrode resulted in less than 100% efficiency. This result was unexpected, as the electro-oxidation of most simple organic compounds yields one hydrogen ion per electron. One hundred percent current efficiency was expected for the generation of hydrogen ions from such oxidations.

An investigation of reactions occurring at and around the platinum electrodes, both anode and cathode, in acetic anhydride solutions was undertaken in an effort to explain this loss of hydrogen ions.

Experimental techniques

The following experimental techniques were employed:

1) Coulometric titrations: A platinum electrode (5 cm^2 platinum foil) was substituted for the mercury generating electrode used in the coulometric titrations described in part I of this thesis. This platinum electrode was used either as the anode or as the cathode in various coulometric-acidimetric titrations. Coulometric procedures were essentially those described in part I. All solutions were stirred at all times unless otherwise stated.

The coulometric efficiency for the generation of hydrogen ions was determined by generating anodically (oxidizing the electrolyte solution) for a known time interval and back-titrating the hydrogen ions formed with electrogenerated acetate ion. The acetate ion was generated by reducing acetic acid present in the electrolyte solution. The course of the back-titration was followed by means of the glass electrode-reference electrode pair described in part I of this thesis. The end point was taken as the point of maximum slope of the potential vs. generating time curve. The ratio of equivalents of hydrogen ions found in the back-titration to coulombs of electricity involved in the anodic generation of the hydrogen ions is the generation efficiency of hydrogen ions.

2) Observations of color formation: The reaction of perchloric acid with acetic anhydride gave brightly colored solutions. Ultraviolet spectra of such solutions showed a strong absorption maximum at 282 mμ and a long tail into the visible region. The increase of this absorption maximum with time was followed with a Beckman DU Spectrophotometer. In other instances visual color changes were observed.

3) Volumetric and gravimetric studies: The reaction of perchloric acid with acetic anhydride was followed by titrating aliquots of the reaction mixture in acetic anhydride-acetic acid (10 mole %) with standard base. A glass electrode-reference electrode pair was used to determine the end point of the titration.

The reaction of perchloric acid with acetic anhydride was also studied by analyzing aliquots for perchlorate at various time intervals. Excess potassium acetate in acetic acid was added to precipitate the sparingly soluble potassium perchlorate. This precipitate was washed once with acetic acid, dried (120°C) and weighed.

4) Chronopotentiometric studies: Observing the potential of a working electrode, through which a constant current is passed, with respect to a reference electrode as a function of time is chronopotentiometry (10,11).

Two important quantities are determined in chronopotentiometry. The first is the quarter-wave potential which is characteristic of a particular electrode reaction, for reversible reactions. For irreversible electrode reactions the quarter-wave potential may be used to identify an electrode reaction under suitable conditions. (Studies should be performed at constant current density and with similar solution conditions, namely, concentration of electroactive species, solvent composition and ionic strength.) The second important quantity is the transition time (the time at which the concentration of electroactive species at the electrode surface drops to zero) which depends on the concentration of the electroactive species, for a diffusion controlled electrode process.

In chronopotentiometry electrode reactions may be studied by producing the electroactive species directly at the electrode. By reversing the current, this species can be studied in much the same manner as if it had been introduced externally. This technique permits the study of unstable products of electrode reactions.

In this thesis chronopotentiometry was used in a qualitative manner to identify electrode reactions by their characteristic potentials and to follow relative concentrations by changes in transition times. The procedure followed in the chronopotentiometric studies was standard (10, 11, 12).

All solutions were deaerated with nitrogen before study. All measurements were made in unstirred solutions.

Experimental - Reagents and Chemicals

As in part I of this thesis, except for the sodium perchlorate, all chemicals used were commercial products of the highest purity and were used without further purification.

All batches of sodium perchlorate tested contained significant impurities. One recrystallization from boiling acetic acid reduced these impurities to an acceptably low level. The recrystallized sodium perchlorate contained acetic acid of crystallization which was removed by heating to 150° C.

Two brands of acetic anhydride were used. Acetic anhydride from the General Chemical Division of Allied Chemical and Dye

Corporation contained traces of acetone as well as several percent (by volume) acetic acid. This analysis was made by vapor phase chromatography on a Perkin Elmer Vapor Fractometer, Model 154, using an all-purpose column of diisodecyl phthalate on diatomaceous earth at 100°C. Potentiometric end points of acidimetric titrations in this acetic anhydride were considerably poorer than in acetic anhydride from J. T. Baker Chemical Company. Vapor phase chromatographic analysis showed that J. T. Baker Company acetic anhydride contained no acetone and only a trace of acetic acid. Most experiments were performed in the latter brand of acetic anhydride.

Various mixtures of acetic acid and acetic anhydride were used to prepare supporting electrolyte solutions used in the study of electrode reactions in these solvents. The compositions of the following electrolyte solutions, referred to in part II, are:

acetic anhydride electrolyte: 0.1 VF sodium perchlorate and 0.05-0.2 VF acetic acid in acetic anhydride solvent;

acetic acid-acetic anhydride electrolyte: 0.1-0.6 VF sodium perchlorate (the concentration of the sodium perchlorate was adjusted between these limits to keep the conductivity of the electrolyte solution as constant as possible) in a mixed solvent of acetic acid and acetic anhydride (the acetic acid given as mole %).

The concentrated perchloric acid (60% by weight) contains 3.7 moles of water per mole of perchloric acid. When concentrated perchloric acid is added to acetic anhydride, there is a reaction between the water present in the perchloric acid and the acetic anhydride to form acetic acid.

Solutions of acetylium perchlorate were prepared by adding silver perchlorate to excess acetyl chloride in acetic anhydride and filtering off the silver chloride precipitate. Such solutions were used immediately after preparation.

Experimental - Equipment (chronopotentiometric studies)

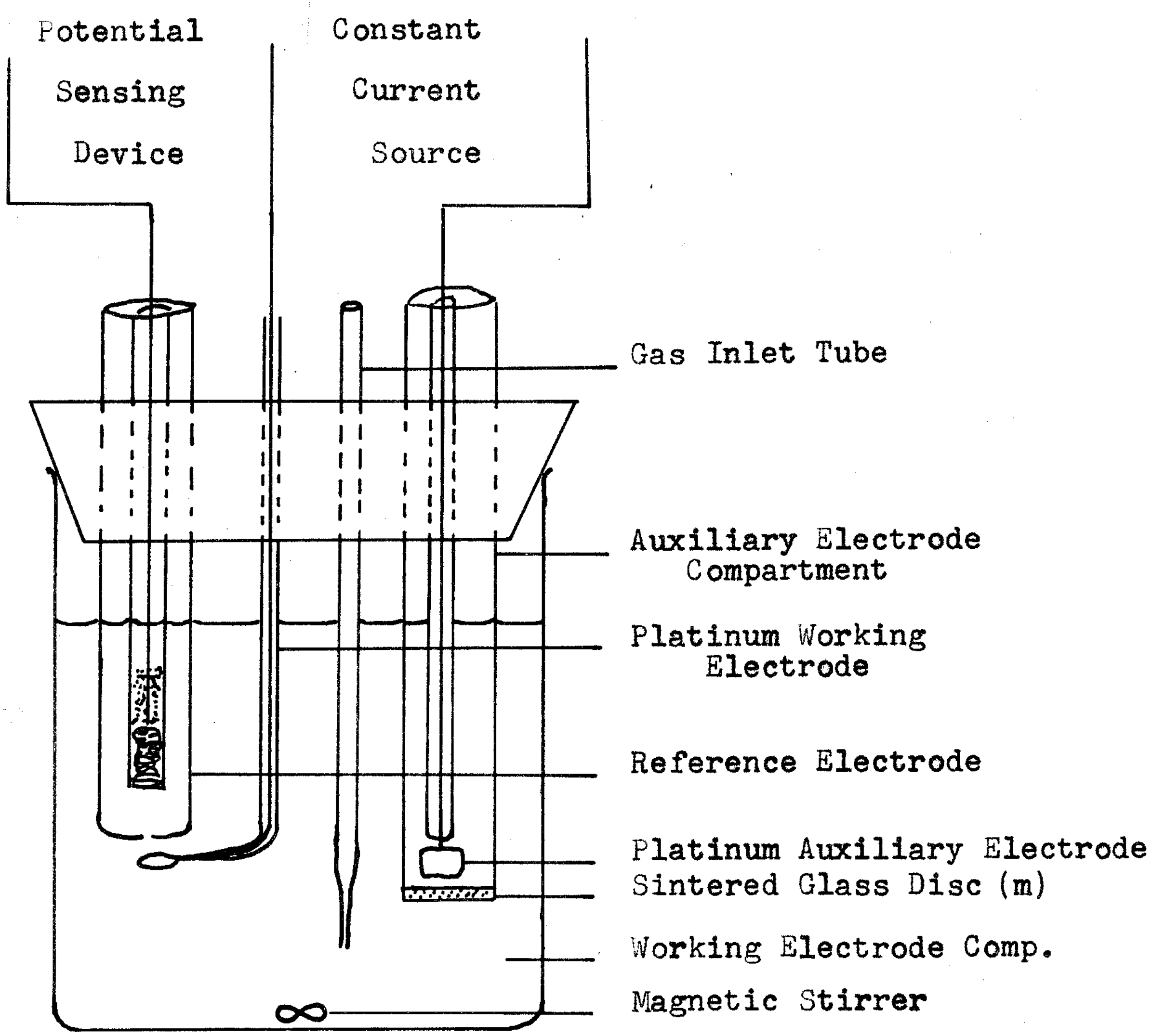
The chronopotentiometric equipment was conventional (12). Electrolysis current was supplied by a bank of four 45 volt dry batteries connected in series. A series of fixed resistances was inserted in the circuit in such a way that currents from 10^{-2} to 10^{-6} amp could be obtained. Current values were calibrated, while electrolysis was in progress by measuring the potential drop across a standard resistance by means of a potentiometer.

The changing potential of the working electrode vs. the reference electrode was followed during electrolysis by means of a Moseley Autograph X-Y recorder. The plot of potential vs. time is referred to as a chronopotentiogram. The potential of the working electrode-reference electrode couple was fed through a follower amplifier to the recorder to limit the current flow between reference and working electrodes (to prevent polarization of the reference electrode).

The chronopotentiometric cell is shown in Fig. II-1. The working electrode and auxiliary electrode were of platinum foil and the two cell compartments were separated by a sintered glass disc. The reference electrode (ref.) was the same as described in part I of this thesis.

A bright platinum foil in the shape of a flat disc, 0.2 cm^2 in area (one side), was used as the working electrode. This electrode was mounted horizontally in the solution directly below the reference electrode to limit the effects of the high iR potential in the cell. The potentials reported are not corrected for these iR effects or for any junction potentials which may appear between the reference electrode and the bulk of solution.

No special efforts were made to condition the working electrode before electrolysis. The platinum electrode was oxidized at about + 2 V vs. ref. (pH dependent) with the formation of a thin film which was reduced at about 0 V vs. ref. (also pH dependent). In studies of a particular electrode reaction, with different methods of forming the electroactive species, the same electrode surface (oxidized or reduced) was used. For example, in the studies of the oxidation of acetate ion



CHRONOPOTENTIOMETRIC CELL

FIG. II - 1

formed (a) in the reduction of acetic acid and (b) in a solution of sodium acetate, a reduced platinum electrode was employed.

Cathode Reaction

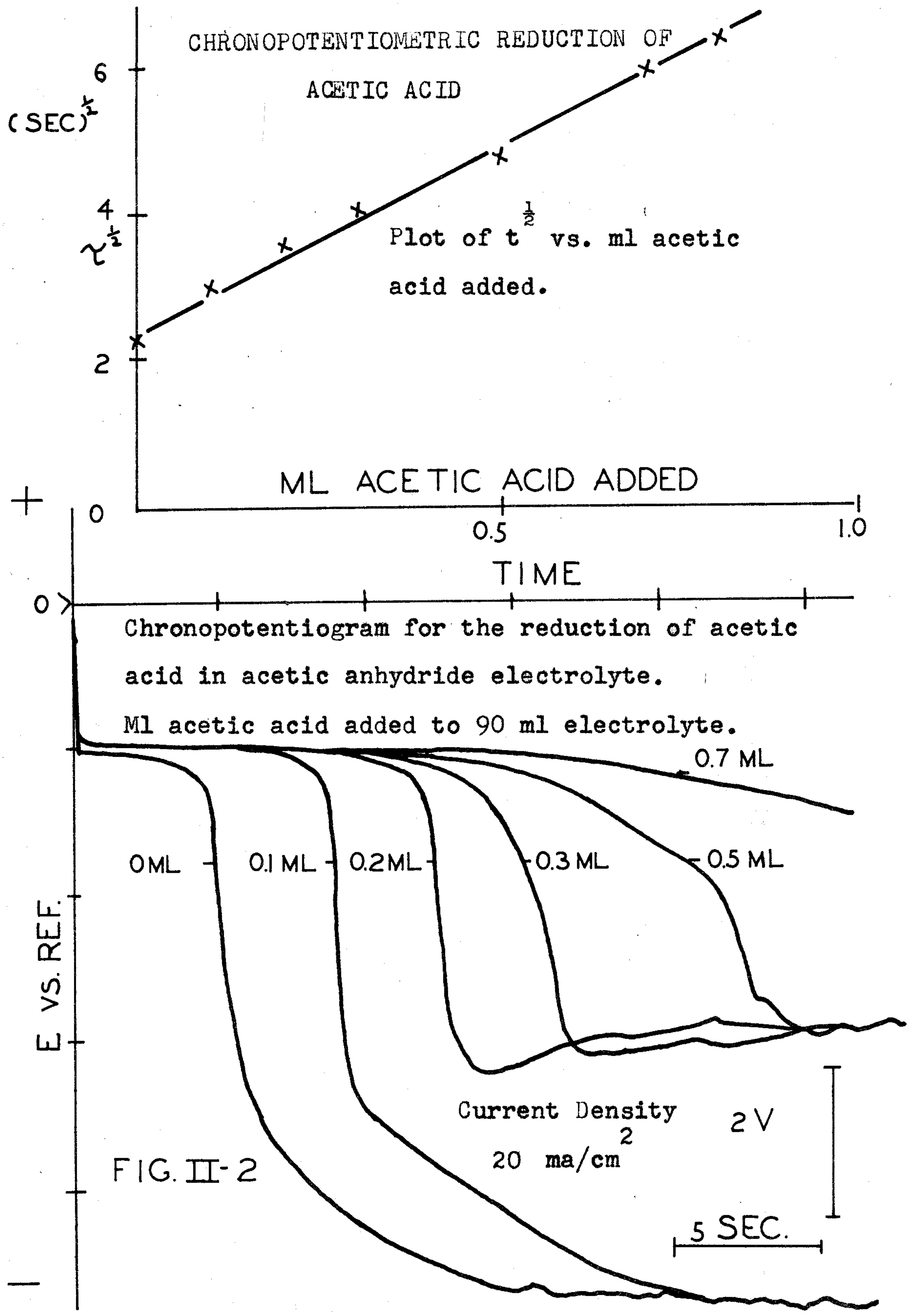
The most reasonable reaction for the reduction of acetic acid at a platinum electrode in acetic acid-acetic anhydride electrolyte is the following:

$$CH_3CO_2H + e^- = 1/2\ H_2 + CH_3CO_2^- \ .$$

The verification of the above reaction provides an interesting introduction to the application of chronopotentiometric techniques to the study of electrochemical reactions.

In the acetic anhydride electrolyte it is the acetic acid which is first reduced. This is seen in Fig. II-2. As the concentration of acetic acid was increased, the transition time (τ) for its reduction increased. A plot of $\tau^{1/2}$ vs. concentration of acetic acid is linear, as it should be for a diffusion controlled electrode reaction (10). Extrapolation to zero transition time determines the residual concentration of acetic acid in the acetic anhydride electrolyte. The concentration of acetic acid in acetic anhydride (J. T. Baker Co.) was found to be 0.08 VF (or 0.5% by volume).

A solution of acetic acid in acetic anhydride electrolyte was reduced for given time intervals after which the current was reversed.



Plot of $t^{\frac{1}{2}}$ vs. ml acetic acid added.

Chronopotentiogram for the reduction of acetic acid in acetic anhydride electrolyte.

Ml acetic acid added to 90 ml electrolyte.

Current Density

20 ma/cm^2

FIG. II-2

The resulting oxidation chronopotentiogram exhibits two transition times (Fig. II-3). The first potential pause occurs at -0.8 V vs. ref., the second occurs at +1.5 V vs. ref.

To identify these potential pauses it is useful to compare Figure II-3 with chronopotentiograms of the oxidation of hydrogen gas and acetate ion. Figure II-4 shows the oxidation of sodium acetate in acetic electrolyte. The potential pause is at +1.5 V vs. ref. The second potential pause in the oxidation of the reduction products of acetic acid is the oxidation of acetate.

Figure II-5 shows the chronopotentiogram of the oxidation of a saturated solution of hydrogen gas in acetic anhydride electrolyte. The potential pause is at 0.0 V vs. ref., considerably different from the oxidation potential pauses of reduced acetic acid solutions in acetic anhydride electrolyte (Fig. II-3).

Reduced solutions of acetic acid in acetic anhydride, saturated with hydrogen, were oxidized (Fig. II-6). Two potential pauses are observed, but neither appears to be due to the oxidation of acetate. The first pause, at -0.8 V vs. ref., is the same as encountered in Figure II-3. The second pause, at 0.0 V vs. ref., is the oxidation of hydrogen gas.

When a solution of perchloric acid in acetic acid was reduced and then oxidized (the transition time for the reduction of the perchloric acid being greater than the reduction time), the resulting

Chronopotentiogram for the oxidation of a reduced solution of acetic acid in acetic anhydride electrolyte.

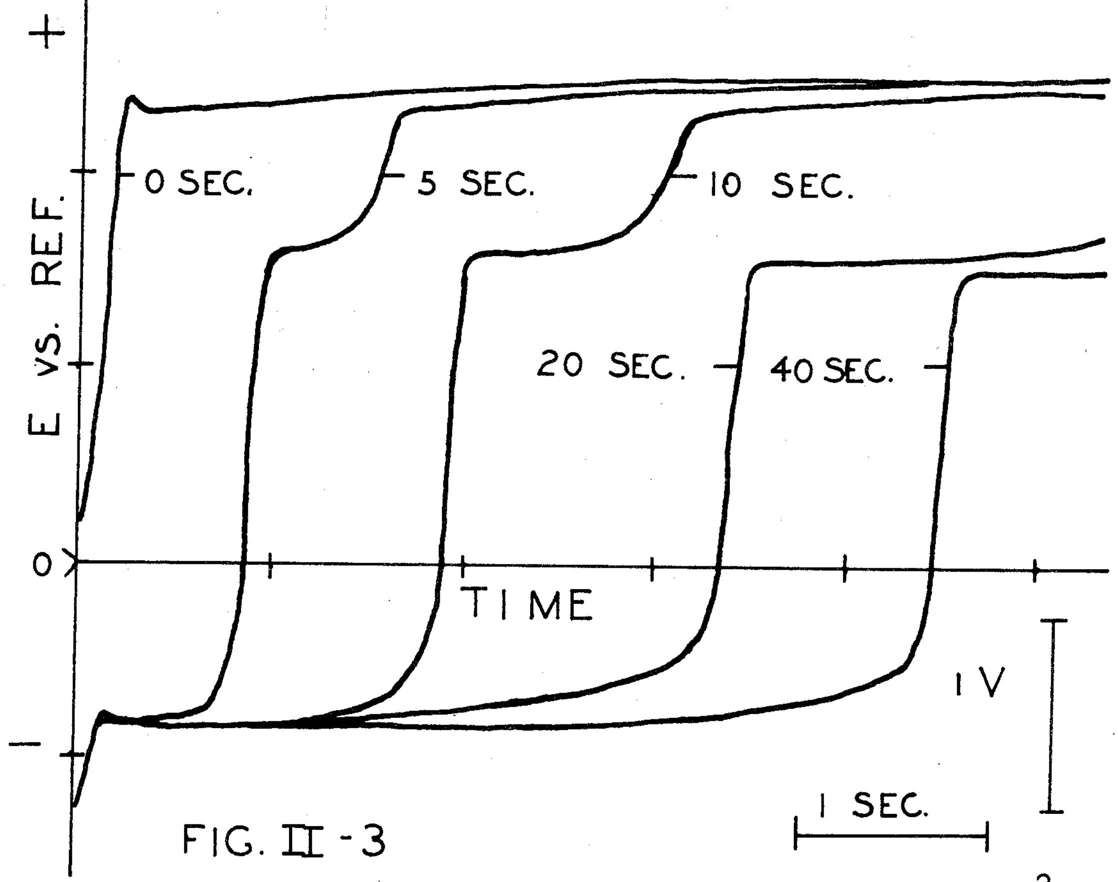


FIG. II-3

Current Density: 4 ma/cm^2

Reduction time (in seconds) before current reversal given with the curves.

Potential pauses at -0.8 V vs. ref. and 1.5 V vs. ref.

0.2 VF acetic acid in 90 ml acetic anhydride electrolyte.

Chronopotentiogram for the oxidation
of acetate in acetic anhydride
electrolyte.

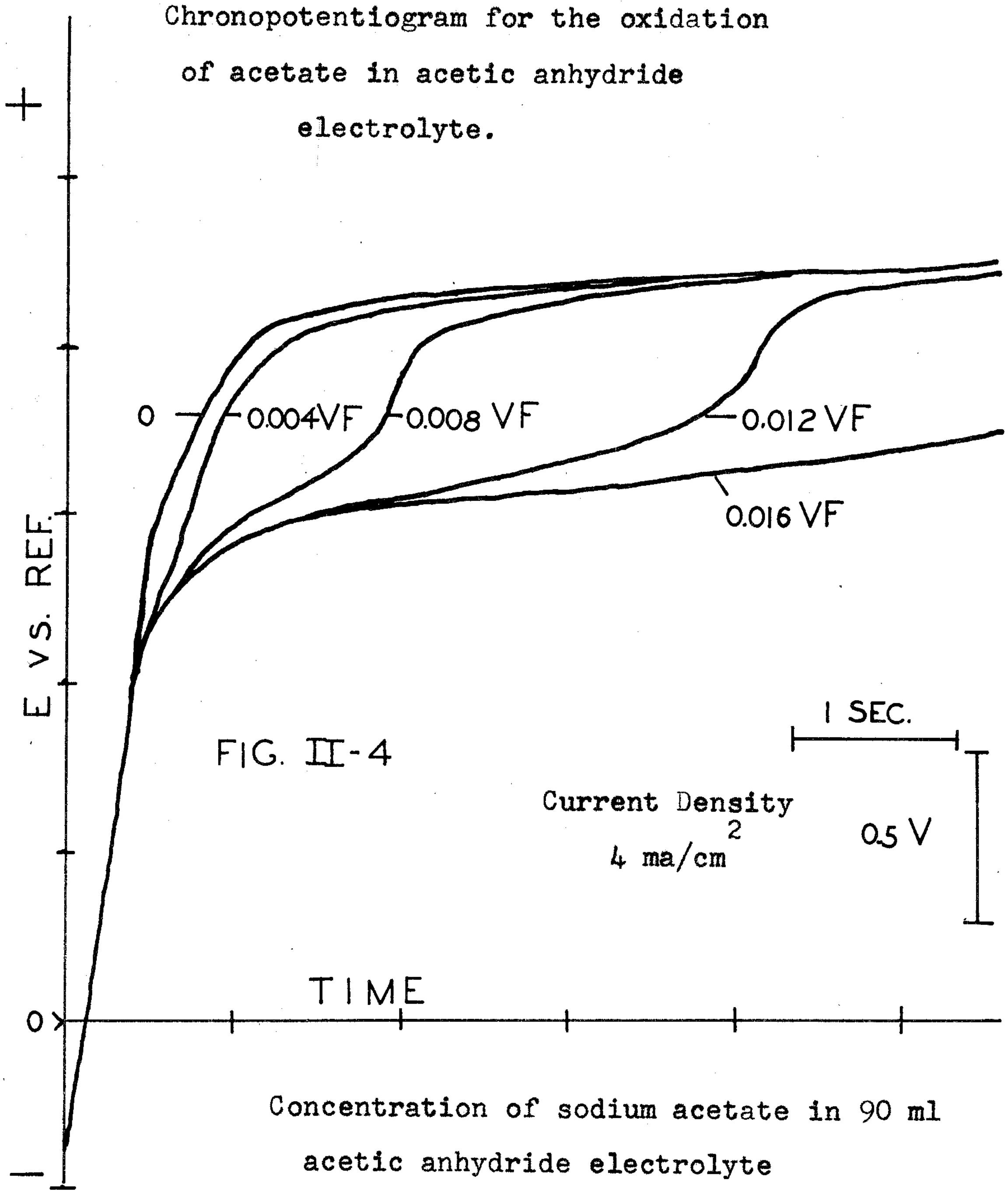


FIG. II-4

Current Density
4 ma/cm^2

Concentration of sodium acetate in 90 ml
acetic anhydride electrolyte
given with the curves.
Potential Pause at 1.5 V vs. ref.

Chronopotentiogram for the oxidation of hydrogen gas in acetic anhydride electrolyte.

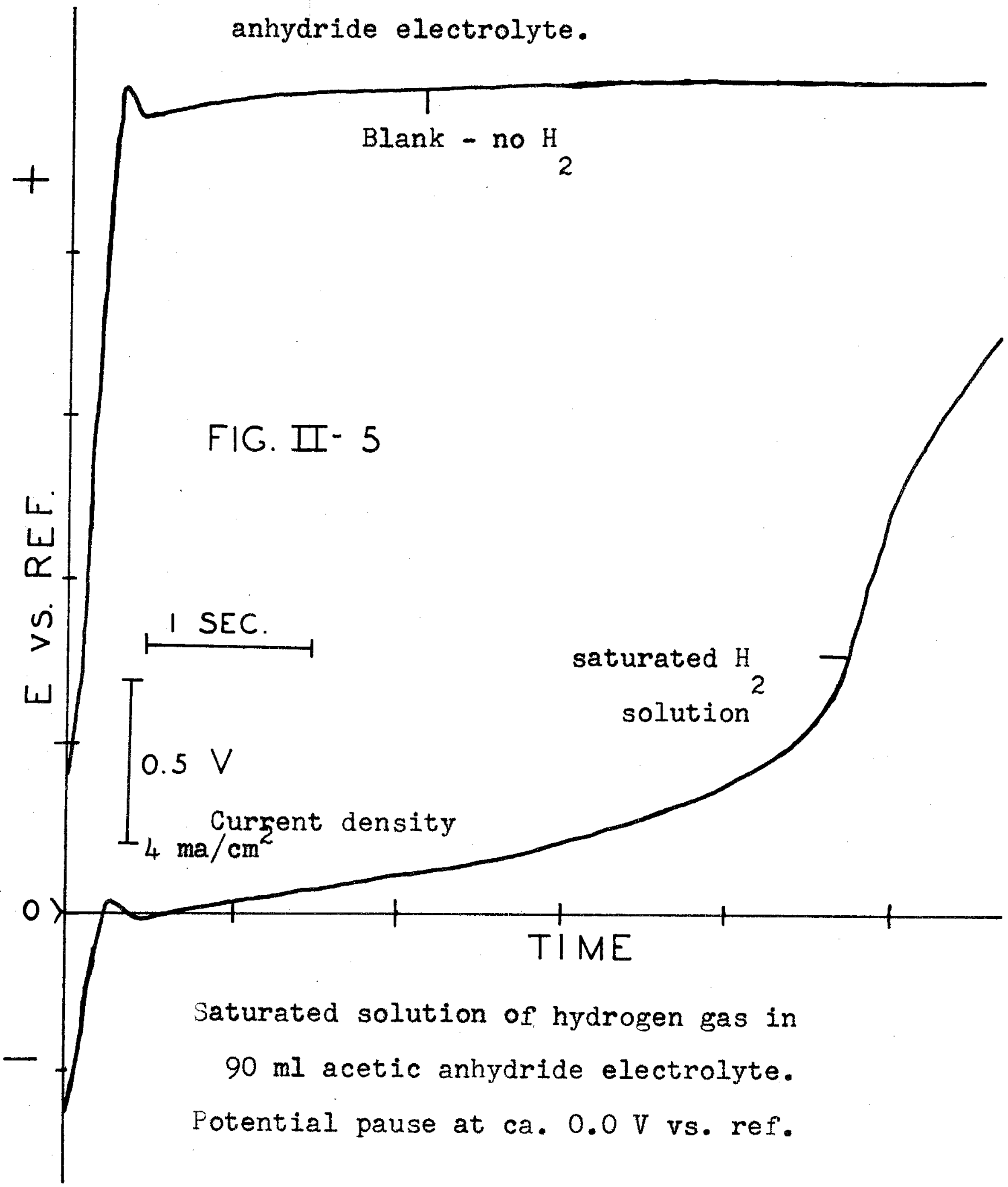


FIG. II- 5

Saturated solution of hydrogen gas in 90 ml acetic anhydride electrolyte. Potential pause at ca. 0.0 V vs. ref.

Chronopotentiogram for the oxidation of a reduced solution of hydrogen gas and acetic acid in acetic anhydride electrolyte.

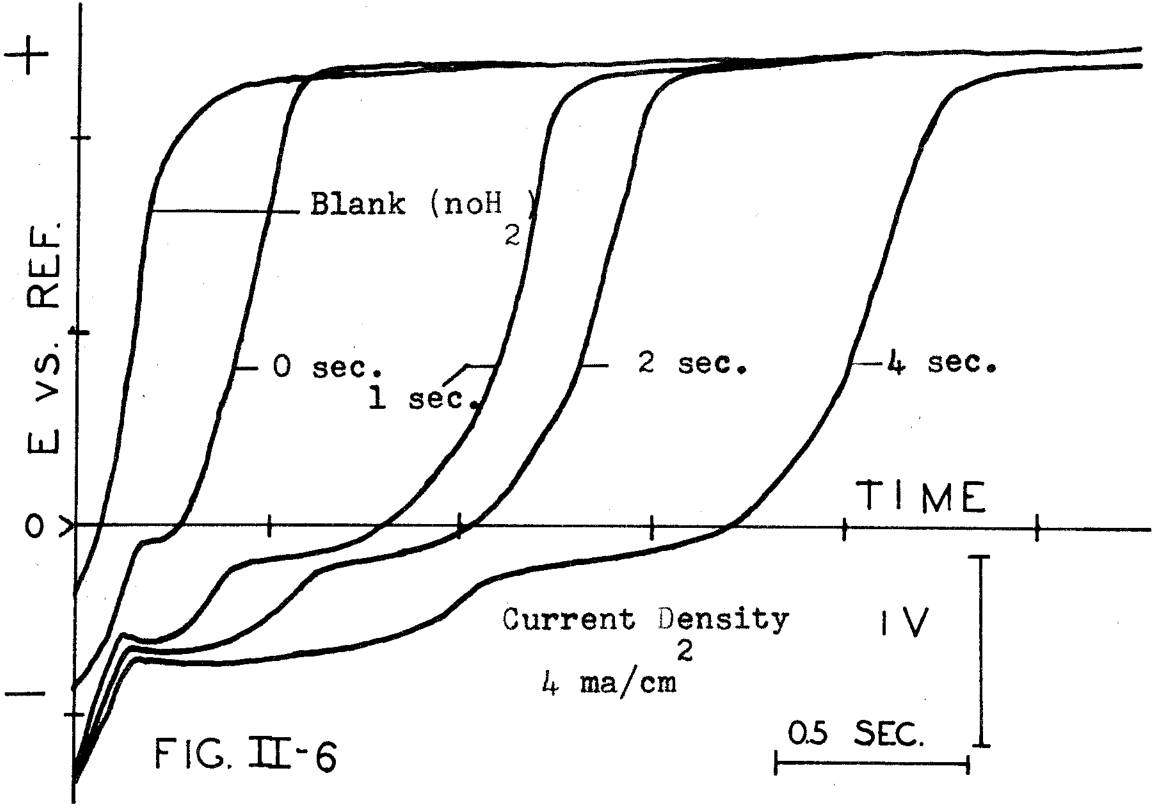


FIG. II-6

Reduction time (in seconds) before current reversal given with the curves.

Potential pauses at -0.8 V vs. ref. and ca. 0.0 V vs. ref.

0.2 VF acetic acid in 90 ml acetic anhydride electrolyte, partially saturated with hydrogen gas.

oxidation chronopotentiogram (Fig. II-7) exhibits one potential pause at 0.0 V vs. ref., the same potential as the oxidation of hydrogen gas in acetic anhydride. The electro-oxidation reaction at this potential is:

$$\frac{1}{2}H_2 + ClO_4^- = H^+ ClO_4^- + e^-.$$

In solutions of acetic anhydride electrolyte, containing acetate ion, hydrogen gas is oxidized at -0.8 V vs. ref.

$$\frac{1}{2}H_2 + CH_3CO_2^- = CH_3CO_2H + e^-.$$

In neutral or acidic solutions hydrogen gas is oxidized to perchloric acid at 0.0 V vs. ref.

$$\frac{1}{2}H_2 + ClO_4^- = HClO_4 + e^- .$$

Acetate ion is oxidized at 1.5 V vs. ref.

$$CH_3CO_2^- \longrightarrow \frac{1}{2}C_2H_6 + CO_2 + e^- \qquad (13) .$$

When a solution of acetic acid in acetic anhydride electrolyte is reduced and then the current reversed, the two oxidation potential pauses observed (Fig. II-3) correspond to the oxidation of hydrogen gas, in the presence of excess acetate ion, to acetic acid

$$\frac{1}{2}H_2 + CH_3CO_2^- = CH_3CO_2H + e^- \quad \text{at -0.8 V vs. ref.,}$$

and to the oxidation of acetate ion

$$CH_3CO_2^- \longrightarrow \frac{1}{2}C_2H_6 + CO_2 + e^- \quad \text{at 1.5 V vs. ref.}$$

Acetic acid is reduced to acetate and hydrogen gas at a platinum cathode in acetic anhydride electrolyte. Hydrogen gas has limited solubility in acetic ahydride. Some hydrogen gas formed in the reduction escapes from the solution before it can be reoxidized, leaving an excess of acetate near the electrode. Were it not for this loss of

Chronopotentiogram for the oxidation of a reduced solution of perchloric acid in acetic anhydride electrolyte.

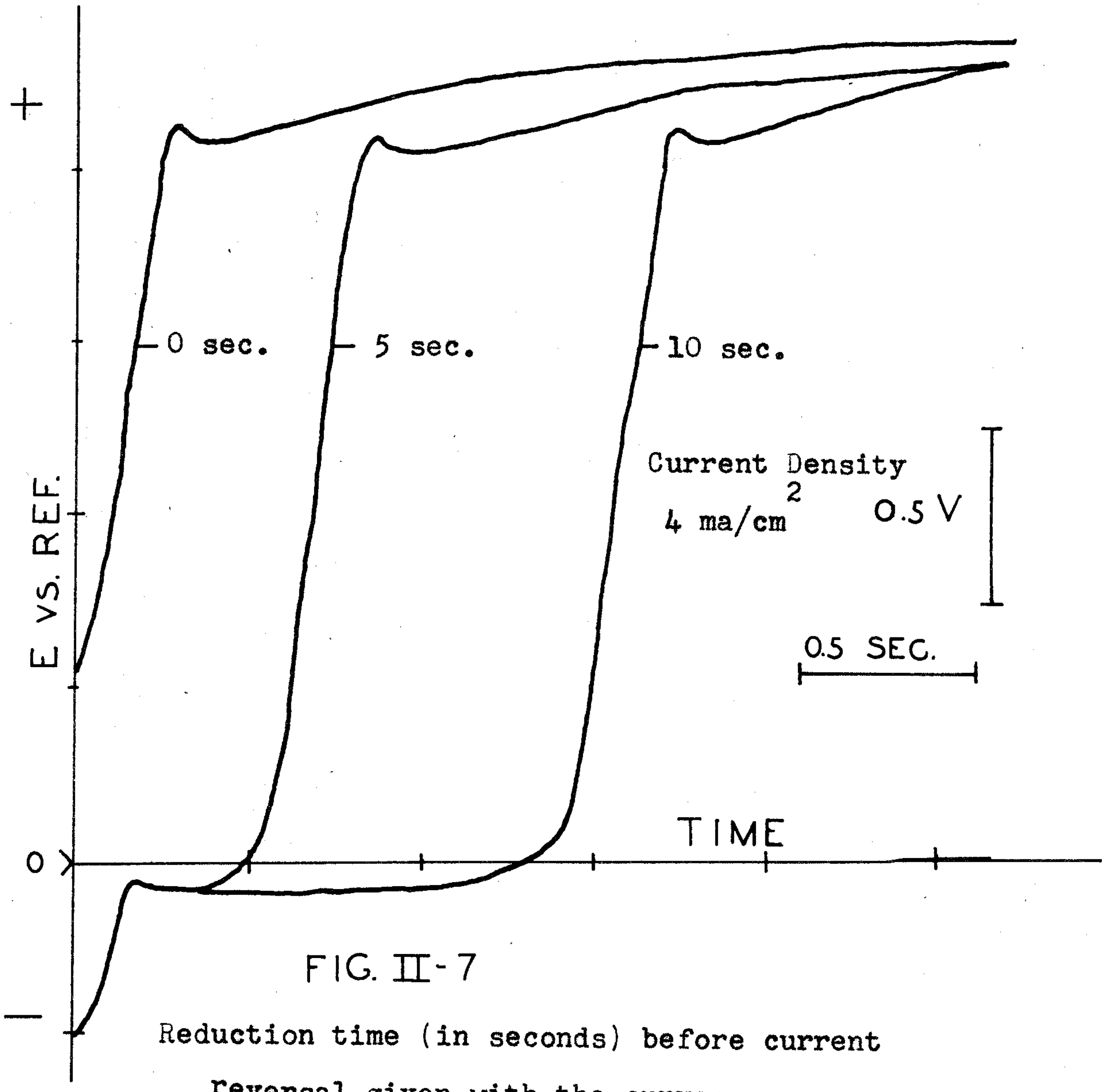


FIG. II-7

Reduction time (in seconds) before current reversal given with the curves.

Potential pause at ca. 0.0 V vs. ref.

0.1 VF perchloric acid in 90 ml acetic anhydride electrolyte.

Curves taken within 30 min. of mixing solution.

hydrogen gas the only reaction expected for the oxidation of the reduction products of acetic acid would be:

$$\frac{1}{2}H_2 + CH_3CO_2^- = CH_3CO_2H + e^- \qquad \text{at -0.8 V vs. ref.}$$

This study has shown that two of the products of the reduction of acetic acid in acetic anhydride electrolyte are hydrogen gas and acetate ion. It has not been shown that these are the only products of the reduction, but that these are the only products which appear to be oxidized. Since all other reduction products of acetic acid (acetaldehyde and ethanol) should be rather easily oxidized, it is assumed that hydrogen gas and acetate ion are the only products of the reduction.

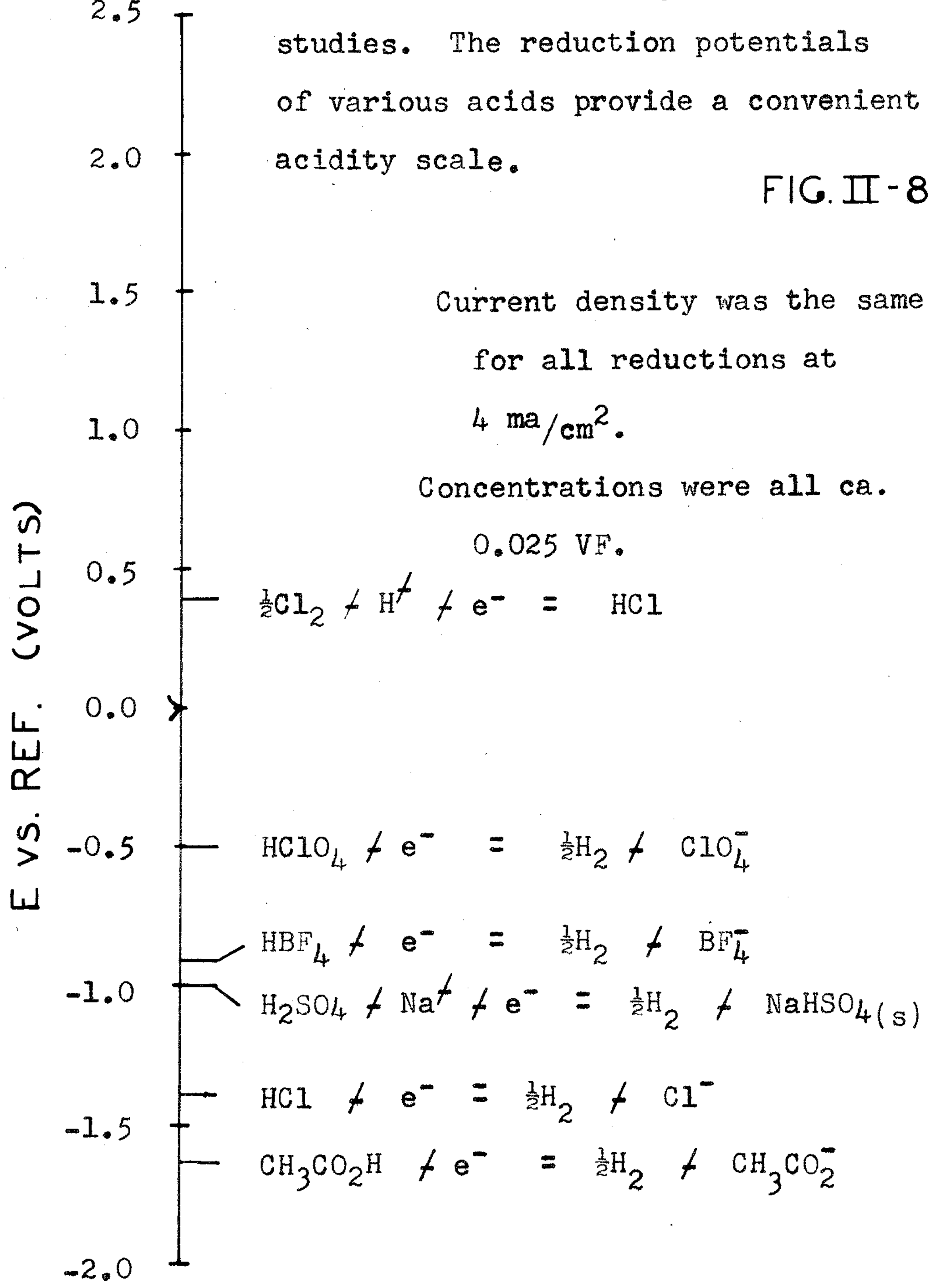
A potential scale for oxidations and reductions at a platinum electrode can be established for the acetic anhydride electrolyte from observations of the potentials of various electrode reactions. Such a potential scale is shown in Figure II-8 and 9. No attempt was made to correct oxidation and reduction scales for liquid junction potentials or cell resistance effects. For these observations of potentials of electrochemical reactions in the acetic anhydride electrolyte, the current density was kept constant so that effects of liquid junction potentials and cell resistance were constant. The reduction scale provides a convenient acidity scale. The potential of the reduction of an acid depends on the dissociation of the acid. The following acids decrease in acidity in this solvent:

Potential scale for reductions at a platinum electrode in acetic anhydride electrolyte from observations of the potentials of electrode reactions in chronopotentiometric studies. The reduction potentials of various acids provide a convenient acidity scale.

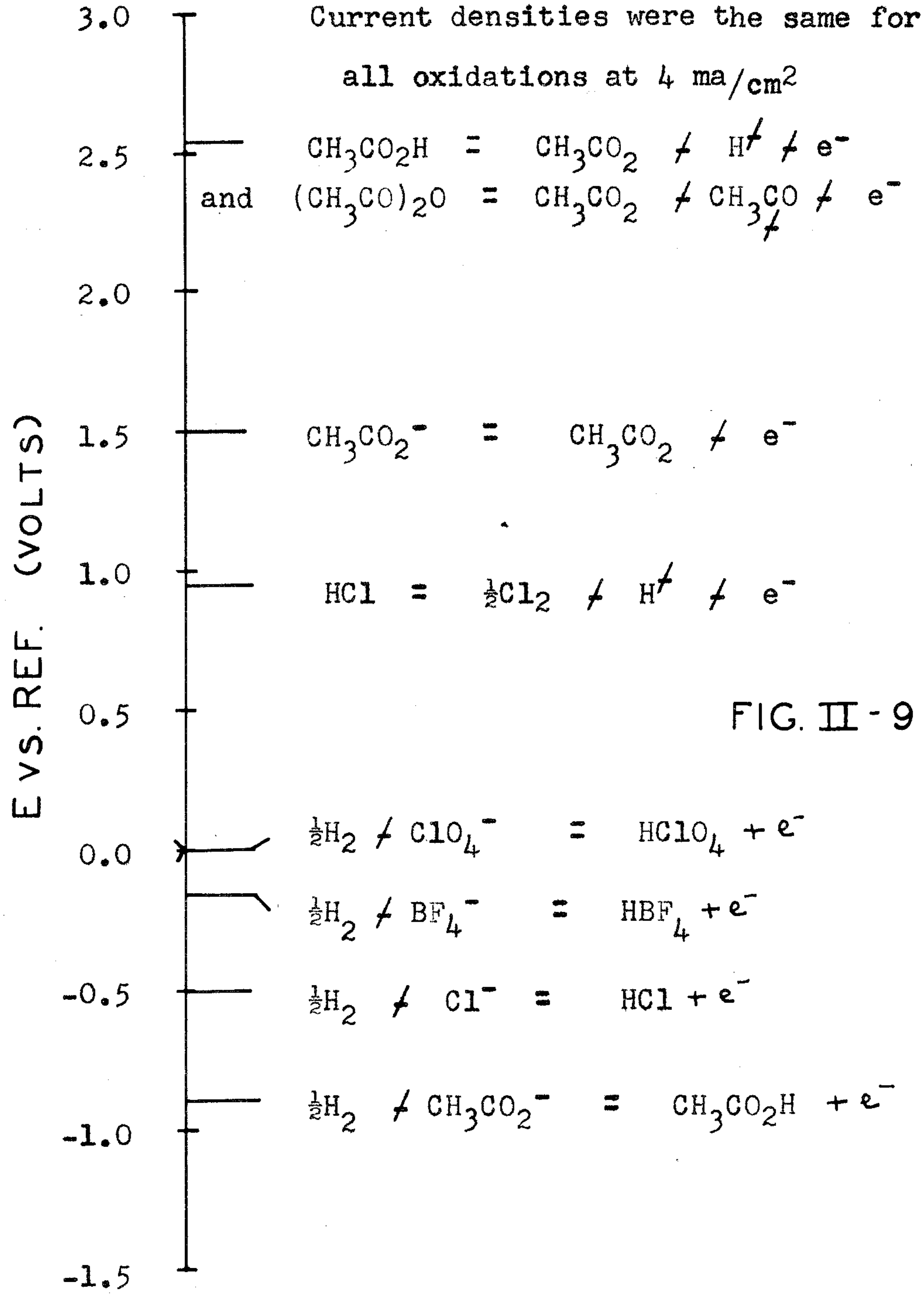
FIG. II-8

Current density was the same for all reductions at 4 ma/cm^2.

Concentrations were all ca. 0.025 VF.



Potential scale for oxidations at a platinum electrode in acetic anhydride electrolyte from observations of the potentials of electrode reactions in chronopotentiometric studies.



Current densities were the same for all oxidations at 4 ma/cm^2

FIG. II - 9

$$HClO_4 > HBF_4 > HCl > CH_3CO_2H \ .$$

This potential (acidity) scale will be used in studies of the anode reaction, which follow.

Anomalous behavior was observed in the reduction of conc. sulfuric acid in acetic anhydride electrolyte. Studies of this reduction and of possible uses of acetic anhydride for reductions at very reducing potentials are treated in Appendix I.

Anode Reaction

Oxidation at a platinum electrode of the acetic anhydride electrolyte is not so simple as the reduction. Either the acetic acid or the acetic anhydride is oxidized, probably the former, but, as will be shown, it makes little difference in the final product if only a small amount of acetic acid is present.

Analogous to the probable electro-oxidation of acetate (13)

$$CH_3CO_2^- = CH_3CO_2 + e^- \ ,$$

acetic acid and acetic anhydride are probably oxidized:

$$CH_3CO_2H = CH_3CO_2 + H^+ + e^-$$

$$(CH_3CO)_2O = CH_3CO_2 + CH_3\overset{+}{C}O + e^- \ .$$

The acetoxy radical is very unstable, decomposing immediately to methyl radical and carbon dioxide. The methyl radical combines mainly with other methyl radicals to give ethane in acetonitrile (13).

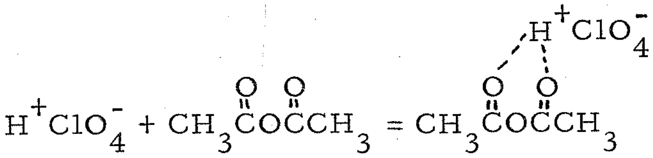
In the titration of samples of inorganic bases with the products of electrolyte oxidation, some hydrogen ions disappeared before they could react with the base, giving high results for the amount of base determined. Five to eight percent of the total hydrogen ions generated were lost in the titration of known amounts of standard base - the same samples were titrated with 100% titration efficiency with the mercury anode.

In the above oxidation reactions hydrogen ion (or its equivalent - acetylium ion) is generated with 100% current efficiency. Between the generation and the determination of hydrogen ions, some are lost.

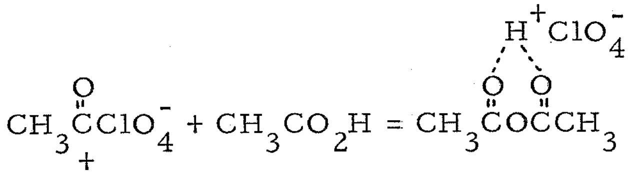
The reason for this loss has been investigated and appears to be due to a condensation of acetylium ions with the solvent to form slightly dissociated products.

This condensation probably occurs in the following manner: the ionic electrode reaction products are ion-paired and in equilibrium with the solvent (acetic anhydride with a small amount of acetic acid):

$$H^+ClO_4^- + CH_3CO_2H = CH_3CO_2H_2^+ClO_4^- \qquad (a)$$

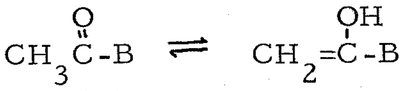


$$H^+ClO_4^- + CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 = CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 \cdot H^+ClO_4^- \qquad (b)$$

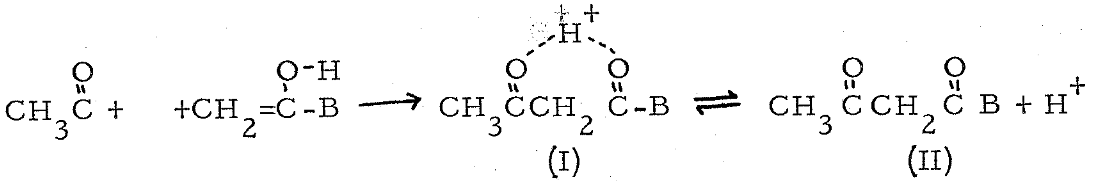


$$CH_3\overset{O}{\overset{\|}{C}}ClO_4^- {}^{+} + CH_3CO_2H = CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 \cdot H^+ClO_4^- \qquad (c)$$

The effect of the electrode oxidation plus the solvation equilibria (a) and (b) is to decrease the acetic acid concentration near the electrode. From the last equilibrium reaction, the acetylium ion concentration increases as the concentration of acetic acid decreases. Acetylium ion, a very strong electrophile, condenses rapidly, probably with the enol form of acetic acid or acetic anhydride:

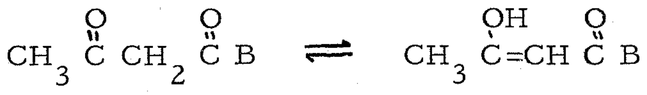


$$CH_3\overset{O}{\overset{\|}{C}}\text{-}B \rightleftharpoons CH_2{=}\overset{OH}{\overset{|}{C}}\text{-}B \quad \text{(enol-keto equilibrium)}$$

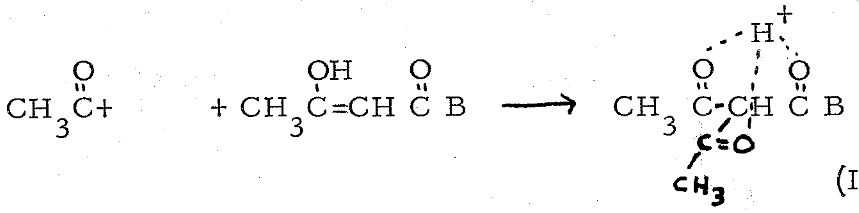


$$CH_3\overset{O}{\overset{\|}{C}}{}^{+} + CH_2{=}\overset{O\text{-}H}{\overset{|}{C}}\text{-}B \longrightarrow \underset{(I)}{CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}\text{-}B \cdot H^+} \rightleftharpoons \underset{(II)}{CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}B} + H^+$$

where B is OH or $O\overset{O}{\overset{\|}{C}}CH_3$. The protonated condensation product (I) is a weaker acid than perchloric acid but is somewhat dissociated and is titrated with sodium acetate in acetic anhydride solvent. Further condensation of acetylium with the enol form of (II) can occur:



$$CH_3\overset{O}{\overset{\|}{C}}\,CH_2\overset{O}{\overset{\|}{C}}\,B \rightleftharpoons CH_3\overset{OH}{\overset{|}{C}}{=}CH\overset{O}{\overset{\|}{C}}\,B$$



(III)

This protonated condensation product (III) is a very weak acid in this solvent system - no stronger than HCl - and is not appreciably dissociated. The condensation can continue to higher condensation products.

The rate of the condensation reaction depends on the acetylium concentration, which depends on the acetic acid and hydrogen ion concentration, and on the amount of enol form of the other reacting substance.

The protonated condensation product (I) is a moderately strong acid in this solvent. Further condensations form weaker and weaker acids (III, etc.). The further condensation products are not titrated with sodium acetate in this solvent system.

Evidence supporting the above hypotheses is the following:

1) <u>Coulometric efficiency for the generation of hydrogen ions</u>

The factors influencing hydrogen ion generation efficiency were studied in the absence of base, a condition which led to the poorest efficiencies. The hydrogen ions were generated by oxidizing the electrolyte at the platinum anode, and were back-titrated with electrogenerated acetate ion to determine the amount of perchloric acid which had disappeared. In each of the following studies all variables but one were held constant.

There was only a slight dependence of percent generation efficiency on current density and on the amount of acid generated (Fig. II-10a and II-10b).

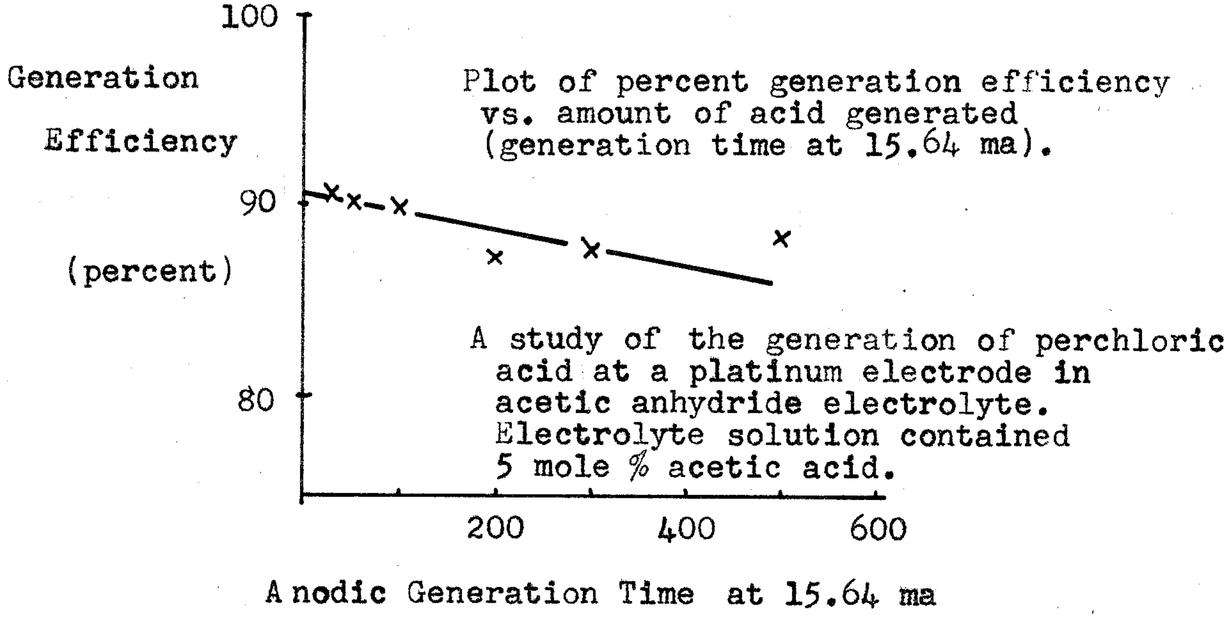
The effect of acetic acid concentration was more pronounced. As shown in Figure II-10c, the addition of acetic acid improved the titration efficiency from 69% with 0.8 mole % acetic acid to 90% with 66 mole % acetic acid. The end points in the back-titration became much less distinct and more acidic as the concentration of acetic acid was increased until, with 66 mole % acetic acid, the end point was too ill-defined to perceive. This behavior results from the acidity of acetic acid, 0.1 VF in sodium perchlorate:

$$\mathrm{Na^+ClO_4^- + CH_3CO_2H = H^+ClO_4^- + Na^+\,(CH_3CO_2)^-} \quad .$$

Perchloric acid is more completely dissociated in acetic acid-acetic anhydride solvent than is sodium acetate (9). The titration efficiency does not exceed 90% up to 66 mole % acetic acid because of two opposing effects. As the acetic acid concentration is increased, the condensation reaction becomes less rapid, but the solvent for the back-titration becomes more acidic. This means that, although fewer of the more

FIG. II-10A

Effect of amount of acid generated on the generation efficiency of perchloric acid.

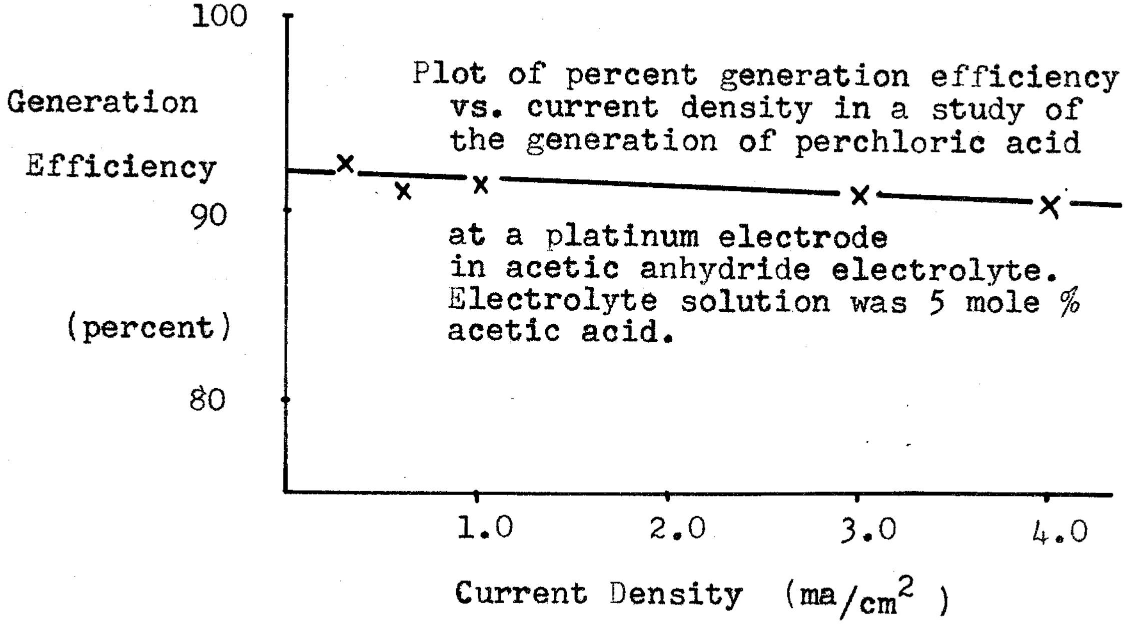


Plot of percent generation efficiency vs. amount of acid generated (generation time at 15.64 ma).

A study of the generation of perchloric acid at a platinum electrode in acetic anhydride electrolyte. Electrolyte solution contained 5 mole % acetic acid.

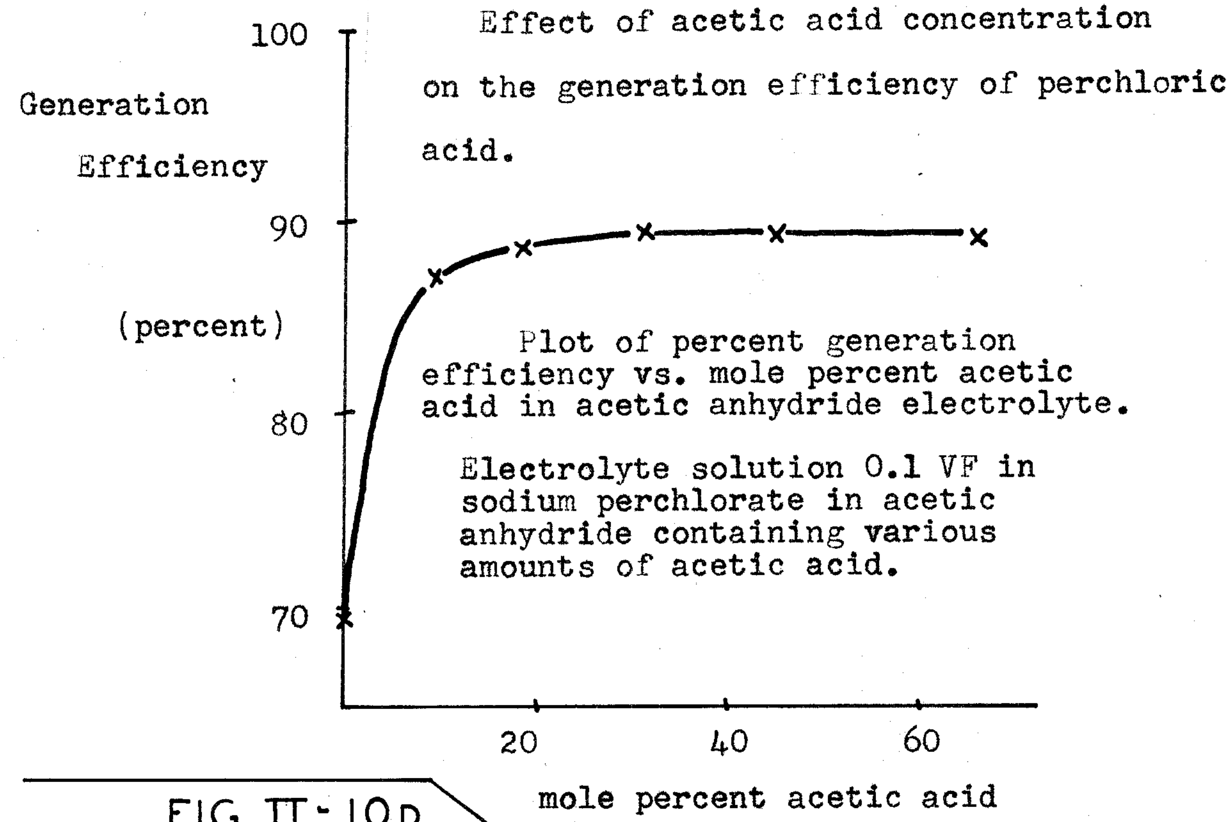
FIG. II-10B

Effect of current density on the generation efficiency of perchloric acid.



Plot of percent generation efficiency vs. current density in a study of the generation of perchloric acid at a platinum electrode in acetic anhydride electrolyte. Electrolyte solution was 5 mole % acetic acid.

FIG. II-10c

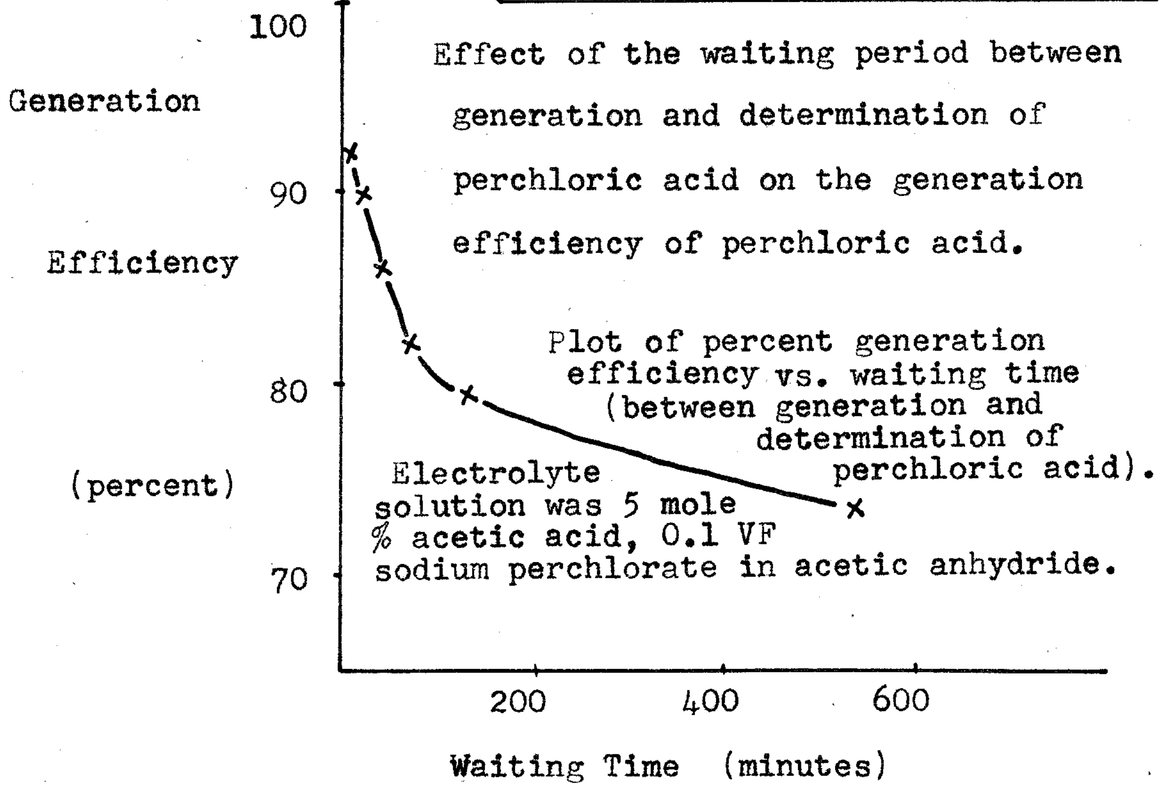


Effect of acetic acid concentration on the generation efficiency of perchloric acid.

Plot of percent generation efficiency vs. mole percent acetic acid in acetic anhydride electrolyte.

Electrolyte solution 0.1 VF in sodium perchlorate in acetic anhydride containing various amounts of acetic acid.

FIG. II-10D



Effect of the waiting period between generation and determination of perchloric acid on the generation efficiency of perchloric acid.

Plot of percent generation efficiency vs. waiting time (between generation and determination of perchloric acid).

Electrolyte solution was 5 mole % acetic acid, 0.1 VF sodium perchlorate in acetic anhydride.

slightly dissociated condensation products form, only the strongest acids are determined in the back-titration. As the solvent becomes more acidic, fewer of the protonated condensation products are determined in the back-titration. In glacial acetic acid no condensation should occur, but it is no longer possible to perform the coulometric-acidimetric titration using the potentiometric end point.

Another factor which had a pronounced effect on the hydrogen ion generation efficiency was the time between the generation and the determination of hydrogen ions (Fig. II-10d). Loss of hydrogen ions was most rapid during the period of generation but continued after generation had ceased. This happens because during the generation period the concentration of acetylium ion is high near the electrode and the condensation occurs rapidly. After the generation of hydrogen ions has ceased and they have been uniformly distributed throughout the solution, the condensation continues at a slower rate.

The condensation is rapid in the vicinity of the generating electrode during the electrolysis of the electrolyte. This is seen in the effect of stirring on generation efficiency. The acetic anhydride-acetic acid (5 mole %) electrolyte was either stirred or not stirred during the period of anodic generation (2 min.) and during the waiting period before the back-titration (10 min.).

anodic generation period (2 min.)	waiting period (10 min.)	generation efficiency %
stirred	stirred	89.9
		large difference
unstirred	stirred	82.3
		small difference
unstirred	unstirred	81.2

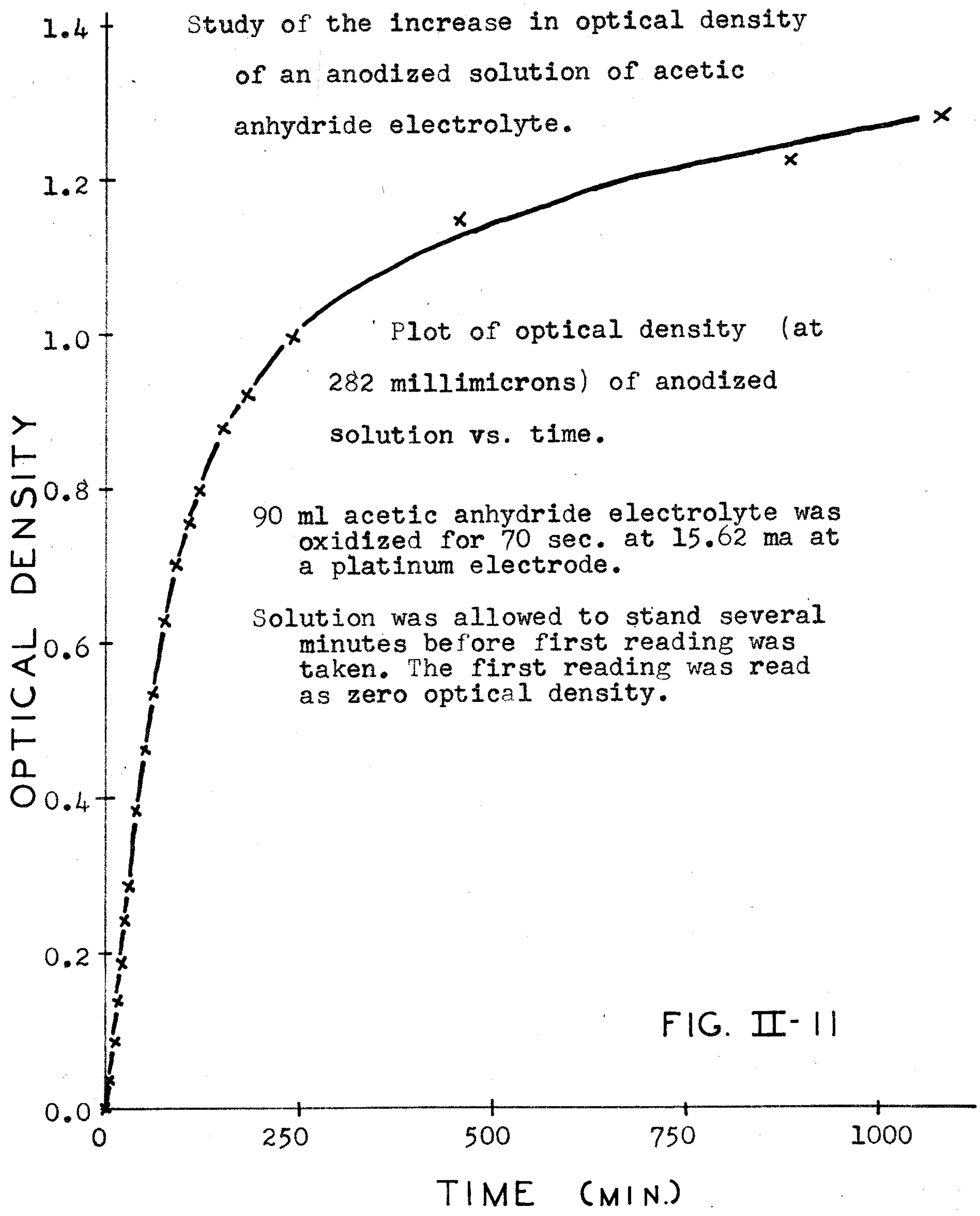
During the generation period acetic acid is removed from the vicinity of the electrode by electrolysis, increasing the concentration of acetylium ions and increasing the rate of condensation. Stirring during the generation period helps to maintain the acetic acid concentration and slows the rate of condensation. This accounts for the fairly large difference between stirred and unstirred solutions during the generation period. Stirring during the waiting period ensures uniformity of the solution and the condensation continuing at a slower rate. The small difference observed between stirred and unstirred solutions during the waiting period implies that most of the condensation has already occurred during the generation period. The condensation forms products which are only slightly dissociated. The rate of further condensation is decreased by the formation of these slightly dissociated products as they effectively remove hydrogen ions from the condensation reaction (hence, decrease the concentration of acetylium ions). If the condensation did not occur for the most part during the generation period, a large effect would be expected from local concentrations of acetylium ion near the electrode in the unstirred solution during the waiting period.

2) Observations of color formation

When the acetic anhydride electrolyte was oxidized at either a platinum or mercury electrode, in the absence of base, the solution turned yellow. As the solution stood, the yellow color changed to orange and finally to red. The same behavior was observed when a few drops of conc. perchloric acid were added to acetic anhydride.

The ultraviolet-visible spectra of both solutions are similar. Each has a strong absorption maximum at 282 mμ and a long tail into the visible region. With time the height of this maximum increases and the tail extends farther into the visible region. A study of the increase in optical density (at 282 mμ) as a function of time is shown for an anodized solution in Fig. II-11. This solution was oxidized for 70 sec. at 15.62 ma and allowed to stand several minutes before the first reading was taken. The first reading was read as zero optical density. Only the slow condensation reaction of acetylium ions uniformly distributed throughout the solution was being studied - not the rapid reaction of locally high concentrations of acetylium ion near the electrode during generation.

If the optical density (at 282 mμ) is assumed to be proportional to the concentration of condensation product(s), then the rate of increase of optical density can be approximately calculated:



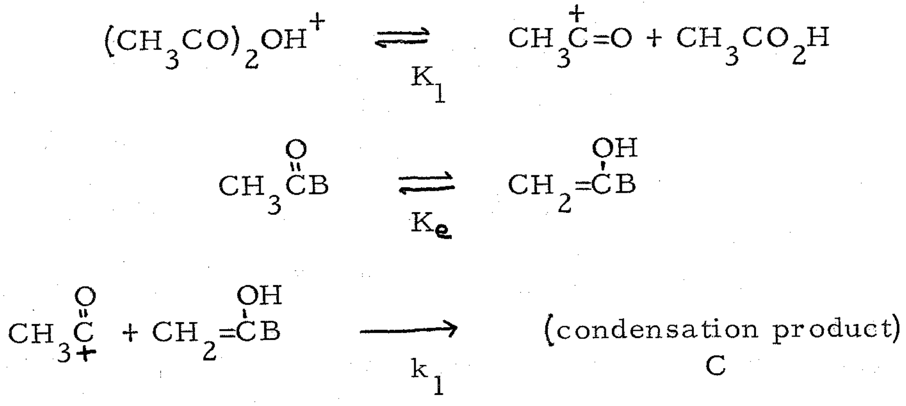
Study of the increase in optical density of an anodized solution of acetic anhydride electrolyte.

Plot of optical density (at 282 millimicrons) of anodized solution vs. time.

90 ml acetic anhydride electrolyte was oxidized for 70 sec. at 15.62 ma at a platinum electrode.

Solution was allowed to stand several minutes before first reading was taken. The first reading was read as zero optical density.

FIG. II-11



$$(CH_3CO)_2OH^+ \underset{K_1}{\rightleftharpoons} CH_3\overset{+}{C}{=}O + CH_3CO_2H$$

$$CH_3\overset{O}{\overset{\|}{C}}B \underset{K_e}{\rightleftharpoons} CH_2{=}\overset{OH}{\overset{|}{C}}B$$

$$CH_3\overset{O}{\overset{\|}{\underset{+}{C}}} + CH_2{=}\overset{OH}{\overset{|}{C}}B \xrightarrow[k_1]{} \underset{C}{\text{(condensation product)}}$$

where [ ] represent concentrations

B is OH or $O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$

$$\frac{dc}{dt} = k_1 \, [CH_3\overset{+}{C}{=}O] \; [CH_2{=}\overset{OH}{\overset{|}{C}}B]$$

$$[CH_3\overset{+}{C}{=}O] = \frac{K_1 \, [(CH_3CO)_2OH^+]}{[CH_3CO_2H]}$$

$$[CH_2{=}\overset{OH}{\overset{|}{C}}B] = K_e \, [CH_3\overset{O}{\overset{\|}{C}}B]$$

$$\frac{dc}{dt} = k_1K_1K_e \; \frac{[CH_3\overset{O}{\overset{\|}{C}}B] \, [(CH_3CO)_2OH^+]}{[CH_3 \; CO_2H]}$$

$$(CH_3CO)_2OH^+ \underset{K_2}{\rightleftharpoons} H^+ + (CH_3CO)_2O$$

$$\frac{dc}{dt} = \frac{k_1K_1K_e}{K_2} \; [H^+] \; \cdot \; \frac{[CH_3\overset{O}{\overset{\|}{C}}B] \, [(CH_3CO)_2O]}{[CH_3 \; CO_2H]}$$

$$\frac{dc}{dt} = A\,[H^+]\;\frac{[CH_3\overset{\overset{O}{\|}}{C}B]\,[(CH_3CO)_2O]}{[CH_3\,CO_2H]}$$

The quantities in the fraction on the right in the last equation are approximately constant for the anodized solution. Optical density of the solution has been assumed to be directly proportional to C.

$$\frac{d(O.D.)}{dt} = B\,[H^+]$$

The change in optical density of the solution is, thus, directly proportional to the hydrogen ion concentration. Initially, before much condensation has occurred, the hydrogen ion concentration is constant and the optical density increases linearly (zero order with respect to hydrogen ion). As the condensation proceeds, the slightly dissociated products of the condensation remove hydrogen ions from the above reactions. As the concentration of hydrogen ions decreases, the rate of increase of optical density becomes less, as observed in Fig. II-11. The optical density continues to increase as long as there are hydrogen ions present.

That this color effect is not due to an organic free radical resulting from the oxidation of acetic anhydride by perchloric acid is seen in a qualitative study of this color development in various acids. The following acids were added to acetic anhydride to form 0.1 VF solutions:

Acid	Solution color
acetylium perchlorate	yellow, orange, red, dark red within 20 min.
perchloric acid	yellow, orange, red within 20 min.
fluoboric acid	yellow after 10 min., slowly turning orange
hydrogen iodide	yellow after 20 min. (deaerated solution)
sulfuric acid	yellow after refluxing for one hour

These qualitative results indicate that it is hydrogen ion that is responsible for the color development. The above series of acids is in order of decreasing acidity.

If a solution 0.1 VF in $HClO_4$ in acetic anhydride is allowed to stand for several weeks, it becomes a very dark red and a brown residue adheres to the walls of the vessel. This brown residue is the final product of the condensation. Burton and Praill report (14) a reaction of perchloric acid with acetic anhydride observing a brown solution and brown needles separating after several days. The brown substance gave an iodoform test, characteristic of methyl carbonyls. The development of color was retarded by the addition of acetic acid. Burton and Praill also draw attention to the fact that reaction of acetylium perchlorate with acetic anhydride is more rapid than with benzene or toluene but less rapid than with m-xylene (15). The solution of acetylium perchlorate in acetic anhydride darkens very rapidly depositing a crystalline perchlorate and some tar. From the hypotheses advanced in this thesis, the perchlorate residue should be the conjugate acid of some polycarbonyl, i.e. (condensation product)$\cdot HClO_4$. The residue is insoluble in cold water but soluble in sodium hydroxide (reprecipitated on addition of excess acid) and in ethanol. An orange precipitate is formed with 2,4-dinitrophenyl hydrazine in ethanol. No melting point was observed for the brown residue which charred at 200°C. The DNP derivative charred at 70°C.

3) Study of the reaction of perchloric acid with acetic anhydride

Studies of the reaction of perchloric acid with acetic anhydride have not been reported, except in passing. This reaction is a side reaction in acetylations with mixtures of perchloric acid and acetic anhydride (14,15,16). Burton and Praill have found considerable evidence that some Friedel-Crafts acetylations are due to the acetylium ion. These authors have mentioned the side reaction of acetylium ion with acetic anhydride but have not investigated it thoroughly (14,15). Acetylium perchlorate has been shown by these authors to be a very good acetylating agent (16).

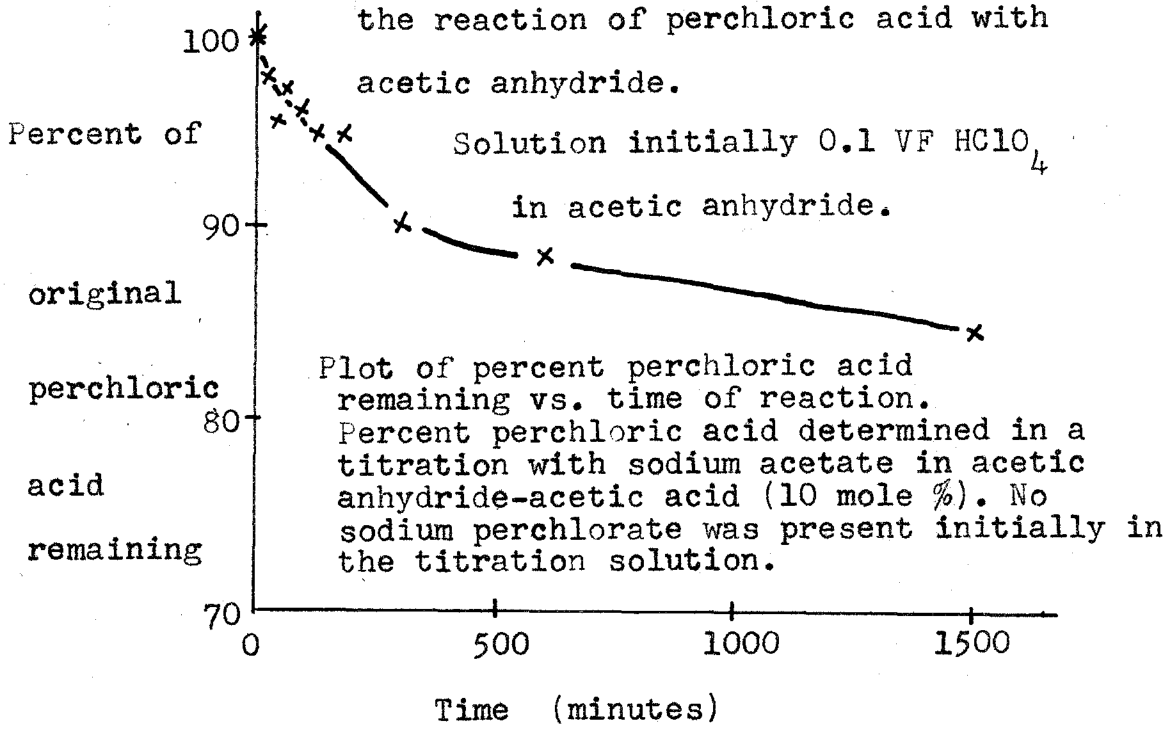
Solutions of perchloric acid in acetic anhydride and solutions of anodized acetic anhydride electrolyte exhibit the same color phenomena. This fact is not a surprise in light of the hypotheses which postulate a condensation of acetylium ion (whose concentration depends on the hydrogen ion concentration) with acetic anhydride. The coulometric generation efficiency, as determined by back-titration of the anodized electrolyte, has been shown to be dependent on the time that the solution was allowed to stand before the back-titration (Fig. II-10d). A similar disappearance of perchloric acid was seen in the reaction of perchloric acid with acetic anhydride.

Volumetric-acidimetric determination of perchloric acid in acetic anhydride.

The concentration of perchloric acid in a solution, originally 0.1 VF $HClO_4$ in acetic anhydride, was followed as a function of time by titration of aliquots with standard base. Figures II-12a and II-12b show the results of such determinations.

Titration of these aliquots of perchloric acid in acetic anhydride, taken at various times, with sodium acetate in a titration solution of acetic anhydride-acetic acid (10 mole %) shows a decrease of perchloric acid with time (Fig. II-12a). This disappearance of perchloric acid in acetic anhydride solutions was seen in the effect of

FIG. II - 12A

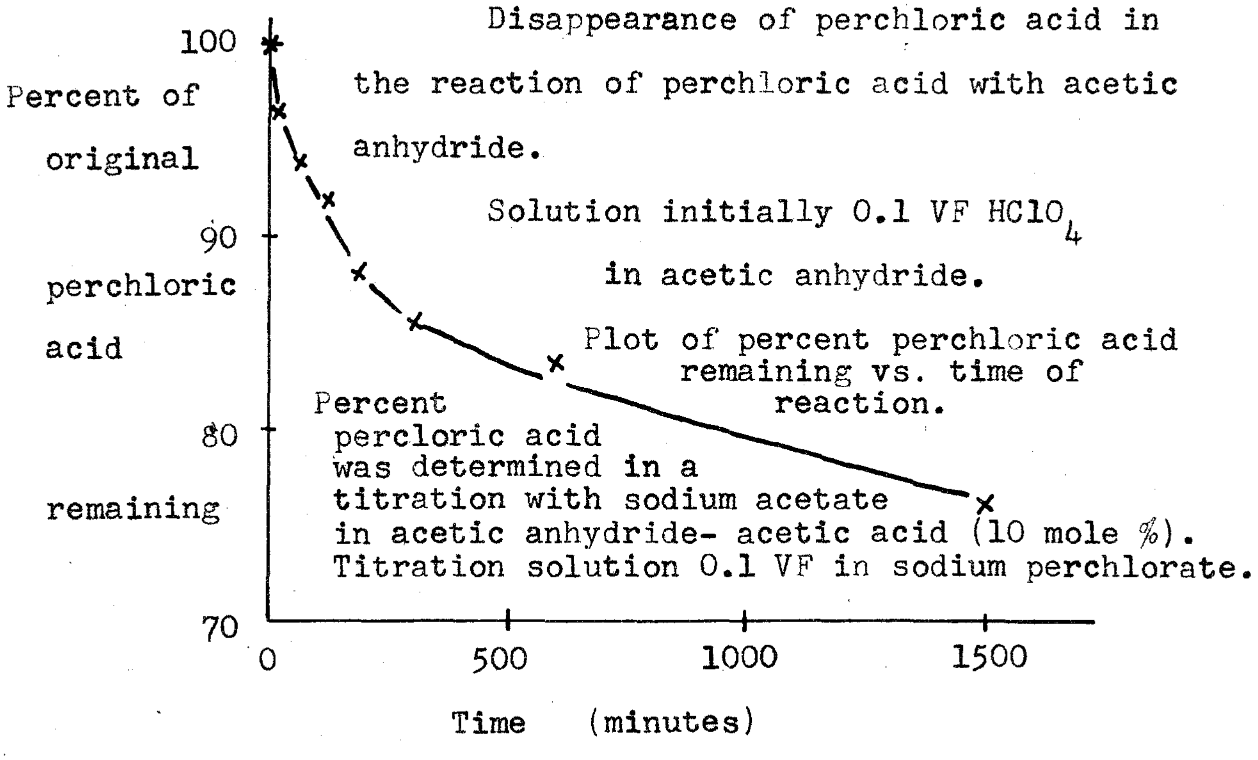


Disappearance of perchloric acid in the reaction of perchloric acid with acetic anhydride.

Solution initially 0.1 VF $HClO_4$ in acetic anhydride.

Plot of percent perchloric acid remaining vs. time of reaction. Percent perchloric acid determined in a titration with sodium acetate in acetic anhydride-acetic acid (10 mole %). No sodium perchlorate was present initially in the titration solution.

FIG. II - 12B



Disappearance of perchloric acid in the reaction of perchloric acid with acetic anhydride.

Solution initially 0.1 VF $HClO_4$ in acetic anhydride.

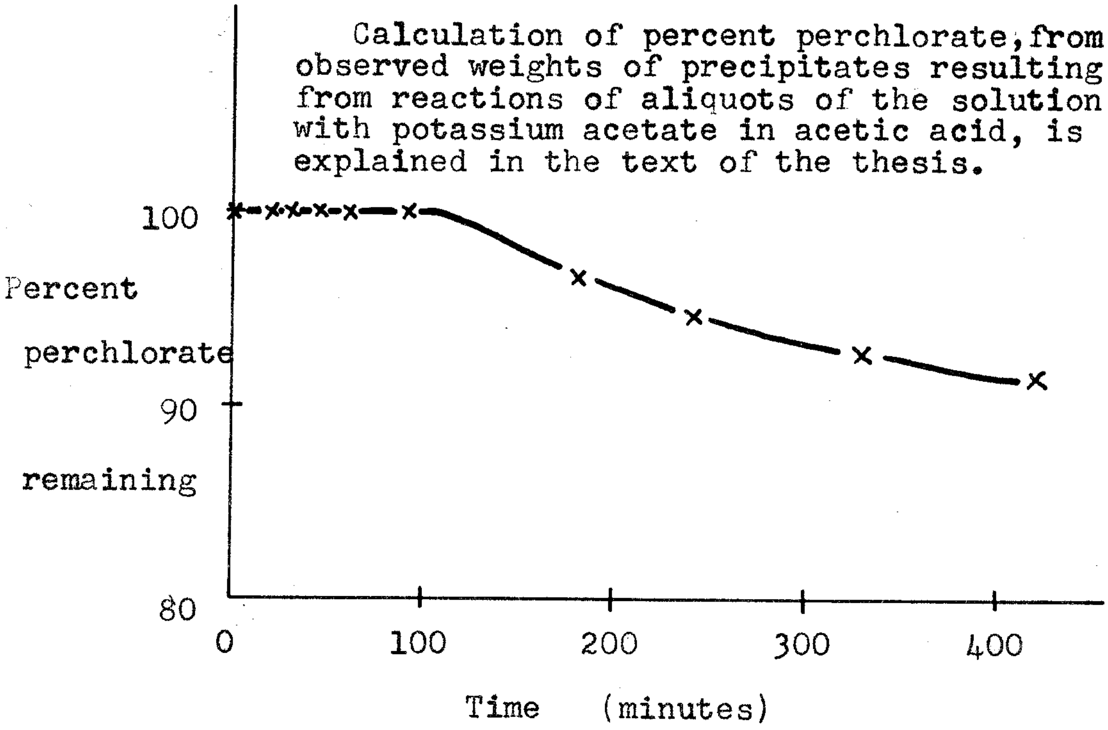
Plot of percent perchloric acid remaining vs. time of reaction.

Percent percloric acid was determined in a titration with sodium acetate in acetic anhydride- acetic acid (10 mole %). Titration solution 0.1 VF in sodium perchlorate.

Disappearance of perchlorate ion in the reaction of perchloric acid with acetic anhydride.

Solution initially 0.3 VF perchloric acid in acetic anhydride.

Plot of calculated percent perchlorate remaining in the perchloric acid- acetic anhydride solution vs. time of reaction.



Calculation of percent perchlorate, from observed weights of precipitates resulting from reactions of aliquots of the solution with potassium acetate in acetic acid, is explained in the text of the thesis.

FIG. II - 12c

waiting time on the coulometric generation efficiency (Fig. II-10d). Figure II-12b illustrates the results of the titrations of aliquots of the solution of perchloric acid in acetic anhydride with sodium acetate under the same conditions as Figure II-12a except that the titration solution contained 0.1 VF $NaClO_4$. The addition of sodium perchlorate to the acetic acid-acetic anhydride solvent increases the acidity of the titration solution. In the titration of the aliquots of the perchloric acid solution in acetic anhydride, the perchloric acid seemed to disappear more rapidly when the titration was performed in the sodium perchlorate titration solution than when the titration was performed in the titration solution without sodium perchlorate. The reason for this is probably the acidity of the various condensation products. As the condensation of acetylium with acetic anhydride proceeds, a number of different condensation products may be formed which vary in their degree of dissociation (i.e., their hydrogen ion dissociation constants vary). As the acidity of the solvent is increased by increasing either the acetic acid or sodium perchlorate concentration, fewer of the hydrogen ions are determined in the titration. The acidity of the titration solution has been noted before in the effect of acetic acid on the coulometric generation efficiency (Fig. II-10c).

Gravimetric studies of the reaction of perchloric acid with acetic anhydride.

The condensation reaction leads to the colored products observed in both the anodized electrolyte and in the reaction of perchloric acid with acetic anhydride. There was still the possibility that the disappearance of hydrogen ions was due to the following reaction:

$$HClO_4 + 8\,H^+ + 8\,e^- + 4\,(CH_3CO)_2O = HCl + 8\,CH_3CO_2H$$

$$8\,CH_3CO_2H = 8\,CH_3CO_2 + 8\,H^+ + 8\,e^-$$

$$8\,CH_3CO_2 = 4\,C_2H_6 + 8\,CO_2$$

$$HClO_4 + 4\,(CH_3CO)_2O = HCl + 4\,C_2H_6 + 8\,CO_2$$

Perchloric acid is a strong acid in acetic anhydride. Hydrochloric acid is little stronger than acetic acid in acetic anhydride (see acidity scale, Fig. II-8) and does not react completely with sodium acetate. The reduction of perchloric acid to hydrochloric acid results in the loss of hydrogen ions in the acetic acid-acetic anhydride solvent.

The reaction of perchloric acid with acetic anhydride was followed by analyzing aliquots of the reaction mixture for perchlorate at various time intervals by precipitation of potassium perchlorate. A more concentrated solution of perchloric acid, 0.3 VF $HClO_4$ in acetic anhydride, was used in this experiment (0.1 VF $HClO_4$ in acetic anhydride was used in the volumetric determinations of hydrogen ions). The color was much more intense in this more concentrated solution. The percent perchlorate found as a function of time is shown in Figure II-12c. These values assume all perchlorate which reacted was reduced to chloride. As potassium chloride would also appear in the precipitate, a correction was made in the observed weight of the precipitate. The following formulae were used to calculate the percent potassium perchlorate in the precipitate of weight w_t at time t :

$$\frac{w_o}{M_{KClO_4}} = \text{mmoles of chlorine species present} = A = \text{constant}$$

$$\frac{x}{M_{KClO_4}} + \frac{y}{M_{KCl}} = A$$

$$x + y = w_t$$

$$\frac{x}{w_o} \cdot 100 = \%\ \text{perchlorate remaining}$$

where w_o = weight of $KClO_4$ found in an aliquot at t = 0.

M_{KClO_4} = molecular weight of $KClO_4$.

M_{KCl} = molecular weight of KCl.

x = weight of $KClO_4$ at time t .

y = weight of KCl at time t.

No change was observed in the perchlorate concentration during the period in which the hydrogen ion loss was most rapid. A decrease in the perchlorate concentration was seen after about two hours. At this time the hydrogen ion concentration should be 90-95% of the initial concentration. After three hours aliquots of this perchloric acid-acetic anhydride mixture showed the presence of chloride in qualitative tests (precipitation with silver perchlorate).

The conclusion to be drawn from these experiments is that reduction of perchlorate does occur but only rather slowly. The reduction of perchlorate is not rapid enough to account for the loss of hydrogen ions during the coulometric titrations.

Another possible, but not likely, interpretation of the experimental results is that perchlorate is not reduced, but the protonated form of the condensation product is ion-paired with perchlorate ion. This ion-pair could be so slightly dissociated that the perchlorate ion does not react with the potassium acetate. The chloride test could be due to traces of chloride absorbed from the laboratory atmosphere. At any rate, the reduction of perchlorate is only a minor factor in the loss of hydrogen ions.

4) Chronopotentiometric studies of the electrode reaction

Experiments were performed to identify the anodized solutions of acetic anhydride electrolyte with solutions of perchloric acid in acetic anhydride. A very convenient method of doing this was to compare the reduction chronopotentiogram of an acetic anhydride electrolyte solution which had just been oxidized with the reduction chronopotentiogram of perchloric acid in acetic anhydride.

Chronopotentiometric reduction studies of a number of acids in acetic anhydride electrolyte have been used to establish an acidity scale for this solvent (Fig. II-8). The potential at which hydrogen ion is reduced depends on the concentration of hydrogen ion and, hence, on the dissociation of the acid. This acidity scale will be used to show the condensation products of acetylium ion with acetic anhydride to be weaker acids than perchloric acid.

Figure II-13 shows the reduction of perchloric acid in acetic anhydride electrolyte. One transition time is observed, with a potential pause at -0.5 V vs. ref., for the reduction of perchloric acid (solvated). These curves were taken after all water in the system had reacted with the acetic anhydride, but before appreciable condensation had occurred.

Figure II-14 shows the reduction of acetylium perchlorate in acetic anhydride electrolyte. Two transition times are observed, the first potential pause at -0.6 V vs. ref. and the second at -0.8 V vs. ref. The potential pause at -0.6 V vs. ref. is the reduction of perchloric acid, formed in the reaction of acetylium ion with the small amount of acetic acid in the acetic anhydride electrolyte:

Chronopotentiogram for the reduction of perchloric acid in acetic anhydride electrolyte.

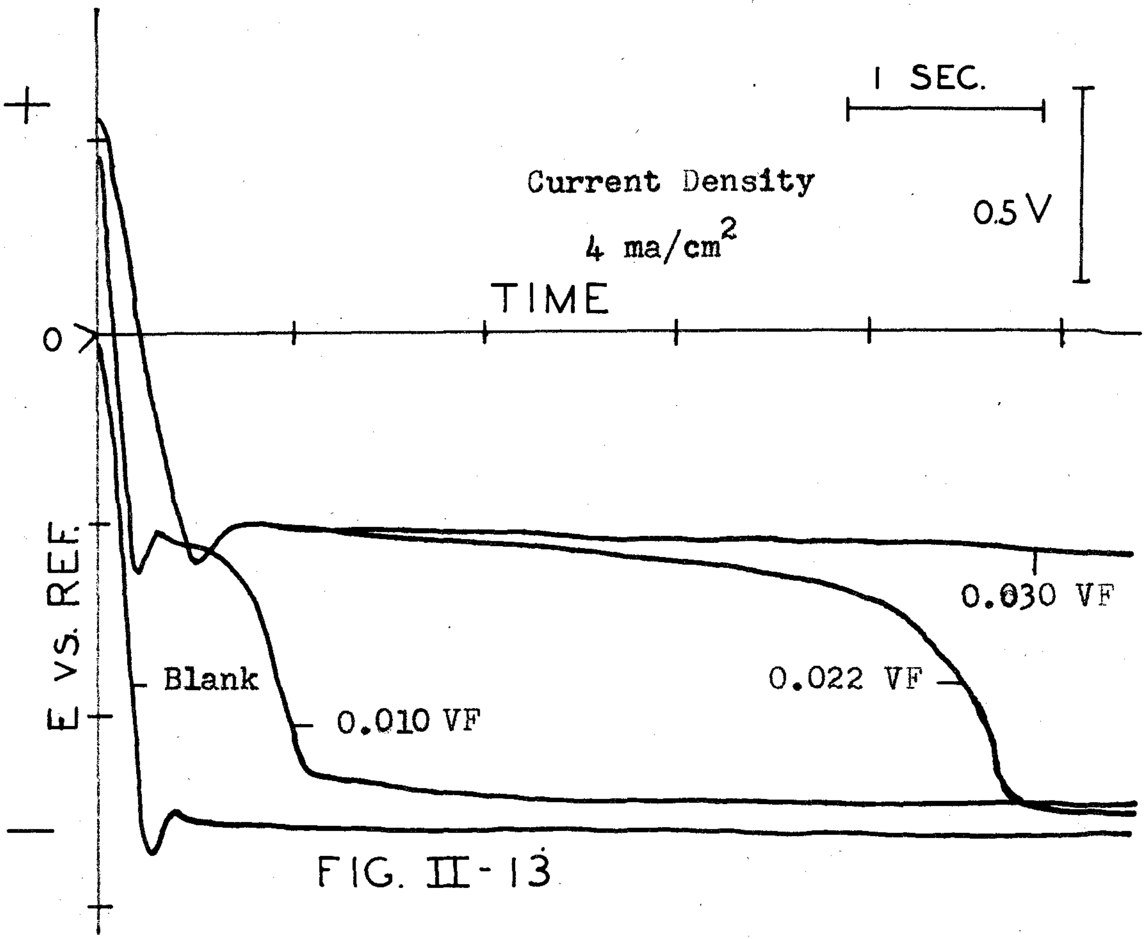


FIG. II-13

Concentration of perchloric acid in 90 ml acetic anhydride electrolyte given with the curves.

Potential pause at -0.5 V vs. ref.

Curves taken after all water in the system had reacted, but before any appreciable condensation had occurred.

Chronopotentiogram for the reduction of a solution of acetylium perchlorate in acetic anhydride electrolyte.

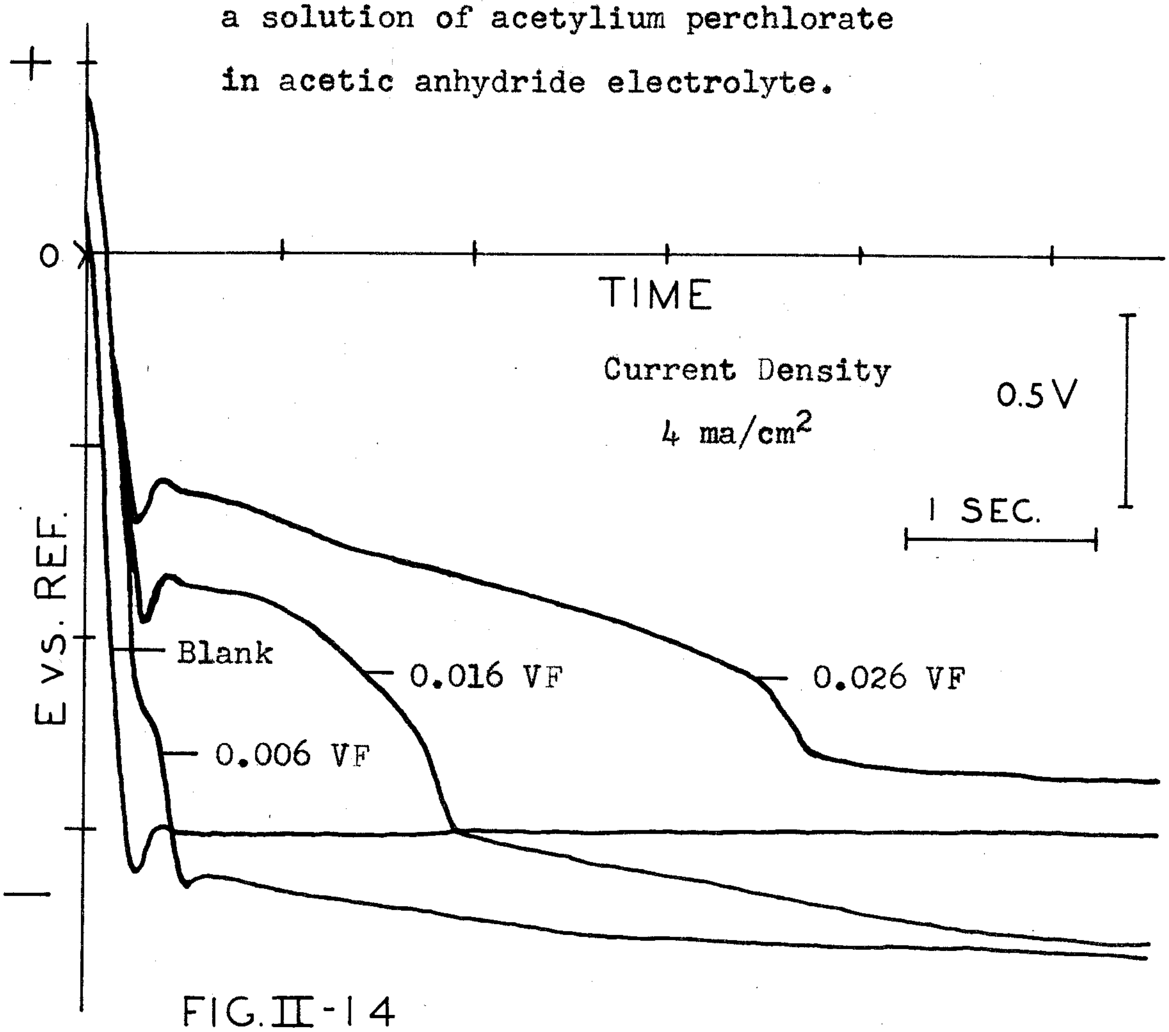
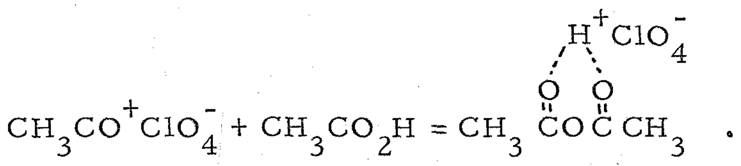


FIG. II-14

Concentration of acetylium perchlorate in 90 ml acetic anhydride electrolyte given with the curves.

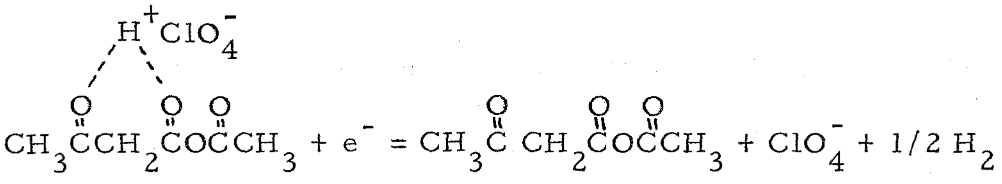
Potential pauses at -0.6 V vs. ref. and -0.8 V vs. ref.

Curves taken as soon as possible after Preparation of solution of acetylium perchlorate.



$$CH_3CO^+ClO_4^- + CH_3CO_2H = CH_3\overset{H^+ClO_4^-}{\overset{O\quad O}{\overset{\|\quad\;\|}{CO\,C}}}CH_3 \quad .$$

The potential pause is at -0.6 V vs. ref. instead of -0.5 V vs. ref., as observed in the reduction of perchloric acid in acetic anhydride, because of the lower concentration of perchloric acid in the acetylium-acetic anhydride mixture. For the reversible reduction of hydrogen ions this difference in concentration would not affect the potential of the reduction - but hydrogen ion does not appear to be reduced reversibly in this solvent system. The second potential pause, at -0.8 V vs. ref., is most likely the reduction of the protonated form of the first condensation product of acetylium ion and acetic anhydride:



$$CH_3\overset{H^+ClO_4^-}{\overset{O\qquad\quad O}{\overset{\|\qquad\quad\|}{C\,CH_2C}}}O\overset{O}{\overset{\|}{C}}CH_3 + e^- = CH_3\overset{O}{\overset{\|}{C}}\,CH_2\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 + ClO_4^- + 1/2\ H_2$$

That this second potential pause appears almost immediately (i.e., as fast as solution could be prepared for study) for solutions of acetylium perchlorate in acetic anhydride is good evidence for a rapid reaction between acetylium ion and acetic anhydride when the concentration of acetylium is significant. The potential of the reduction, -0.8 V vs. ref., places the protonated form of the first condensation product of acetylium ion with acetic anhydride just above fluoboric acid on the acidity scale, Fig. II-8. It is a considerably weaker acid than perchloric acid in this solvent system.

The acetic anhydride electrolyte was saturated with hydrogen gas. The hydrogen was oxidized at the platinum electrode, then the current reversed and the potential time behavior of the cathode observed. Figure II-15 shows the reduction chronopotentiogram of an oxidized solution of hydrogen gas in the acetic anhydride electrolyte. The potential pause is at -0.5 V vs. ref. and is the reduction of perchloric acid to hydrogen gas. This is the same potential that was observed for the reduction of a solution of perchloric acid in acetic anhydride electrolyte.

The reduction chronopotentiogram of an oxidized solution of acetic anhydride electrolyte is seen in Figure II-16. Two transition times are observed, with potential pauses at -0.5 V and -0.8 V vs. ref. The potential pause at -0.5 V vs. ref. is the reduction of perchloric acid and the pause at -0.8 V vs. ref. is probably the reduction of the protonated form of the first condensation product. This second pause is only observed after oxidations long enough so that the acetylium ions which were generated in the electrode process had time to condense with acetic anhydride before the current was reversed. It should be noted that a significant amount of condensation occurs in a relatively short time - 40 seconds.

In the reduction of the oxidized acetic anhydride electrolyte, the only potential pauses that are observed are those due to the

Chronopotentiogram for the oxidation of hydrogen gas and for the reduction of perchloric acid in acetic anhydride electrolyte.

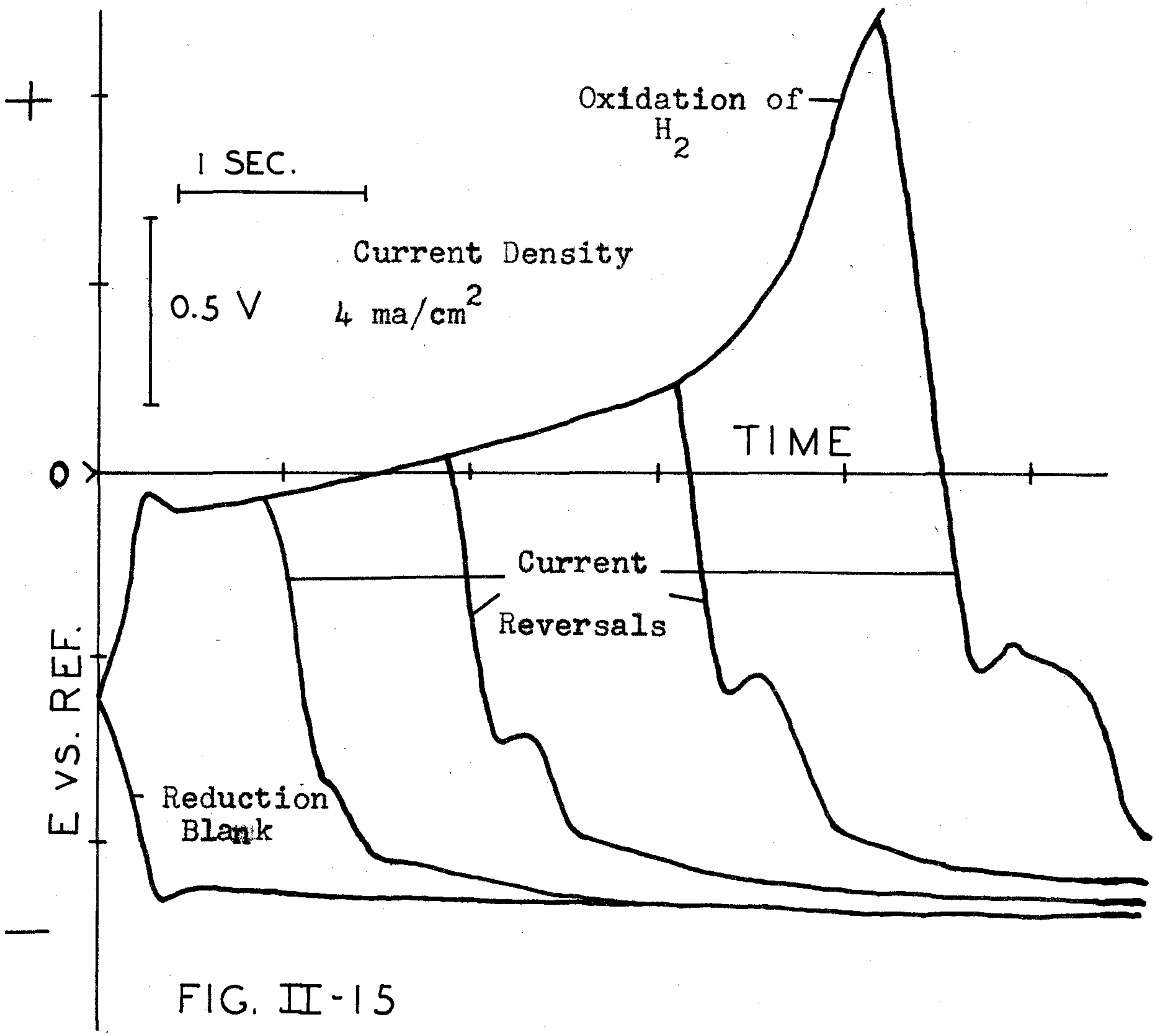


FIG. II-15

Current reversals shown at various points on the oxidation potential pause of a saturated solution of hydrogen gas in 90 ml acetic anhydride electrolyte. Potential pauses at 0.0 V vs. Ref.(oxidation) and -0.5 V vs. ref. (reduction).

Chronopotentiogram for the reduction of an oxidized solution of acetic anhydride electrolyte.

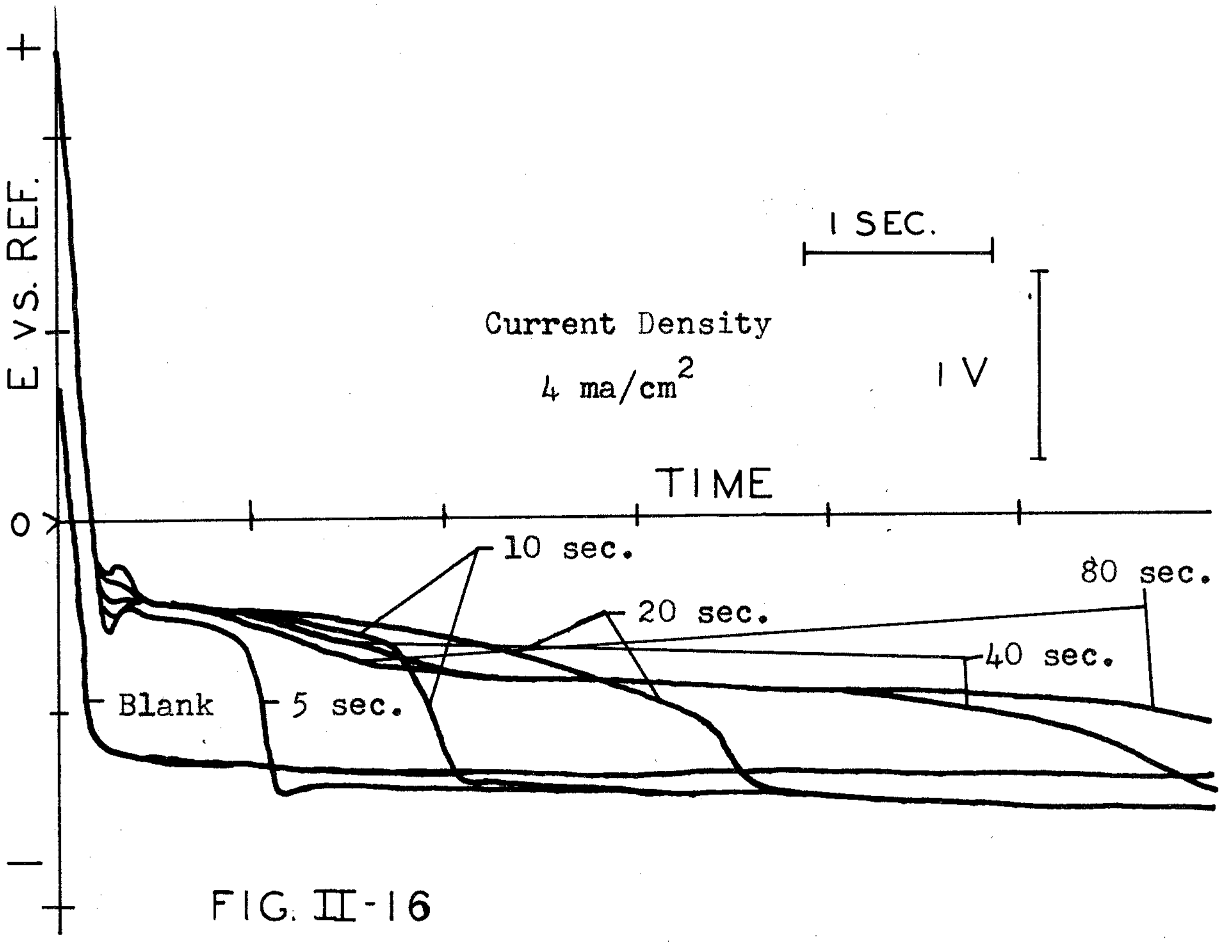


FIG. II-16

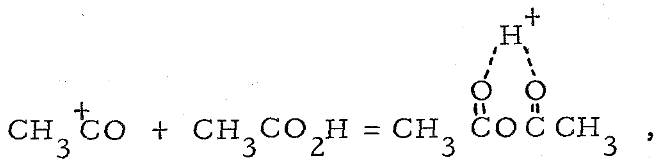
Oxidation time (in seconds) before current reversal given with the curves.

Potential pauses at -0.5 V vs. ref. and -0.8 V vs. ref.

90 ml acetic anhydride electrolyte taken.

reduction of hydrogen ions. No potential pauses are observed for the reduction of any other products of the electrolyte oxidation. No evidence was observed for the existence of acetoxy radical at the electrode. This does not necessarily imply that acetoxy radical cannot be reduced at an electrode, for it is probably so unstable that it decomposed before the current could be reversed. In the study of the oxidation of acetate, no potential pause before the reduction of the acetic acid is observed in the reduction chronopotentiogram of an oxidized solution of sodium acetate in acetic anhydride (Fig. II-17). Again no evidence for the existence of acetoxy radical is observed.

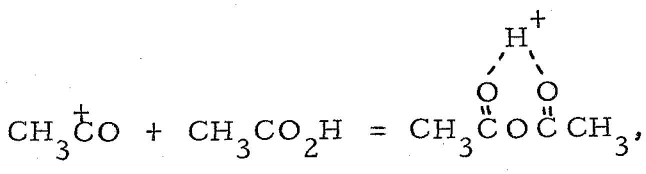
No separate potential pause is observed for the reduction of acetylium ion, another proposed product of the oxidation of acetic anhydride electrolyte. There are several explanations for this. Acetylium ion might be reduced at the same potential as perchloric acid; or an appreciable amount of acetylium is in a fast equilibrium with perchloric acid,



$$CH_3\overset{+}{C}O + CH_3CO_2H = CH_3\overset{\overset{H^+}{O\quad O}}{\overset{\|\quad\|}{C\,O\,C}}CH_3$$

, which is reduced;

or acetylium ion may not be reduced before acetic acid; or, finally, acetylium ion may react so rapidly with the solvent to form either



$$CH_3\overset{+}{C}O + CH_3CO_2H = CH_3\overset{\overset{H^+}{O\quad O}}{\overset{\|\quad\|}{C\,O\,C}}CH_3,$$

reduced at -0.5

Chronopotentiogram for the reduction of an oxidized solution of sodium acetate in acetic anhydride electrolyte.

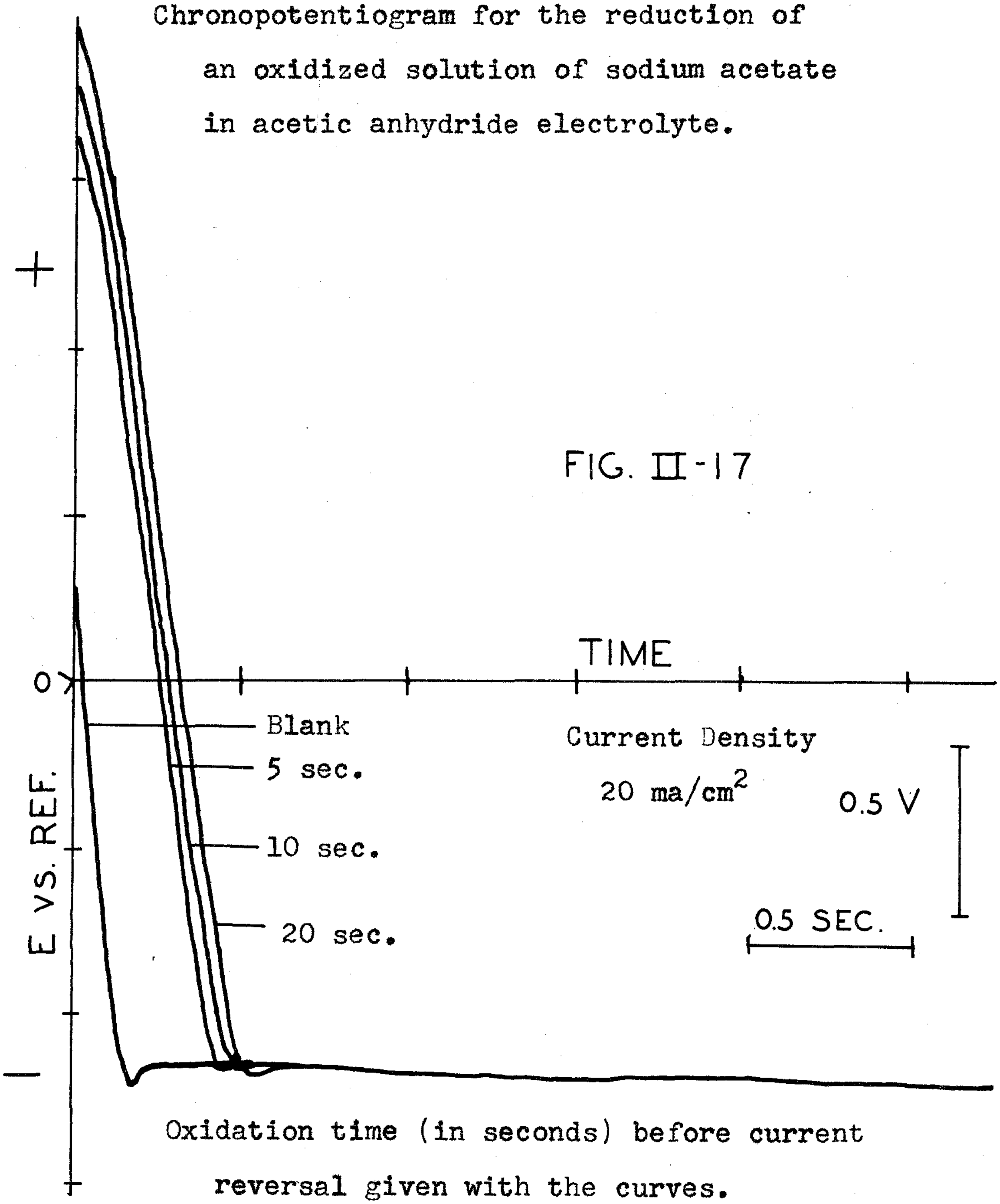


FIG. II-17

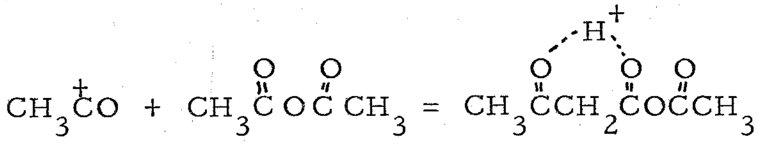
Current Density
20 ma/cm^2

Oxidation time (in seconds) before current reversal given with the curves.

No potential pause before reduction background.

0.05 VF sodium acetate in acetic anhydride electrolyte (90 ml). Transition time for the oxidation of acetate ion - 35 sec.

V vs. ref. or



$$CH_3\overset{+}{C}O + CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 = \overset{H^+}{CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3}$$

at -0.8 V vs. ref. that the acetylium ion has disappeared before the current is reversed. In light of the observed rapid reaction between acetylium ion and the solvent, the last of the above alternatives seems the most likely, but the others are not excluded.

The reduction product of perchloric acid and of the protonated form of the first condensation product is hydrogen gas. This is seen when a reduced solution of perchloric acid in acetic acid is oxidized (Fig. II-7). If a solution of perchloric acid in acetic anhydride is allowed to react for several hours, the reduction chronopotentiogram is similar to that of acetylium perchlorate in acetic anhydride or of the oxidized acetic anhydride electrolyte - namely, a two step reduction chronopotentiogram. Oxidation of a reduced solution of perchloric acid in acetic anhydride electrolyte (three hours after mixing perchloric acid with acetic anhydride) shows only a single potential pause, at 0.0 V vs. ref. - the oxidation of hydrogen gas (Fig. II-18) - in the oxidation chronopotentiogram.

A reduced solution of acetylium perchlorate in acetic anhydride electrolyte shows, on reversal of current, a similar oxidation chronopotentiogram (Fig. II-19). The potential pause is at 0.0 V vs. ref. and is the oxidation of hydrogen gas.

Chronopotentiogram for the reduction of hydrogen ions and for the oxidation of hydrogen gas in acetic anhydride electrolyte.

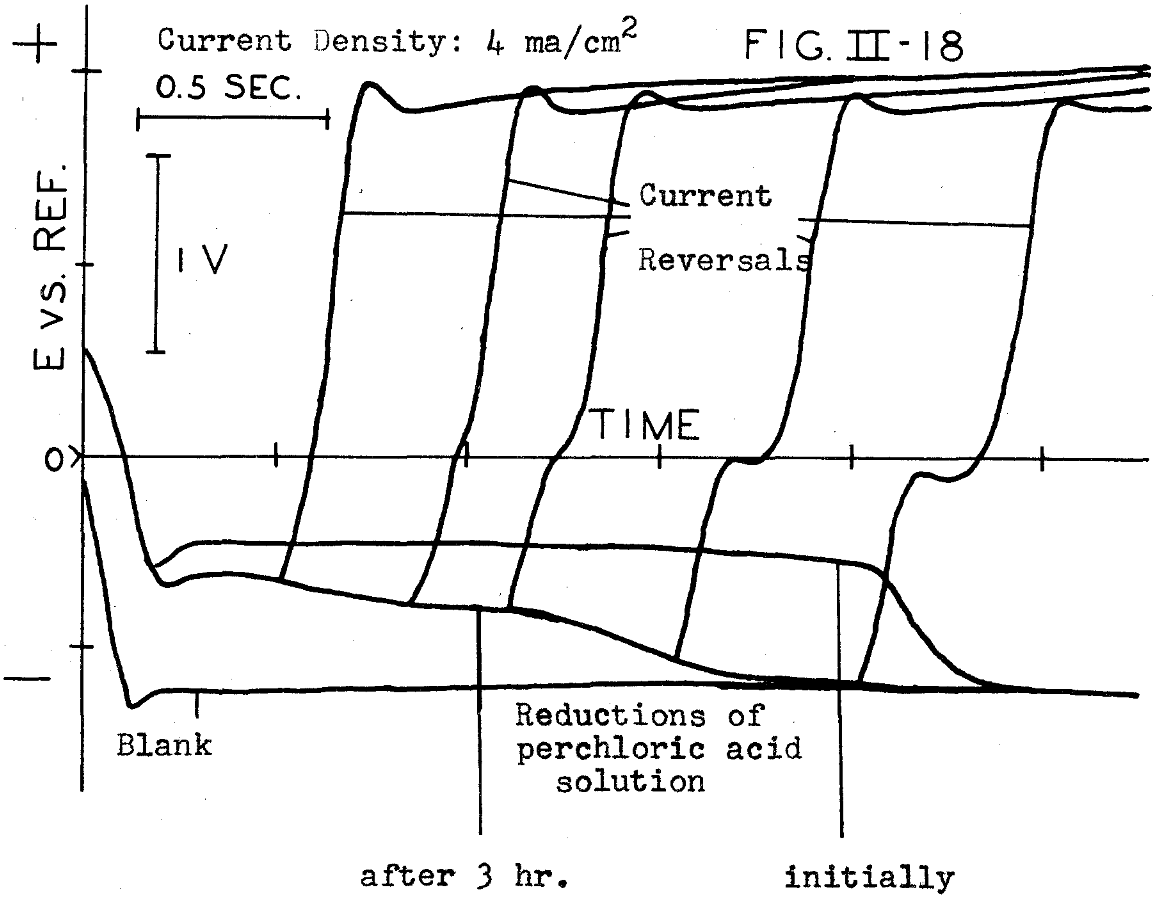


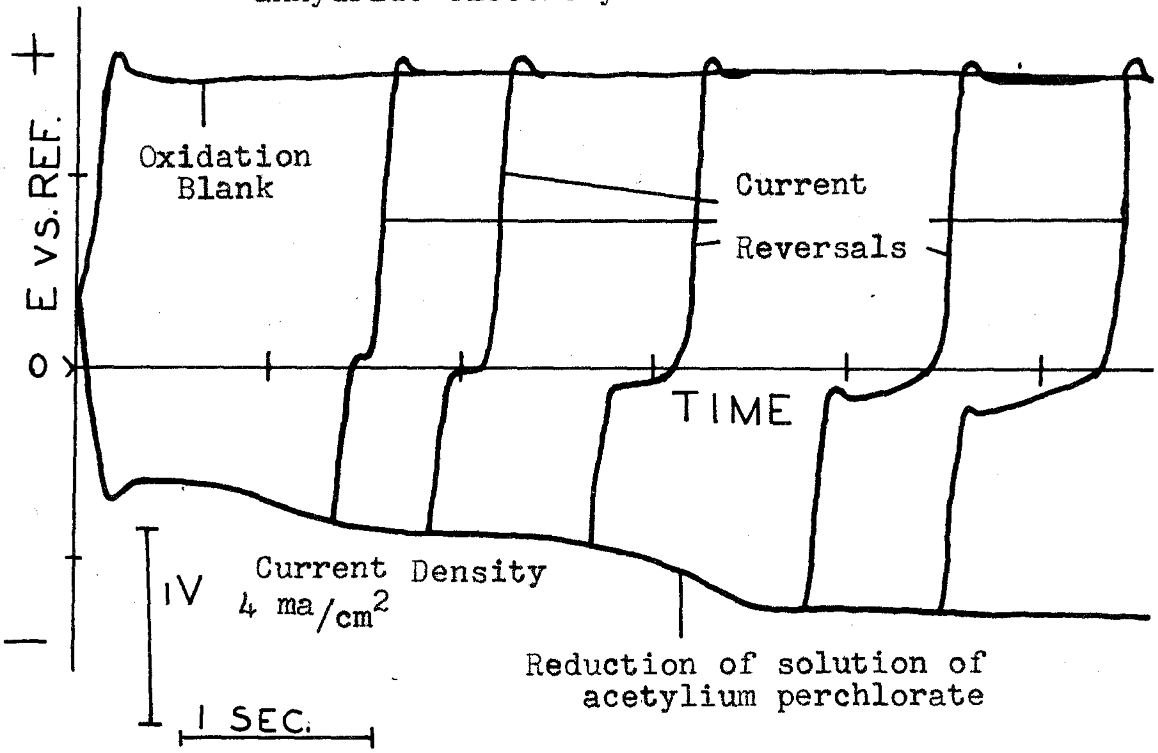
FIG. II-18

Current reversals shown at various points on the reduction potential pause of a solution of perchloric acid in acetic anhydride electrolyte.

0.015 VF perchloric acid in 90 ml acetic anhydride electrolyte allowed to stand 3 hr. before current reversal study.

Potential pauses at -0.5V vs. ref. and -0.8 V vs. ref. (reductions) and ca. 0.0 V vs. ref. (oxidations).

Chronopotentiogram for the reduction of a solution of acetylium perchlorate and oxidation of hydrogen gas in acetic anhydride electrolyte.



Current reversals shown at various points on the reduction potential pause of a solution of acetylium perchlorate in acetic anhydride electrolyte.

0.025 VF acetylium perchlorate in 90 ml acetic anhydride electrolyte.

Potential pauses at -0.6 V vs. ref. and -0.8 V vs. ref. (reductions) and ca. 0.0 V vs. ref. (oxidation).

FIG. II-19

Chronopotentiometric studies of the condensation reaction

The disappearance of hydrogen ions from the perchloric acid-acetic anhydride mixture has been followed by volumetric and coulometric titrations. Since the transition time for a diffusion controlled electrode reaction is proportional to the square of the concentration of the electroactive species, the disappearance of hydrogen ions from the reaction mixture can also be followed chronopotentiometrically.

Figure II-20 shows a chronopotentiometric study of the reduction of a solution of perchloric acid in acetic anhydride at various times after mixing. Little change is observed in the first few minutes - as the water in the conc. $HClO_4$ reacted with the acetic anhydride. The shift in the background reduction potential (reduction of acetic acid) is due to the increased acetic acid concentration (from the reaction of the water with acetic anhydride). The reduction of perchloric acid occurs at -0.5 V vs. ref. as seen before. After 50 min. a second potential pause is seen at -0.8 V vs. ref., the reduction of the protonated form of the first condensation product. The transition time for this second potential pause increases at the expense of the reduction pause of perchloric acid, but there is an overall decrease in the total transition time. The explanation of this behavior is probably the following: initially the perchloric acid (solvated) is reduced.

Chronopotentiogram for the reduction of a solution of perchloric acid at various times after mixing with acetic anhydride electrolyte.

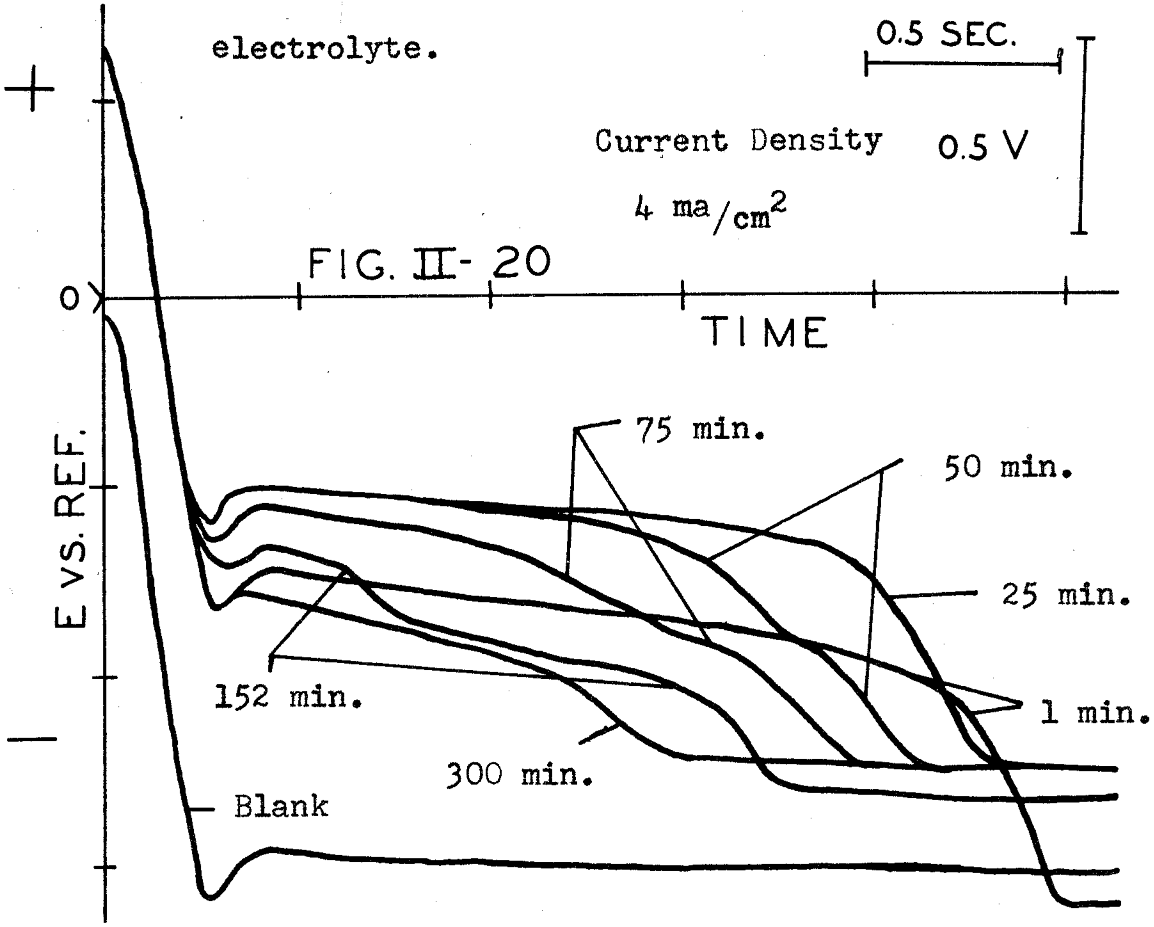


FIG. II- 20

Curves taken at various times (in minutes) after mixing perchloric acid with acetic anhydride electrolyte.

Solution initially 0.015 VF perchloric acid in 90 ml acetic anhydride electrolyte.

Potential pauses at -0.5 V vs. ref. and -0.8 V vs. ref.

As time passes the condensation of acetylium ion with acetic anhydride proceeds - reduction of this solution shows two potential pauses, reduction of a strong acid at -0.5 V vs. ref. (perchloric acid) and a weaker acid at -0.8 V vs. ref. (the protonated form of the first condensation product). As more time passes the condensation continues with the formation of higher, less dissociated condensation products. These slightly dissociated condensation products are not reduced before the electrolyte background. There is an over-all decrease in the transition time as these products form.

In acidimetric titrations of perchloric acid in acetic anhydride, the amount of acid determined depends on the acidity of the titration solution. This can be seen by mentally shifting the electrolyte background reduction potential in Fig. II-20. As the acidity of the electrolyte is increased (background reduction potential shifted upward on the figure), the reduction potential pauses disappear. This disappearance of the reduction potential pauses occurs as the solution becomes as acidic as the various condensation products. Only for acids considerably stronger than the solution is an end point observed in the acidimetric titrations with sodium acetate. For low concentrations of acetic acid in acetic anhydride, both perchloric acid and the protonated form of the first condensation product are titrated with sodium acetate, only the slightly dissociated, higher condensation products are lost. As the acidity of the solvent is increased (by increasing the concentration of acetic acid or sodium perchlorate), it becomes harder to observe an end point for the titration of the protonated form of the first condensation product. As the acidity of the solvent increases further, the error in the determination of this end point increases until the end point is almost indistinguishable.

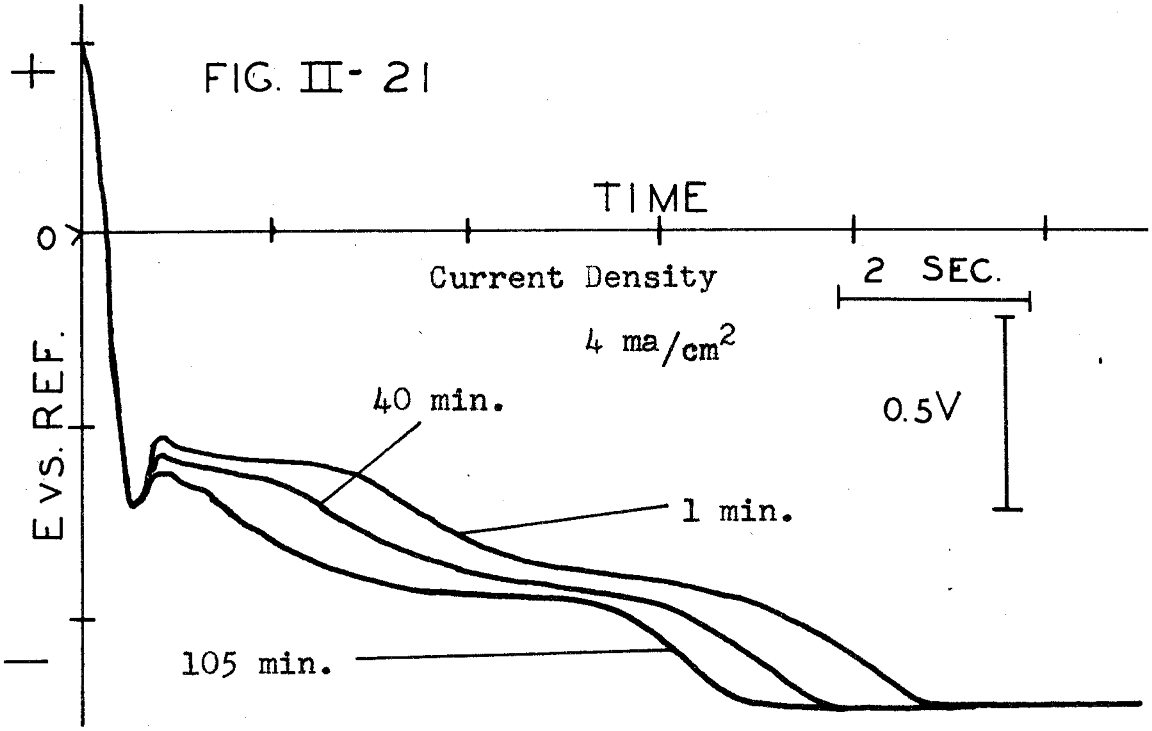
The decrease of perchloric acid concentration is seen also in the reaction of acetylium perchlorate with acetic anhydride electrolyte (Fig. II-21). A more rapid decrease in the transition time for the reduction of perchloric acid is observed than in Figure II-20. This is because at higher acetylium ion concentrations the condensation is more rapid. There is a very distinct potential pause for the reduction of the protonated form of the first condensation product. There is also a decrease in the total transition time as the less dissociated higher condensation products form.

Fluoboric acid is a much weaker acid than perchloric acid in acetic anhydride. The condensation is much slower. Figure II-22 shows the reduction of a mixture of fluoboric acid and acetic anhydride electrolyte at several times after mixing. There is only a slight decrease in the overall transition time after 2-1/2 hours.

The reduction of oxidized acetic anhydride electrolyte showed the same behavior as the reduction of perchloric acid in acetic anhydride (Fig. II-16 and II-20). At longer oxidation times (> 20 sec.) the transition time for the reduction of perchloric acid decreased as

Chronopotentiogram for the reduction of a solution of acetylium perchlorate at various times after mixing with acetic anhydride electrolyte.

FIG. II- 21



Curves taken at various times (in minutes) after preparation of the solution of acetylium perchlorate in acetic anhydride electrolyte.

Solution initially 0.04 VF acetylium perchlorate in 90 ml acetic anhydride electrolyte.

Potential pauses at -0.5 V vs. ref. and -0.8 V vs. ref.

Chronopotentiogram for the reduction of a solution of fluoboric acid at various times after mixing with acetic anhydride electrolyte.

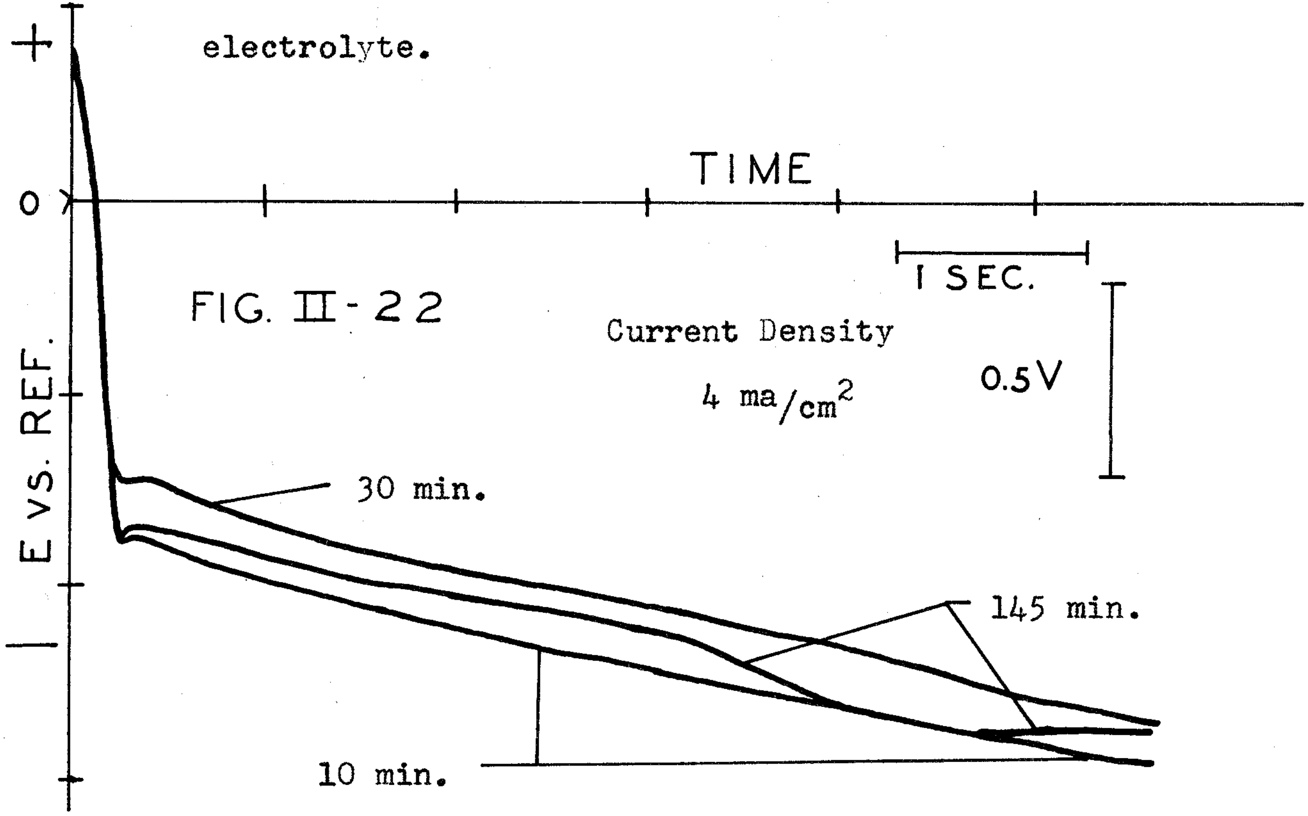


FIG. II-22

Curves taken at various times (in minutes) after mixing fluoboric acid with acetic anhydride electrolyte.

Solution initially 0.02 VF fluoboric acid in 90 ml acetic anhydride electrolyte.

Potential pause at -0.9 V vs. ref.

the transition time for the reduction of the protonated form of the first condensation product increased. This behavior indicates that the condensation in the vicinity of the electrode is fairly rapid, for such changes in the transition times of the two reduction potential pauses, seen after 40 sec. oxidation, were seen only after several hours in the case of perchloric acid-acetic anhydride mixtures. The difference in the rates of condensation is probably due to the increased acetylium ion concentration near the electrode. The homogeneously distributed perchloric acid solutions were 0.025 VF in $HClO_4$ and 0.2 VF in acetic acid. The concentration of perchloric acid and acetylium ion in the immediate vicinity of the electrode at the end of a 40 second oxidation period was about 0.4 VF. Since the rate of condensation depends linearly on the hydrogen ion concentration, it should be much faster at this higher acid concentration. Also, the rate of condensation is inversely proportional to the acetic acid concentration, which decreases near the electrode during oxidation.

The rapid condensation near the electrode is even better seen at higher acid concentrations. A mixture of perchloric acid and acetic anhydride was oxidized and the current reversed (Fig. II-23). The reduction chronopotentiogram shows no increase in perchloric acid concentration even at short oxidation times (> 5 sec.). The residual perchloric acid concentration stays about constant. At longer oxidation times only an increase in the transition time for the reduction of

Chronopotentiogram for the reduction of an oxidized solution of perchloric acid in acetic anhydride electrolyte.

Oxidation time (in seconds) before current reversal given with the curves.

Potential pauses at -0.5 V vs. ref. and -0.8 V vs. ref.

0.018 VF perchloric acid in 90 ml acetic anhydride electrolyte within 30 min. of mixing.

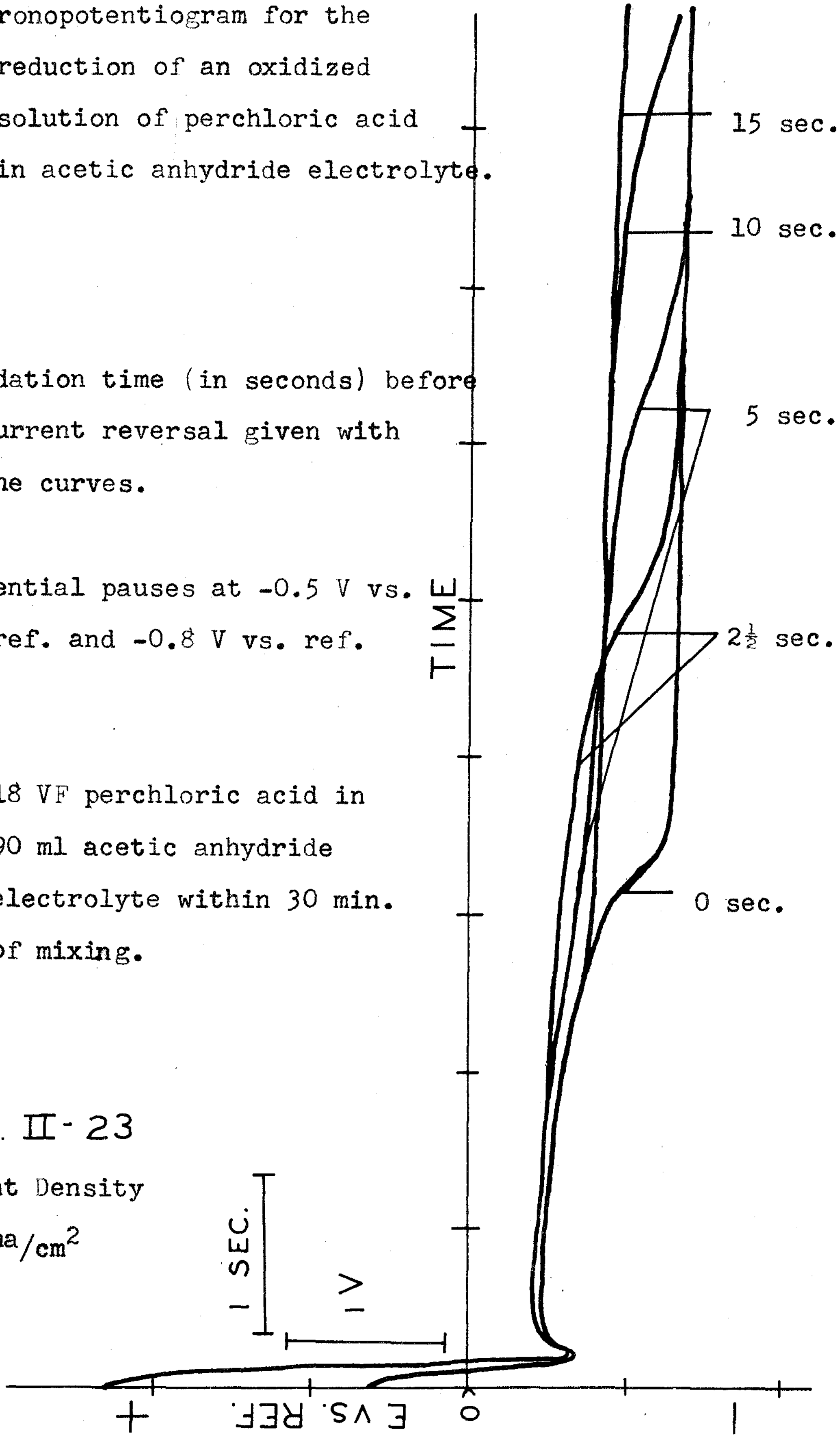


FIG. II-23

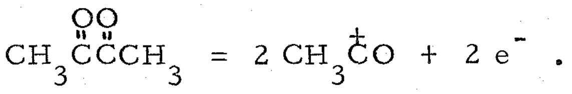
Current Density

4 ma/cm^2

the protonated form of the first condensation product is observed. The oxidation of the electrolyte forms acetylium which reacts almost immediately with the acetic anhydride. There is no significant formation of perchloric acid in the electrode reaction at this low acetic acid concentration.

Acetic acid suppresses the condensation reaction by decreasing the concentration of acetylium ion. When acetic acid was added to the acetic anhydride electrolyte, the mixture oxidized and then reduced, the reduction chronopotentiogram, shown in Fig. II-24, results. The double reduction potential pause, corresponding to the reduction of perchloric acid and the protonated form of the first condensation product, becomes only the single potential pause of the reduction of perchloric acid as the concentration of acetic acid is increased.

One final study of this condensation was the reduction of an oxidized solution of biacetyl in acetic anhydride (Fig. II-25). The product of the oxidation of biacetyl (2, 3 Butanedione) was, most likely, acetylium ion:



$$CH_3\overset{O}{\overset{\parallel}{C}}\overset{O}{\overset{\parallel}{C}}CH_3 = 2\,CH_3\overset{+}{C}O + 2\,e^- \;.$$

The acetylium ions react with acetic acid near the electrode to give perchloric acid or with the solvent to give the protonated form of the first condensation product. In the long oxidations the concentration of

Effect of acetic acid concentration on the chronopotentiogram for the reduction of an oxidized solution of acetic anhydride electrolyte.

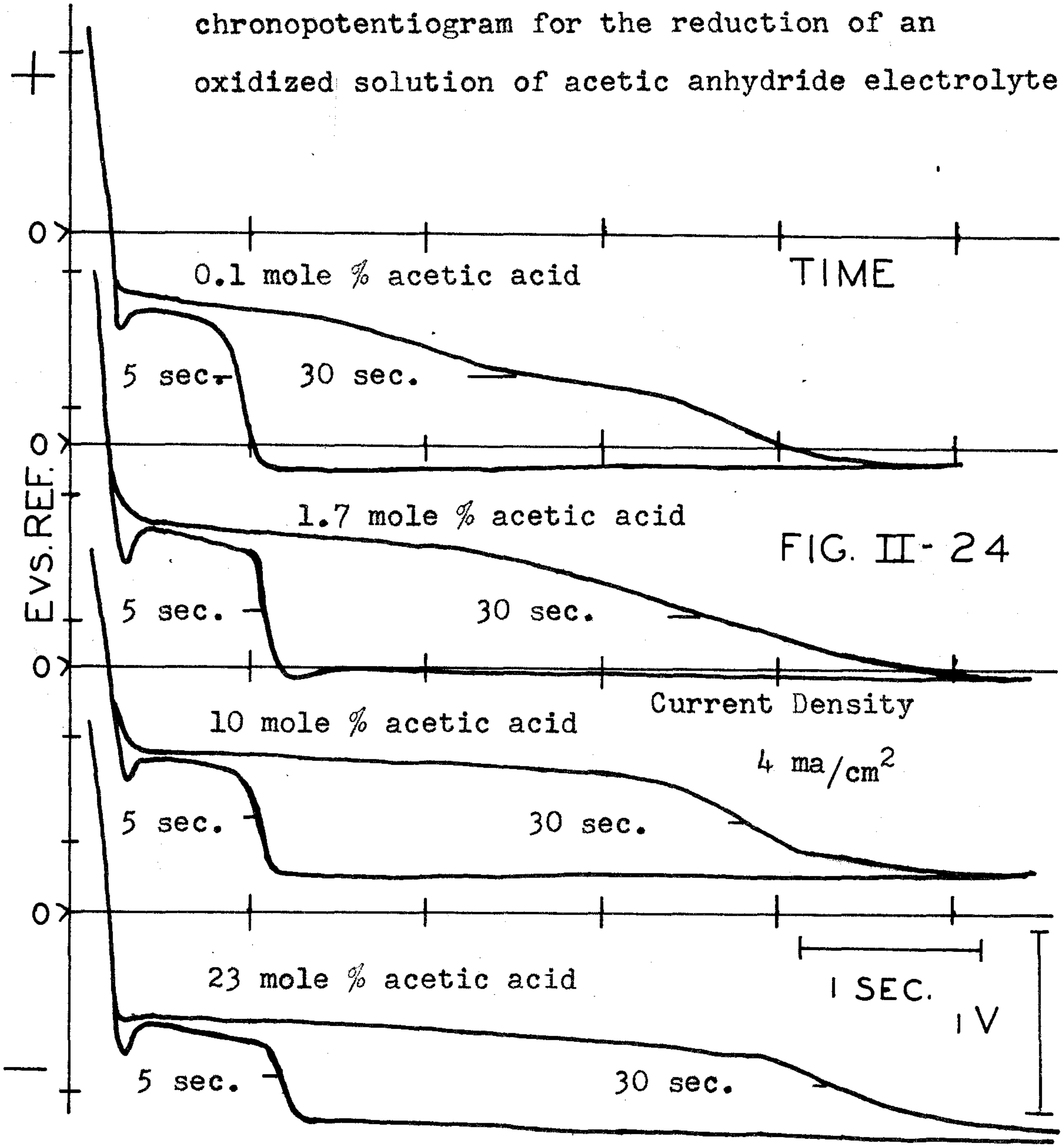


FIG. II-24

Oxidation time (in seconds) before current reversal given with the curves.

Potential pauses at -0.5 V vs. ref. and -0.8 V vs. ref.

90 ml acetic anhydride-acetic acid electrolyte taken . The concentration of acetic acid present in the electrolyte given in mole %.

Chronopotentiogram for the reduction of an oxidized solution of biacetyl (2,3-butanedione) in acetic anhydride electrolyte.

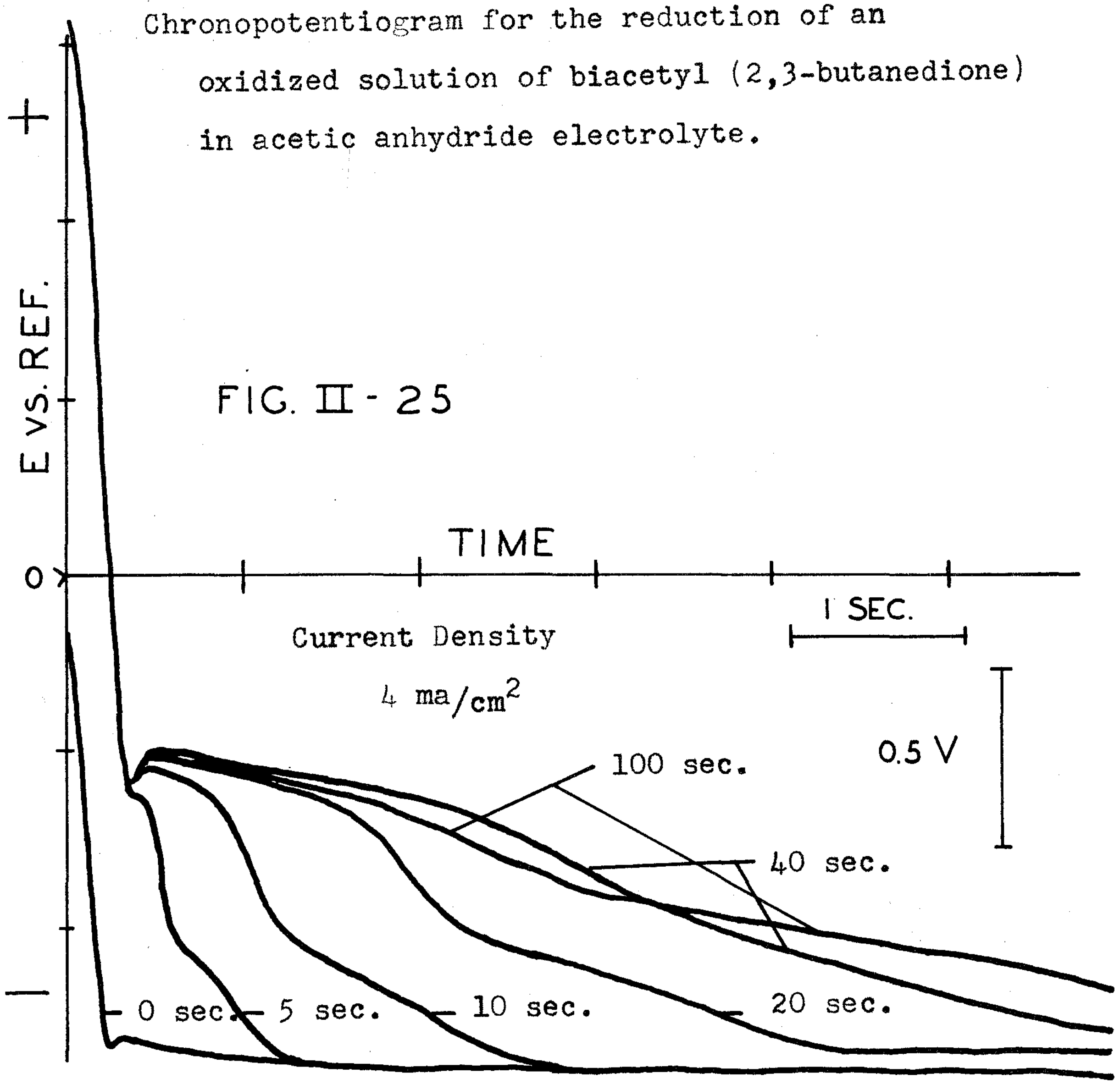


FIG. II - 25

Oxidation time (in seconds) before current reversal given with the curves.

Potential pauses at -0.5 V vs. ref. and -0.8 V vs. ref.

0.2 VF biacetyl in 90 ml acetic anhydride electrolyte.

acetylium generated at the electrode approaches the acetic acid concentration (near the electrode) and the condensation reaction predominates.

Conclusion

Sufficient experimental evidence has been presented to lend credibility to the proposed hypothesis of reactions which occur at and around platinum electrodes in acetic anhydride solutions.

The observed loss of perchloric acid generated at a platinum anode in the coulometric-acidimetric titrations of bases in acetic anhydride is attributed to a condensation of acetylium with acetic anhydride forming weakly acidic products. This condensation occurs when local excesses of perchloric acid form near the electrode. In these regions the acetylium ion concentration is high enough for the condensation to occur rather rapidly.

Such local excesses of perchloric acid were probably avoided when mercurous ions were generated at the electrode in basic solutions. It is likely that the mercurous ions were able to diffuse away from the electrode before reacting slowly with acetic acid to form hydrogen ions. These hydrogen ions reacted rapidly with the base present in the solution. In acidic solutions oxidation of a mercury electrode showed, qualitatively, the same behavior as the oxidation of the electrolyte at a platinum electrode, but to a lesser degree.

Oxidation of hydrogen gas or hydroquinone at the platinum anode would produce hydrogen ions in excess near the electrode and the condensation would occur. Perchloric acid was generated with 88% efficiency from the oxidation of hydrogen gas.

From these studies of reactions which occur at and around a platinum electrode in acetic anhydride electrolyte, the conclusion can be drawn that a coulometric-acidimetric titration, using the direct generation of hydrogen ions at a platinum electrode in acetic anhydride, cannot be performed satisfactorily. Although there may be more involved alternant procedures for accomplishing such titrations, the success achieved with the mercury anode makes such alternatives unappealing.

APPENDIX I - Reductions in Acetic Anhydride

Chronopotentiometric reduction studies were used to establish an acidity scale in part II of the thesis. In these studies the reduction potentials of several acids were found to be related to the strength of the acid. A reduction potential pause was observed for hydrogen ion at a potential related to the degree of dissociation of the acid in acetic anhydride. The potential pause for the reduction of hydrogen ion was followed by the potential pause for the reduction of acetic acid. Perchloric acid, fluoboric acid and hydrochloric acid all exhibited this behavior, but sulfuric acid did not.

Anomalous behavior was observed in the reduction of conc. sulfuric acid in acetic anhydride electrolyte (Fig. A-1). With the addition of sulfuric acid to the acetic anhydride electrolyte, a potential pause was observed at -1.0 V vs. ref., but the potential pause for the reduction of acetic acid disappeared. Instead the potential became more reducing until something was reduced at -3.0 V vs. ref. The reduction at -1.0 V vs. ref. is the reduction of sulfuric acid to hydrogen gas and bisulfate.

Why the reduction potential pause for acetic acid should disappear is not at all obvious. One suggestion is the following: sulfuric acid is probably more closely associated with acetic acid than acetic

Chronopotentiogram for the reduction of a solution of sulfuric acid in acetic anhydride electrolyte.

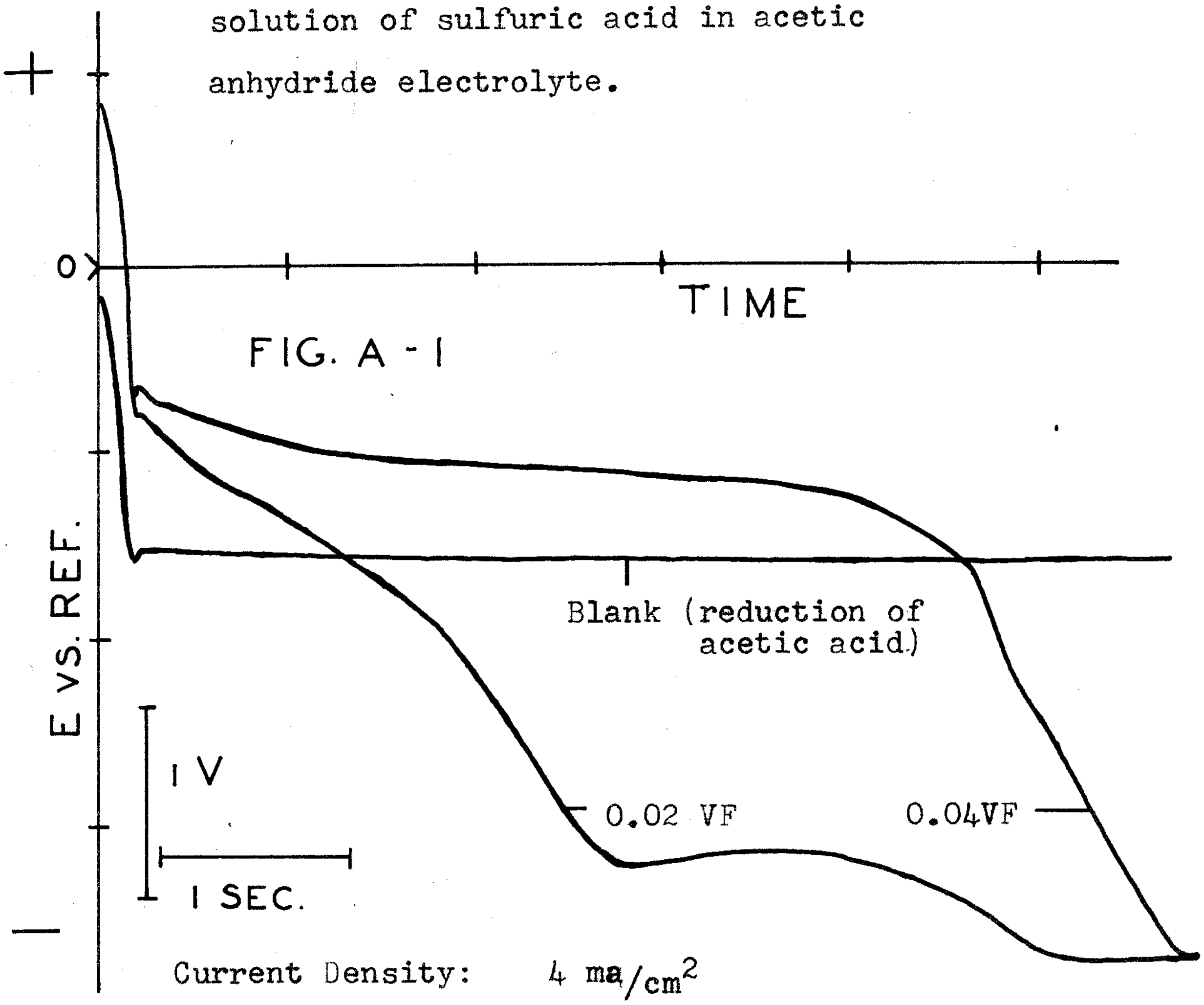


FIG. A - 1

Concentration of sulfuric acid in 90 ml acetic anhydride electrolyte given with the curves.

Potential pause at -1.0 V vs. ref. is the reduction of sulfuric acid. Potential pause at -1.6 V vs. ref. is the reduction of acetic acid. Note disappearance of this latter pause on addition of sulfuric acid.

anhydride because of the greater opportunities for hydrogen ion transfer between sulfuric acid and acetic acid. What little acetic acid is present in the acetic anhydride electrolyte (< 0.1 VF acetic acid) is probably coordinated with the sulfuric acid (> 0.02 VF). The reduction of sulfuric acid in the acetic anhydride electrolyte (0.1 VF in sodium perchlorate) leads to the formation of the sparingly soluble (in acetic anhydride) sodium bisulfate. This salt precipitates and with it precipitates the acetic acid, closely associated with the bisulfate ion in the sodium bisulfate crystal. Thus, there is no acetic acid left in the vicinity of the electrode to be reduced and the potential of the cathode becomes more reducing until the next electrode process occurs. Further work is needed to test this hypothesis, but it seems like the most reasonable explanation of the rather strange disappearance of acetic acid.

A brief investigation of reduction chronopotentiometry in acetic anhydride showed that a transition time could be observed for the reduction of acetic acid (Fig. A-2). Because of the higher concentrations involved (ca. 0.1 VF acetic acid instead of ca. 0.025 VF solutions, as studied in part II) higher current densities (20 ma/cm^2 instead of 4 ma/cm^2) were used to obtain transition times less than 10 sec. After the transition time for the reduction of acetic acid very reducing potentials were reached.

Chronopotentiogram for the reduction of the small amount of acetic acid in acetic anhydride electrolyte.

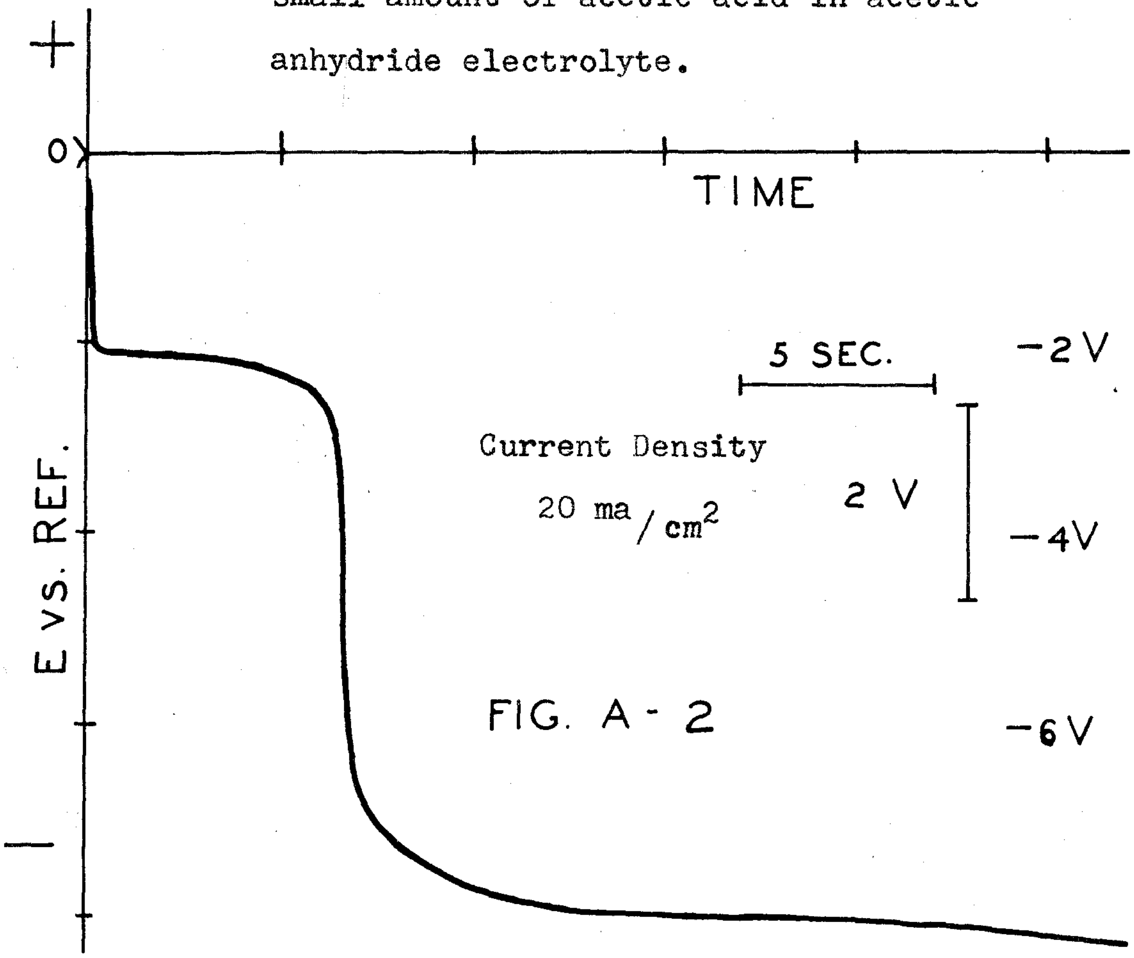


FIG. A - 2

0.1 VF acetic acid in 90 ml acetic anhydride electrolyte.

Potential pause at -2.1 V vs. ref. is the reduction of acetic acid at this current density and concentration of acetic acid.

Note the rather high reducing potentials apparently attained.

Observations of the electrode during the reduction evidenced gas formation (hydrogen) and, after the transition time for the reduction of acetic acid, at higher potentials, a dark material on the electrode surface. When the current flow was stopped, this dark material floated towards the surface. Before reaching the surface, the substance reacted with the solvent evolving a gas (probably hydrogen). The actual identity of this material was not determined but it could have been sodium metal, produced in the reduction of sodium perchlorate.

Small amounts of acetic acid in acetic anhydride can be determined by reduction chronopotentiometry. This has been done in part II of this thesis (page 32 and Fig. II-2).

The acetic anhydride electrolyte, on standing, slowly absorbs water to form acetic acid (Fig. A-3). A shift is observed in the background reduction potential to less reducing potentials (reduction of water?).

Attempts were made to remove the last traces of acetic acid from acetic anhydride electrolyte by reacting magnesium or sodium with the acetic acid to form the respective acetates. Figure A-4 shows the solution obtained with the shortest transition time for the reduction of acetic acid. This solution was prepared by reacting the acetic anhydride electrolyte with a sodium-lead alloy. As seen in Figure A-4, the transition time for the reduction of acetic acid is

Chronopotentiogram for the reduction of acetic acid in acetic anhydride electrolyte. Effect of standing on the transition time for the reduction of acetic acid.

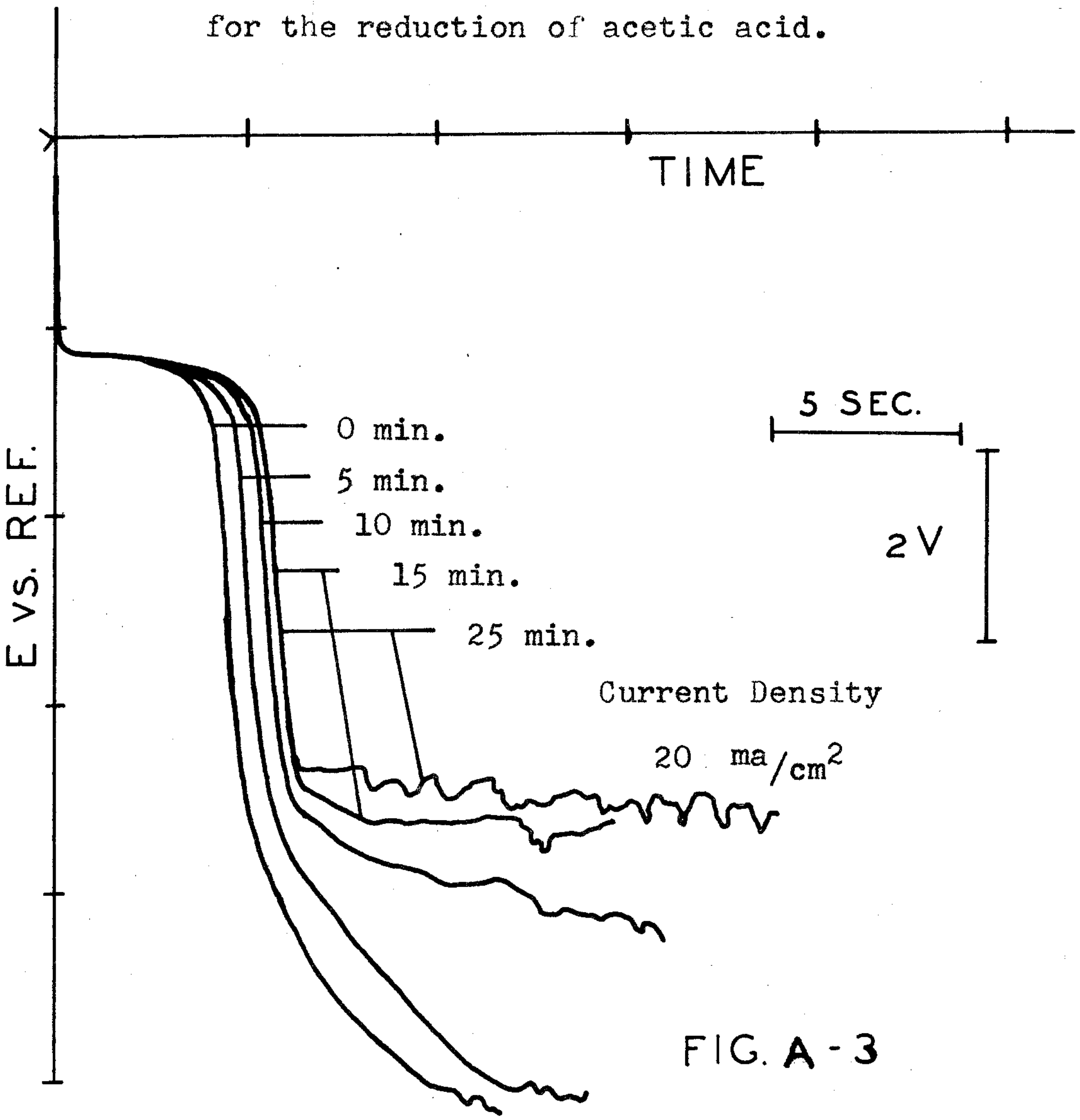


FIG. A-3

Initially 0.08 VF acetic acid in 90 ml acetic anhydride electrolyte.

Solution allowed to stand in room atmosphere and curves taken at various times given (in minutes) from solution preparation.

Chronopotentiogram for the reduction of acetic acid in acetic anhydride electrolyte which has stood several days over sodium-lead alloy.

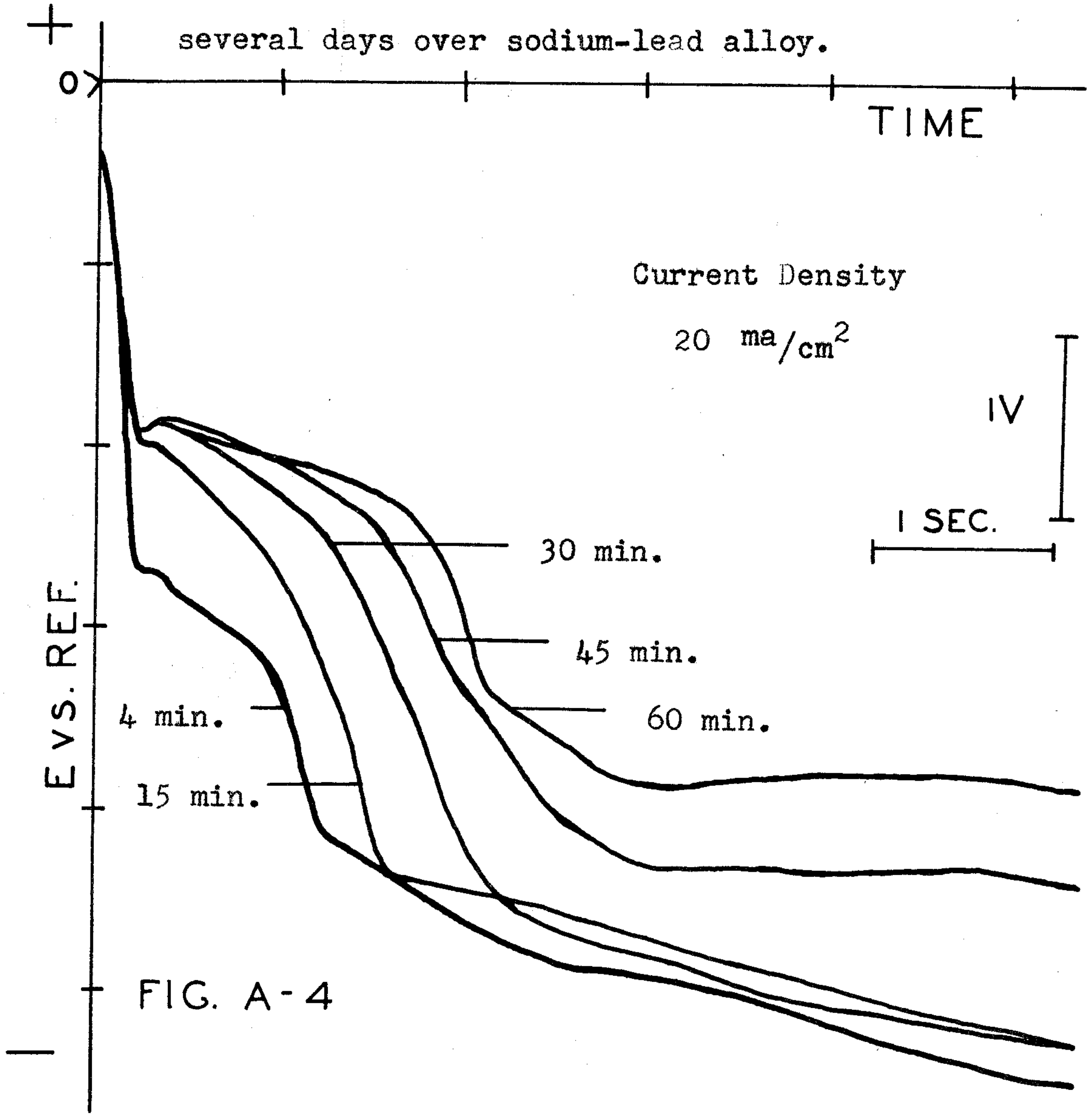


FIG. A-4

Initially 0.08 VF acetic acid in acetic anhydride electrolyte reduced to 0.03 VF on standing several days over sodium-lead alloy.

Solution allowed to stand in room atmosphere and curves taken at various times (in minutes) given with the curves.

only one second at 20 ma/cm^2. Before reacting the electrolyte solution with the sodium lead alloy, the transition time for the reduction of acetic acid was seven seconds at this current density - see Figure A-2. Since the transition time is proportional to the square of the concentration, the reduction of the concentration of acetic acid, by the addition of the sodium-lead alloy, is by a factor of $\sqrt{7}$. This is good, but there should be better ways of removing the acetic acid - ways which do not involve the formation of such high concentrations of base (sodium acetate) in the acetic anhydride. One possibility would be to distill the acetic anhydride from the sodium-lead alloy-acetic anhydride mixture at reduced pressure and moderate temperature (ca. 50°C). Solutions of acetic anhydride electrolyte with very little acetic acid pick up water quite rapidly to form acetic acid (Fig. A-4).

Gutmann and Nedbalek have used "acetic acid free" acetic anhydride for polarographic reductions of a number of salts (17). They claim to reduce lithium, sodium and several tetraalkylammonium ions to the mercury amalgams. From the potentials given it seems to this author that they are merely reducing the small amounts of acetic acid which would be difficult to remove even in a vacuum distillation with 25 plate equivalent efficiency (18). Even a small amount (ca. $5x10^{-3}$ VF) of acetic acid would give the results obtained in the polarographic reductions of various solutions of metal salts. The potential at which the acetic acid would be reduced would depend on the acidity of the particular metal salt being studied. For example, lithium perchlorate is more acidic than sodium perchlorate and it was observed that the lithium perchlorate solution was more easily reduced than the sodium perchlorate solution.

Some of the very reducing potential observed was due to the iR potential of the chronopotentiometric cell. Figure A-5 shows the effect of current density on the oxidation of the acetic anhydride electrolyte. The effect of current density on potential should be:

$$E = b + a \log i + ci$$

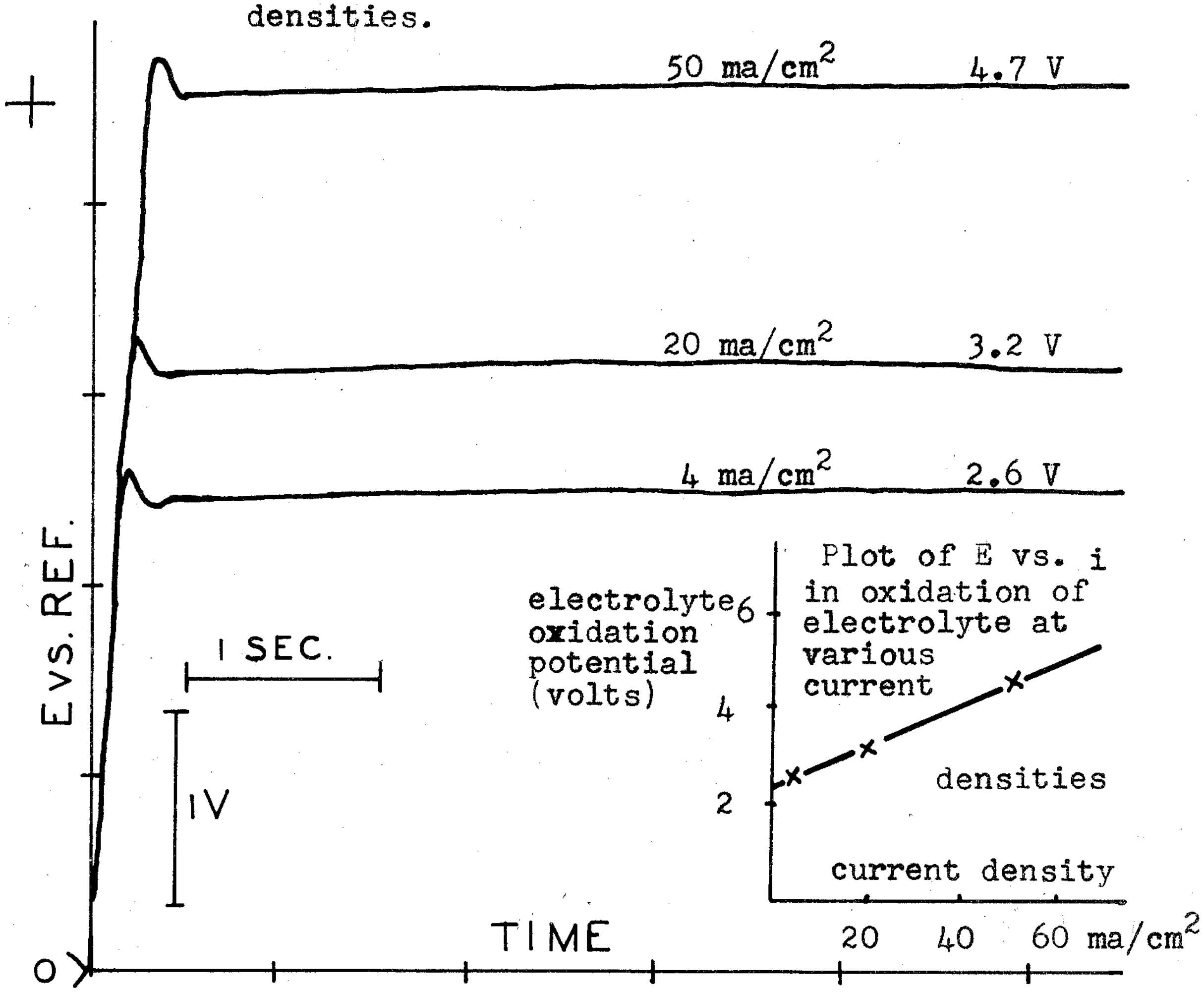
where b, a, and c are constants

E = potential of the oxidation of the electrolyte

i = current density

The approximate linearity of the E vs. i curve shows that the (a log i) term must be negligible compared to (ci). The (ci) term is related to the iR potential of the cell. Studies of reductions in acetic anhydride electrolyte were performed at current densities of 20 ma/cm^2. This corresponds to (ci) $\approx$ 1 volt. Liquid junction potential and overvoltage for the reduction of acetic acid might contribute another volt to the chronopotentiogram of the reduction of the acetic anhydride electrolyte (Fig. A-2). Still, rather high reducing potentials are observed.

Chronopotentiogram for the oxidation of acetic anhydride electrolyte at various current densities.



Curves taken at various current densities.

90 ml acetic anhydride electrolyte taken.

Contribution to observed oxidation potential from iR potential of the solution ca 1 V at 20 ma/cm^2.

FIG. A-5

Rather high reducing potentials may be reached in acetic anhydride because acetic anhydride itself is not reduced, possibly before even sodium ion. These high reducing potentials attainable in acetic anhydride should enable one to use this solvent in reductions of substances which cannot be reduced in more easily reducible solvents. To use acetic anhydride for reductions of this nature, all acetic acid should be removed and care taken to prevent the solvent from absorbing water. Also the fairly reactive nature of acetic anhydride as an acylating agent should be kept in mind. Unfortunately, most inorganic substances are sparingly soluble in acetic anhydride, but the solvent should find use in the reduction of many organic compounds.

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PROPOSITIONS

1. Anodic Acetylations

A method of anodic acetylation is proposed in which acetylium perchlorate (or acetic anhydrium perchlorate) is formed at a platinum anode by the oxidation of hydrogen gas in a solution of sodium perchlorate and acetic acid in acetic anhydride. A number of organic compounds can be acetylated by the acetylium perchlorate so formed.

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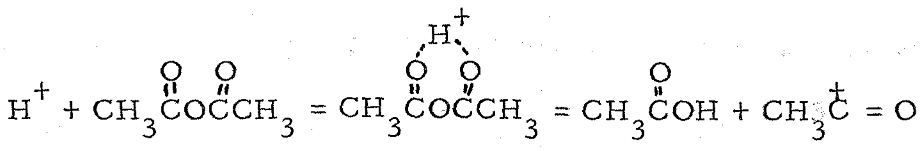
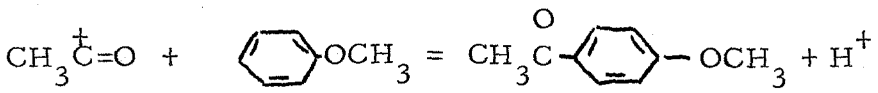
Background for proposition

Allen has discussed several anodic substitutions in his book, "Organic Electrode Processes (1). In these substitution reactions there is no net change in electrons in the substitution product. The electrode reaction serves merely as a means of forming the substituting species. One advantage of the electrode process producing the substituting species is that of concentrating the active species near the electrode surface. Higher concentrations of active species near the electrode might be possible than would be attainable if an attempt were made to distribute the active species uniformly throughout the solution. Reaction rates can be controlled by controlling the rate of generation of the active species (by controlling the current density) and the rate of transfer of material to be substituted toward the electrode (by controlling the rate of stirring). Allen mentions a number of anodic substitutions which have been accomplished: halogenation, thiocyanation and nitration. Another such substitution is proposed, namely, anodic acetylation.

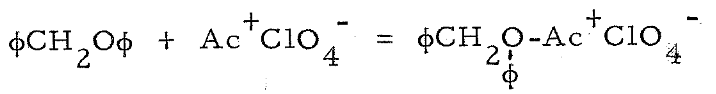
Burton and Praill, in a series of papers, have described the use of acetylium perchlorate (or acetic anhydrium perchlorate) as an O- or C- acetylating agent. This acetylating agent has been prepared by mixing perchloric acid with acetic anhydride (2) or silver perchlorate with acetyl chloride (3) and has been used to acetylate anisole to p-methoxy acetophenone. In the presence of excess acetic anhydride, more than stoichiometric yields of the ketone were observed, based on the amount of perchloric acid present. Perchloric acid had a catalytic effect:



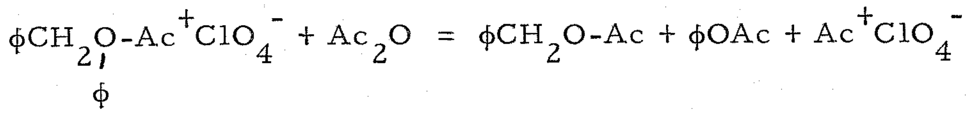
$$H^+ + CH_3\overset{O}{C}O\overset{O}{C}CH_3 = \overset{H^+}{CH_3\overset{O}{C}O\overset{O}{C}CH_3} = CH_3\overset{O}{C}OH + CH_3\overset{+}{C} = O$$



O-acetylations were also accomplished with acetylium perchlorate (4). Benzyl phenyl ether forms an oxonium salt with acetylium perchlorate which, on reaction with acetic anhydride, yields benzyl acetate and phenyl acetate:



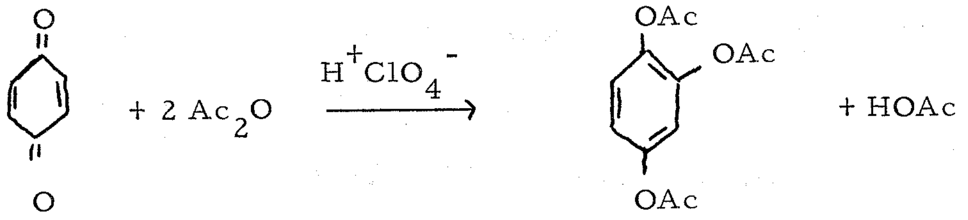
$$\phi CH_2O\phi + Ac^+ClO_4^- = \phi CH_2\underset{\phi}{O}\text{-}Ac^+ClO_4^-$$



$$\phi CH_2\underset{\phi}{O}\text{-}Ac^+ClO_4^- + Ac_2O = \phi CH_2O\text{-}Ac + \phi OAc + Ac^+ClO_4^-$$

(Ac. represents the acetyl radical CH_3CO)

Other acetylation reactions studied included the acetylation of simple quinones (5):



This latter work confirmed earlier studies by Mackenzie and Winter on the perchloric acid catalyzed acetylation of quinone and toluquinone in acetic acid-acetic anhydride solution (6).

Benzene was found to be much less reactive toward acetylium perchlorate than toluene which was much less reactive than m-xylene (7). The reaction of acetylium perchlorate occurred more readily with acetic anhydride than with benzene or toluene.

Allyl phenyl ether was found to substitute acetylium to form p-allyloxyacetophenone (8).

Acetylations of thiophene and anisole have been accomplished in furan with a mixture of acetic anhydride and perchloric acid (9).

Milder conditions have been used in the formation of acetylium perchlorate for acetylation of rings (10). Monohydric, dihydric and trihydric phenol ethers were acetylated with a mixture of sodium perchlorate, acetic anhydride and acetyl chloride in acetic acid.

Part II of this thesis has been an investigation of reactions which occur at and around a platinum electrode in acetic anhydride-acetic acid-sodium perchlorate solutions (11). Some evidence has been presented for a reaction of acetylium perchlorate (or acetic anhydrium perchlorate) with acetic anhydride near the platinum anode. This electrochemical method of producing acetylium perchlorate, namely, the oxidation of the acetic anhydride electrolyte, might be used to advantage in the anodic acetylation of many of the organic compounds studied above. Unfortunately, the high oxidation potentials needed to oxidize the electrolyte would oxidize almost anything which could be easily acetylated.

An alternant method of generating perchloric acid at the electrode in acetic anhydride (hence of generating acetylium perchlorate) is the oxidation of hydrogen gas at a platinum anode. That the oxidation of hydrogen does lead to acetylium reactions has been seen in the low generation efficiency for hydrogen ions from the oxidation of hydrogen gas in acetic anhydride (12). This loss of generating efficiency is due to the reaction of acetylium perchlorate with acetic anhydride to form weakly acidic products.

Details of the proposition

An electrolysis cell, divided into two compartments by a sintered glass disc, is to be partially filled with a solution 0.5 VF in sodium perchlorate, 10 mole % acetic acid and 90 mole % acetic anhydride. The substance to be acetylated is added to the anode compartment. The anode is of platinum gauze of high surface area and the solution in the anode compartment is saturated with hydrogen gas, continuously bubbling through the solution. The solution is stirred. Electrolysis is performed with care being taken to see that the current density does not exceed the limiting current for hydrogen gas oxidation. This can be accomplished by observing the potential of the anode vs. some reference electrode.

Advantages of this method of acetylation

An advantage of this method of acetylation over external addition of perchloric acid is that the rate of reaction of acetylium ion can be controlled by controlling the rate at which it is produced (controlling the current density) or by controlling the rate of transfer of reactants toward and away from the electrode (by stirring at different speeds). Near the electrode - in a region of high acid concentrations - the acetylation reaction occurs fairly rapidly, but in the bulk of solution the acetylation occurs slowly. As long as there is an appreciable amount of substance to be acetylated present, the reaction of acetylium ion with acetic anhydride should not predominate (assuming that the substance to be acetylated is acetylated more easily than acetic anhydride). The electrolysis can be stopped whenever convenient and any further reaction will take place throughout the solution at much slower rate than in the region of high concentration of acid near the electrode during electrolysis.

In order to find out when to stop the electrolysis, the acetylation reaction should be followed with time. This could be done spectrophotometrically by observing the absorption maximum of either reactant or products of acetylation. Once the point of completion of the reaction has been ascertained under a given set of conditions, results could be repeated by generating the same amount of hydrogen ions under the same conditions and the same solution composition. Burton and Praill found that the yield of acetylation product, based on acid concentration, depended greatly on the solution composition (3).

If the electrolysis were not stopped when the desired reaction has taken place, reaction of acetylium ion with acetic anhydride would occur.

Another advantage of this acetylation technique is the possibility of working under less oxidizing conditions than with perchloric acid in acetic anhydride. The potential of the electrode depends on the ratio of concentration of acid to hydrogen gas, as long as the limiting current for hydrogen gas oxidation is not exceeded. The hydrogen ion in perchloric acid solutions is an oxidizing agent which can oxidize some organic compounds (e.g., ferrocene). The hydrogen gas decreases the oxidizing potential of the solution. When working with easily oxidized materials, low current densities should be employed.

Extensions of the method

Burton and Praill were able to form benzoyl perchlorate in the reaction of silver perchlorate with benzyl chloride and to use this reactive substance in acylation reactions (13). With benzoic anhydride and sodium perchlorate in acetic acid or acetonitrile, acylations should be possible similar to those proposed above.

2. Ammonia "Fuel" Cell

A low temperature (between 20° and 100°C) electrochemical device, operated on ammonia and air, could be made to supply low voltage (d.c.) power. Such a device would have some advantages over most hydrogen-oxygen fuel cells.

****

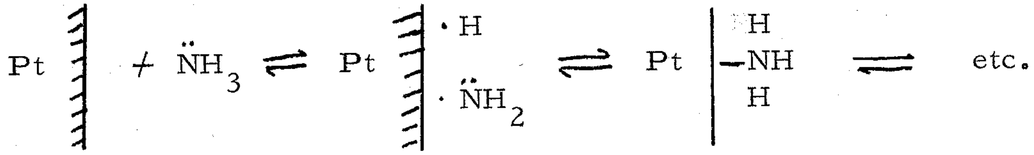
Background for the proposition

For the past 120 years scientists and others have attempted to convert chemical energy directly into electrical energy by means of a fuel cell. Only in the last fifteen years have there been any signs of success in this endeavor. Many review articles are available on this subject. Among the clearest are those by Austin (14) and by Young and Rozelle (15).

Ammonia is, strictly speaking, not a fuel. Liebhafsky and Douglas have restricted the word "fuel" to apply to fossil fuels and substances easily derived therefrom (16, 17). Ammonia could be used in a fuel cell in applications where fuel cost is not a major factor.

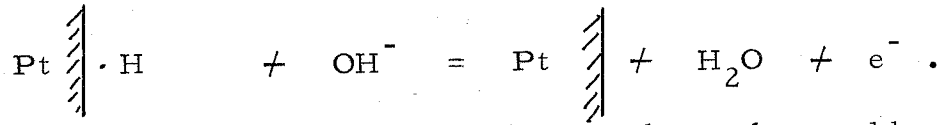
Hydrocarbon fuels would be ideal for use in the fuel cell except for three rather important factors: hydrocarbons are rather unreactive at room temperature; one product of the oxidation of hydrocarbons is carbon dioxide which contaminates the alkaline electrolytes of most fuel cells; and finally, there is some deactivation of the fuel electrode, when hydrocarbon fuels are used, from the formation of carbon deposits on the electrode surface. The second of the above conditions limits the use of carbon containing fuels to acid-electrolyte fuel cells (at least at low temperatures) - but the oxygen electrode of the fuel cell works best in an alkaline electrolyte (18).

Ammonia suffers less from the above limiting conditions than do the hydrocarbons. Ammonia is not unreactive at low temperatures (between 20° and 100°C). Kemball has shown that an exchange reaction between ammonia and deuterium occurs on the surface of platinum or rhodium at room temperatures (19). The exchange reaction proceeds via dissociative adsorption of ammonia on the metal surface:



$$\mathrm{Pt}| + \ddot{N}H_3 \rightleftharpoons \mathrm{Pt}\begin{matrix}\cdot H \\ \cdot \ddot{N}H_2\end{matrix} \rightleftharpoons \mathrm{Pt}\begin{matrix}H \\ -NH \\ H\end{matrix} \rightleftharpoons \text{etc.}$$

If a platinum electrode were used as the fuel electrode in an alkaline electrolyte, the electrode reaction of ammonia should involve the adsorbed hydrogen atoms as follows:



$$\mathrm{Pt}|\cdot H + OH^- = \mathrm{Pt}| + H_2O + e^- .$$

Eventually nitrogen atoms should combine on the surface and be evolved as nitrogen gas. The overall fuel electrode (anode) process is:

$$NH_3 + 3\,OH^- \xrightarrow[\text{Pt surface}]{} \frac{1}{2}\,N_2 + 3\,H_2O + 3\,e^- .$$

An alkaline electrolyte would be advantageous for using ammonia in a fuel cell. Ammonia has a limited but finite solubility in potassium hydroxide solutions. (The solubility of ammonia in 1.5 VF potassium hydroxide solutions has been reported as 0.607 VF at 25°C (20).) With ammonia in solution a two phase electrode reaction only need be considered. One of the serious problems in fuel cell work is to achieve a large three phase contact when using a gaseous fuel at a solid electrode with a liquid electrolyte (16).

Finally, it is hoped that the nitrogen atoms on the surface of platinum will combine with other nitrogen atoms rather than form a stable platinum nitride. Platinum nitride is formed normally only at elevated temperatures, on heating metallic filaments in nitrogen at 1100° to 1300°C(21).

Potential of the fuel electrode

The potential of a reversible ammonia-oxygen fuel cell can be calculated from data in Latimer's book, "Oxidation Potentials" (22):

ammonia-nitrogen gas half cell	E_o(22)	nE_o
$NH_3 + 2\,OH^- = NH_2OH + H_2O + 2\,e^-$	-0.42 V	-0.84 V
$NH_2OH + OH^- = \frac{1}{2}N_2 + 2\,H_2O + e^-$	3.04	3.04
$NH_3 + 3\,OH^- = \frac{1}{2}N_2 + 3\,H_2O + 3\,e^-$	0.733 V	2.20 V

oxygen-hydroxide ion half cell	E_o(22)
$\frac{3}{4}O_2 + \frac{3}{2}H_2O + 3\,e^- = 3\,OH^-$	0.401

cell reaction	E_o	
$NH_3 + \frac{3}{4}O_2 = \frac{1}{2}N_2 + \frac{3}{2}H_2O$	1.134	n=3

This is the standard potential of the reversible ammonia-oxygen fuel cell, and assumes all electrode processes completely reversible. If the reaction were reversible, it should be possible to reverse the cell and produce ammonia electrolytically. This has not been accomplished although the exact conditions proposed here may not have been investigated.

Probably the oxidation of ammonia is not completely reversible. It does not seem too likely that the energy of combination of the nitrogen atoms to form nitrogen molecules should contribute to the electrode potential. A more reasonable electrode reaction may be the oxidation of ammonia to give nitrogen atoms and water:

$$NH_3 + \frac{3}{4} O_2 = N + \frac{3}{2} H_2O \qquad \Delta F_o = 2.9 \text{ kcal} \quad (22)$$

and for a cell with this reaction $\qquad E_o = -0.04$ V .

The partial pressure of nitrogen atoms can be calculated from the dissociation of ammonia gas, assuming nitrogen atoms and hydrogen gas present in equilibrium concentrations from the dissociation:

$$NH_3 = N + \frac{3}{2} H_2 \qquad \Delta F_o = 87.9 \text{ kcal} \quad (22)$$

$$\log K = -63.6$$

$$\frac{[N]\ [H_2]^{3/2}}{[NH_3]} = 10^{-63.6}$$

let $[N] = x$, $[NH_3]$ 1 atm., then $[H_2] = \frac{3x}{2}$

$$\frac{(x)\ {\frac{3x}{2}}^{3/2}}{1-x} = 10^{-63.6}$$

$$(x)^{5/2} = 10^{-63.9}(1-x)$$

$$x \ll 1$$

$$[N] = x = 10^{-25.6} \text{ atm.}$$

The potential of the cell with the reaction

$$NH_3 + \frac{3}{4} O_2 = N + \frac{3}{2} H_2O \qquad E_o = -0.040 \text{ V}$$

can be calculated from the standard potential for the reaction and from the equilibrium concentration of nitrogen atoms, assuming that the hydrogen gas never gets above its equilibrium pressure, i.e., $\frac{3}{2} \times 10^{-25.6}$ atm.

$$E = E_o - \frac{0.059}{3} \log [N]$$

$$E = -0.040 + (0.020)(25.6)$$

$$E = 0.0472 \text{ V}$$

This potential is considerably less than the potential of the reversible ammonia-oxygen fuel cell, but the fuel cell could still be economically feasible in special applications.

Comparison of economics of hydrogen and ammonia fuel cells

(prices quoted are paid by the Chemistry Department at Caltech)

1) Hydrogen-oxygen fuel cell: $H_2 + \frac{1}{2} O_2 = H_2O$

191 cu. ft. of hydrogen gas cost $3.59 — $\Delta F = 57$ kcal/mole of H_2 (22)

$$\frac{(191 \text{ cu ft})(28.3 \text{ liter/cu ft})}{(22.4 \text{ liter/mole})} \cdot \frac{(57 \text{ kcal/mole})}{(3.59 \text{ dollars})} = 3820 \frac{\text{kcal}}{\text{dollar}}$$

2) Reversible ammonia-oxygen fuel cell:

$$NH_3 + \frac{3}{4} O_2 = \frac{1}{2} N_2 + \frac{3}{2} H_2O \qquad n = 3$$

$$E_o = 1.134 \text{ V (see p. 113)}$$

15 lbs. of ammonia

cost $7.75

$$\Delta F = n \quad E$$

$$\Delta F = (3)(23.1)(1.134)\ \frac{\text{kcal}}{\text{mole of } NH_3}$$

$$\Delta F = 78.5 \text{ kcal/mole of } NH_3$$

$$\frac{(15 \text{ lbs})(454 \text{ gm/lb})}{(17 \text{ gm/mole})} \cdot \frac{(78.5 \text{ kcal/mole})}{(7.75 \text{ dollars})} = 4040 \text{ kcal/dollar}$$

The reversible ammonia fuel cell would be more economical than the hydrogen-oxygen fuel cell.

3) One irreversible ammonia-oxygen fuel cell is the following:

$$NH_3 + \frac{3}{4}O_2 = N + \frac{3}{2}H_2O \qquad n = 3$$

E_o = 0.472 V (see p. 115)

$$\Delta F = n \quad E$$

$$\Delta F = (3)(23.1)(0.472)\ \frac{\text{kcal}}{\text{mole of } NH_3}$$

$$\Delta F = 32.7 \text{ kcal/mole of } NH_3$$

$$\frac{(15 \text{ lbs})\ (454 \text{ gm/lb})}{(17 \text{ gm/mole})} \cdot \frac{(32.7 \text{ kcal/mole})}{(7.75 \text{ dollars})} = 1570 \text{ kcal/dollar}$$

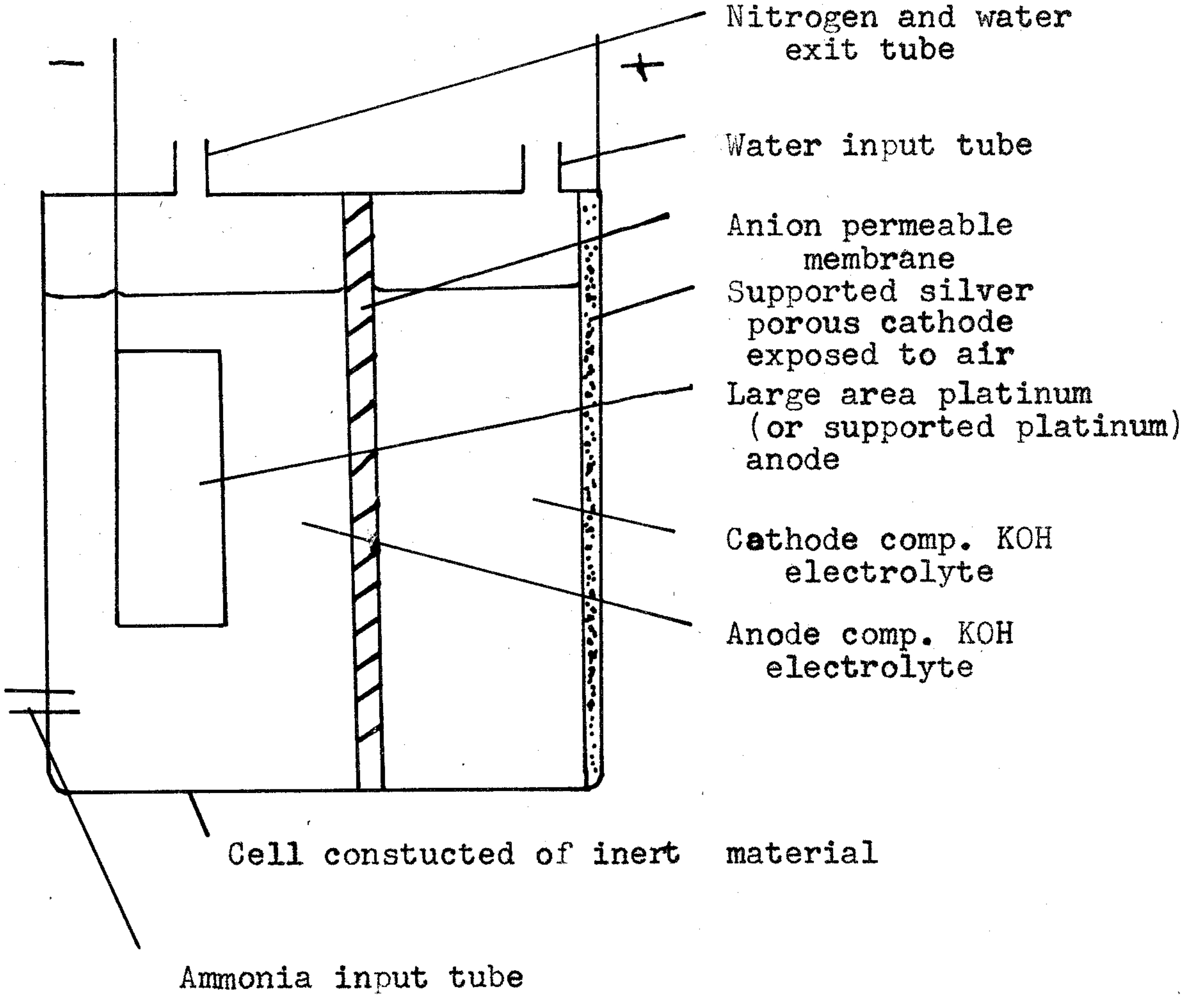
This cell would be less economical than the hydrogen-oxygen fuel cell.

The potential of the actual ammonia-oxygen fuel cell is probably neither of the two values above. The values stated are merely for comparison with the economics of the hydrogen-oxygen fuel cell. The actual potential of the ammonia-oxygen fuel cell would have to be determined by experiment.

Details of the proposition

The electrochemical cell described below is proposed to supply low voltage (d.c.) power when operated on ammonia and air (Fig. P-1).

Electrochemical Device designed to operate on ammonia and air to produce low voltage-d.c. power.



Electrode reactions:

Anode

$$2\ NH_3 + 6OH^- = N_2 + 6\ H_2O + 6\ e^-$$

Cathode

$$\frac{3}{2}\ O_2 + 3\ H_2O + 6\ e^- = 6\ OH^-$$

FIG. P-1

Electrode reactions

anode - fuel electrode (reversible)	E_o(22)
$2\ NH_3 + 6\ OH^- = N_2 + 6\ H_2O\ 6\ e^-$	0.733 V
cathode - air (oxygen) electrode	
$\frac{3}{2}\ O_2 + 3\ H_2O + 6\ e^- = 6\ OH^-$	0.401
cell reaction (reversible)	
$2\ NH_3 + \frac{3}{2}\ O_2 = N_2 + 3\ H_2O$	1.134 V

Electrode materials:

anode - platinum or platinum supported on some inert material, e.g., carbon (18), in such a concentration as to provide electrical conductivity and strength, but not be too expensive. The platinum serves as the catalyst for the dissociative adsorption and oxidation of ammonia.

cathode - silver has been shown to be among the most active catalysts for the electrode reaction of the oxygen-hydroxide ion half-cell in aqueous potassium hydroxide (23). The oxygen must be adsorbed in such a manner as to lead to rapid formation of peroxide and hydroxide. The peroxide should decompose rapidly on the catalyst surface. Groub Ib metals appear to be the most active catalysts. The electrode material should be porous, silver sponge or silver supported on carbon (or some other inert material) in such a way that there is both strength and electrical conductivity.

The porous material is to allow the gaseous oxygen to form as large a three phase contact as possible with the electrode and the solution.

Electrolyte:

Aqueous potassium hydroxide 1-3 VF is to be used so that there is a limited solubility of ammonia in the solution, as well as low solution resistance.

Electrochemical cell:

The electrochemical cell is to be constructed of an inert plastic or stainless steel divided into two compartments which are separated by an anion permeable membrane (see Fig. P-1). One section of the cell is the porous silver electrode and is exposed to atmospheric oxygen. The details of introduction of ammonia, of removal of nitrogen and water from the anode compartment and of addition of water to the cathode compartment need to be worked out.

Anion permeable membrane:

An anion (hydroxide) permeable membrane is necessary to pass hydroxide ions from cathode to anode compartment but to keep ammonia out of the cathode compartment. A heterogeneous anion permeable membrane may be prepared by milling a vinyl chloride-vinyl acetate resin with an anion resin of the quaternary ammonium type (24).

Temperature: ambient (at least 20° C).

Advantages

The direct conversion of the chemical energy of fuels into electrical energy will be a great benefit to mankind. The invention of a fuel cell which will operate on carbonaceous fuels will be such a benefit. The use of ammonia in fuel cells, while a step in the right direction, would find only limited applications because of the relatively high cost of ammonia. Ammonia does have some advantages over hydrogen for use in fuel cells. Ammonia is easier to handle than hydrogen. Ammonia can be liquefied under fairly low pressures and transported easily. Hydrogen is not easily liquefied and is difficult to transport. Also, as mentioned earlier, ammonia has a finite solubility in the alkaline electrolyte. Only a two phase electrode reaction of the fuel, electrode and electrolyte need be considered.

3. Amperometric Titration of Germanium(IV) with Tiron

An amperometric determination of germanium(IV) is proposed in which the unknown germanium solution in phosphate buffer at pH 11 is titrated with a standard solution of Tiron (disodium pyrocatechol-3,5-disulfonate). A dropping mercury electrode polarized at -1.75 V vs. S.C.E. is to be used to determine the end point in this amperometric titration.

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Background for the proposition

Germanium(IV) has been reduced to the metal at a dropping mercury electrode in alkaline solutions. A two step polarographic wave (the second step with a pronounced maximum) was noted for the reduction of germanium(IV) in ammonia-ammonium chloride buffer (25, 26). A single reduction wave was observed by Dahr, in non-complexing media, for the reduction of Ge(IV) in buffers from pH 5 to pH 12 (27). His results show this wave to be very irreversible. Das Gupta and Nair (26) noted the improvement of shape of the polarographic wave with added maximum suppressor. With added gelatin the reduction wave became much sharper.

The two-step reduction wave for Ge(IV) in ammoniacal buffer was also observed by Sauvenir and Duyckaerts who noted that the height of the wave (diffusion current) was dependent on pH but was nearly constant over the pH range 8-9 (28). The heights of the waves were difficult to measure because of the pronounced maximum in the second wave.

Recently Ge(IV) has been reduced in acetate media (29). The wave was most distinct in the pH range 7.0-8.5 and the height of the wave could best be measured in this range. However, it should be noted that this pH range is well outside the maximum buffer region of acetate-acetic acid buffers. The reduction of Ge(IV) depends markedly on pH:

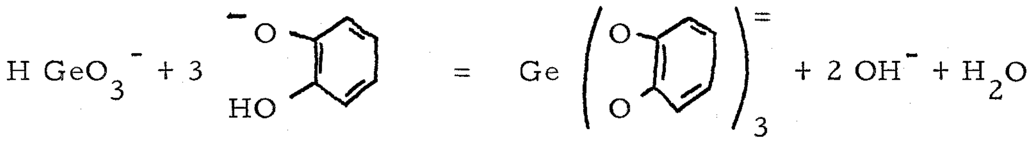
$$H_2GeO_3 + H_2O + 4\,e^- = Ge + 4\,OH^- \;.$$

A fairly high capacity buffer is required to keep the hydrogen ion concentration nearly constant near the electrode.

As a problem in undergraduate research at Princeton University, this author investigated the conditions for possible polarographic determination of germanium (30). A linear calibration curve, relating diffusion current to concentration, was established from reductions of Ge(IV) in phosphate buffer at pH 11. A fairly high concentration of methyl cellulose (0.03%) improved the wave form to almost reversible appearance. The half-wave potential was -1.69V vs. S.C.E.;

diffusion current constant (I) was 3.01 ± 0.07 measured at -1.75 V vs. S.C.E.; the concentration range of constant I was 1.6×10^{-4} to 4.0×10^{-3} VF Ge(IV).

Germanium(IV) combines mainly with hydroxide ions or hydroxyl groups of complexones (31). There is little tendency for germanium(IV) to combine with the basic nitrogen in complexones. Thus, no EDTA-germanium(IV) complex was observed in the reduction of Ge(IV) in EDTA media (25, 30). Polyphenols are good complexing agents for germanium(IV). Bevillard showed that germanium(IV) formed stable complexes with a large number of ortho-diphenols (32). With pyrocatechol a 3:1 complex was formed in basic solution:



The germanium(IV) has been determined by titration of the acid formed when GeO_2 was dissolved in excess pyrocatechol (33). In a similar determination pyrocatechol was added to a Ge(IV) solution at pH 5 and the mixture was back-titrated with NaOH to pH 5 (34).

Aqueous pyrocatechol solutions are not very stable, being slowly air oxidized to the orthoquinone. A similar compound which does form stable aqueous solutions is Tiron (disodium pyrocatechol-3,5-disulfonate). This compound has found use in the colorimetric determinations of iron (35), titanium (36), molybdenum (37, 38) and copper (39).

Schwarzenbach has stated that the use of polyphenols for titrations of germanium and similar compounds looked promising, but that complex formation might be slow (31). In reactions of both copper and molybdenum with Tiron the reactions were reported to be immediate (37, 39). It is not unreasonable to expect that the reaction of Tiron with germanium(IV) in alkaline solutions should be rapid enough for an amperometric titration.

In an amperometric titration of germanium(IV) with Tiron a dropping mercury electrode would be used to determine the germanium concentration. No reduction of the germanium(IV)-pyrocatechol complex was observed before the reduction of water in polarographic studies of this complex (30). The height of the reduction wave of germanium(IV) in a germanium(IV)-Tiron solution, buffered in alkaline medium, should be proportional to the amount of uncomplexed germanium(IV). The amperometric titration curve should exhibit a linear decrease of the diffusion current, as the Tiron concentration is increased, followed by a constant background diffusion current beyond the end point. The end point should occur at a molar ratio of 3 Tiron to 1 Ge(IV).

Details of the proposition

A conventional polarographic assembly is to be used with the dropping mercury electrode polarized at -1.75 V vs. S.C.E. The electrolyte should be 0.2 VF phosphate buffer at pH 11.0, with 0.03% methyl cellulose added to sharpen the wave. Samples of 4×10^{-3} VF Ge(IV) or less should be determined in this titration.

Titrating solution: solutions of Tiron (commercially available from La Motte Chemical Products Co., Baltimore, Md.) are stable for periods of several months (39). Such solutions could be standardized against solutions of electrolytic copper by a number of procedures, including colorimetric (39) and, probably, potentiometric titrations.

Applications

This analytical determination of germanium(IV) will not tolerate many interferences, as most substances are reduced before germanium(IV). EDTA can be added to the solution, without affecting the germanium determination, to mask some interferences. The simplest way to remove interferences is to separate germanium before attempting the determination. This can most easily be accomplished by distilling $GeCl_4$ (b.p. 83.1°C) from 6 VF hydrochloric acid solution or by separating H_2GeO_3 (pK_a 9.1) from metallic cations on a cation exchange column.

The amperometric titration should provide a simple and straightforward analysis for germanium - a substance which has recently become rather important to the electronics industry.

4. Use of N-Methyl Acetamide as a Solvent in Electroanalytical Studies.

N-methyl acetamide has been investigated as a solvent in non-aqueous polarographic studies (40). In view of several very attractive properties of this solvent, extension of the use of this solvent to further electroanalytical applications is proposed. First, several important changes in the polarographic technique are proposed. Second, use of a platinum electrode in both current-potential studies and chronopotentiometric studies is proposed. Using a platinum electrode would enable one to study oxidations as well as reductions in this solvent.

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Background for this proposition

N-methyl acetamide should be a very useful solvent for electrochemical studies of both organic and inorganic substances. It has the following physical properties:

Property	water (20°C)	N-methyl acetamide (40°C) (40,41)
melting point, °C	0°	29°-29.5°
boiling point, °C	100°	206°
dielectric constant	78.5	165.5
viscosity, poises	0.00917	0.02411
density, gm/ml	0.998	0.9421

N-methyl acetamide is a very good solvent for organic compounds. Its methyl groups give it solvent power for hydrocarbons; its carbonyl group relates it to ketones, esters and acids; its amino group relates it to derivatives of ammonia; and its tautomeric hydroxyl group relates it to alcohols and water.

As a solvent for inorganic materials N-methyl acetamide, with its very high dielectric constant, acts very much like water. Alkali halides are completely dissociated in this solvent (41). Substituted ammonium halides are also completely dissociated as N-methyl acetamide, like water acts as a leveling medium for strong acids (42). Hydrogen chloride, picric acid and many univalent salts including nitrates and perchlorates are completely dissociated in the solvent (43). Picric acid appears to be more dissociated in N-methyl acetamide than in water as the former solvent is a stronger base than water. Alkaline earth halides are soluble but may not be completely dissociated (44). Hydrated salts lose their water in solution and appear to be solvated with N-methyl acetamide.

N-methyl acetamide is easily purified (derivatives of formamide are purified only with difficulty) by fractional distillation and subsequent fractional crystallization, the fraction which melted above 29°C only being used (41). The fairly high viscosity of N-methyl acetamide limits rates of diffusion (45) and decreases the equivalent conductance of ions somewhat relative to water. Unusual solvation effects are observed in this solvent (as compared with water) in that the equivalent conductance of the alkaline earth halides is 15-20% greater than potassium ions (44). In water the equivalent conductance of potassium ion is greater than barium ion (at infinite dilution) (46).

The melting point of N-methyl acetamide at 29°C makes it necessary to work with this solvent slightly above room temperature. This is a little inconvenient, but by no means a serious problem.

Sellers and Leonard used N-methyl acetamide as a solvent for polarographic studies of a typical inorganic electrochemical reaction - reduction of cadmium iodide (40). In these studies, using tetraethylammonium bromide as supporting electrolyte, a usable potential range from zero to -1.8 V vs. mercury pool ref. electrode was observed. Excessive exposure to atmospheric moisture was avoided during preliminary investigations but it is felt by this author that the reduction at -1.8 V was probably that of water, a contaminant either in the solvent or in the deliquescent supporting electrolyte. Using the dry-box conditions of Dawson et al. (45) a higher background reduction potential should be attainable. Also, Meites and coworkers have questioned the advisability of the use of tetraalkylammonium salts as supporting electrolytes in polarographic studies (47). The tetraalkylammonium salts seem to be adsorbed on the surface of the mercury drop and may have pronounced effects on the half-wave potentials and diffusion currents obtained.

Details of the proposition

I.) Changes in polarographic procedure:

1) Pains should be taken to exclude water from the solvent.

2) A supporting electrolyte of sodium perchlorate should be used instead of the tetraethylammonium bromide for three reasons:

   a) Sodium perchlorate can be easily prepared pure and dry (by recrystallization from acetic acid, and removal of acetic acid of crystallization).

   b) Sodium perchlorate is not adsorbed on the mercury drop.

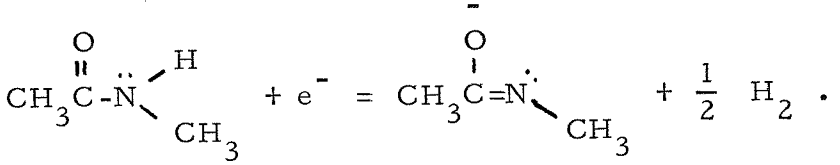
   c) Perchlorate ion will allow the polarographic studies to be performed at more anodic potentials. With a bromide electrolyte the anodic potential is limited by the oxidation to the insoluble mercurous bromide. With perchlorate the anodic limiting potential is that of the oxidation of mercury to mercurous (ic?) ions. This difference in potential could be about half a volt.

With these two changes the potential range for polarographic studies in N-methyl acetamide should be from ca. +0.5 V vs. ref. (oxidation of mercury to mercurous ions) to ca. -2.0 V vs. ref. (reduction of the

N-hydrogen in the solvent). This increase in potential range would permit studies of iron(III), copper(II), and bismuth(III), which Sellers and Leonard found reduced too close to the anodic wave of the system (40). The reduction of the more difficultly reducible compounds, such as some tetraalkylammonium compounds (48), could be studied at the more reducing end of the scale.

II.) Studies at platinum electrodes:

The use of this solvent with a supporting electrolyte of sodium perchlorate should be extended to studies with platinum electrodes. Using perchlorate ion in the supporting electrolyte would permit more oxidizing potentials to be attained than the more easily oxidized halide ions permit. In current-potential studies with a rotating platinum electrode and chronopotentiometric studies, oxidation potentials would be limited only by the oxidation of the solvent. This oxidation, if analogous to the oxidation of acetic acid, should occur only at very oxidizing potentials. The reduction limiting potential will be determined by the potential at which the solvent is reduced. The dissociation constant of N-methyl acetamide should be slightly less than that of water and it is expected that the reduction of the solvent would be:



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}-\ddot{N}\begin{matrix}\diagup H\\ \diagdown CH_3\end{matrix}} + e^- = \mathrm{CH_3\overset{\overset{\bar{O}}{|}}{C}=\dot{\dot{N}}\diagdown CH_3} + \frac{1}{2}\ \mathrm{H_2}\ .$$

Applications

This solvent should find a great number of applications in electrochemical studies. There are advantages of being able to study the electrode reactions of both organic and inorganic compounds in the same media. Solvating properties of this solvent are different from water mainly in the size of the solvent molecule and in the tendency of the solvent to form linear chains rather than three-dimensional clusters. Different solvating properties may show up in different electrochemical behavior of ions which are solvated with water molecules in aqueous solutions.

5. Coulometric Titrations of Strong Acids in Acetic Acid-Acetic Anhydride.

A coulometric titration of strong acids in acetic anhydride-acetic acid (10 mole %) is proposed in which electrogenerated acetate ion is used to titrate the acids. Only acids stronger than hydrochloric acid are determined in this acidic solvent solution. It should be possible to determine components of various binary mixtures of strong acids,

$$HClO_4, HBF_4, HI, p\text{-}CH_3C_6H_4SO_3H, HBr \text{ and } H_2SO_4 ,$$

by this method. Components of such mixtures are impossible to differentiate in most other solvent systems.

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Background for this proposition

Markunas and Cundiff have shown that individual components of mixtures of some acids can be determined by titration in pyridine with tetrabutylammonium hydroxide (49, 50, 51). Two potential inflections were observed in the titration of a mixture of hydrochloric and sulfuric acid with tetrabutylammonium hydroxide in pyridine (49). The first inflection corresponded to the titration of the hydrochloric acid and the first proton of the sulfuric acid and the second inflection to the titration of bisulfate ion. Components of a mixture of hydrochloric acid, benzoic acid and phenol were differentiated by this titration (50). In general, components of a mixture of acids could be determined if (a) they were weaker than nitric acid and (b) they were sufficiently different from each other in acidity (3 or 4 pK units different in their dissociation constants).

In anhydrous acetic acid it is possible to determine components of mixtures of strong acids (52). Components of mixtures of perchloric acid and sulfuric acid, of perchloric acid and hydrochloric acid, and of p-toluene sulfonic acid and nitric acid were readily determined in anhydrous acetic acid by titration with pyridine and dimethyl aniline.

In part II of this thesis perchloric acid was determined by means of a coulometric titration with electrogenerated acetate ion (53). The proposition is to extend this coulometric titration to the determination of other strong acids and mixtures of strong acids.

Details of the proposition

A coulometric titration assembly similar to that employed in part I of this thesis is to be used (54). A platinum electrode is substituted for the mercury electrode and is used as the cathode in the coulometric titrations. The glass-reference electrode assembly is the same as described in part I of this thesis.

The predominant electrode reaction is the reduction of acetic acid in the acetic acid-acetic anhydride-sodium perchlorate electrolyte with the formation of sodium acetate and hydrogen (55).

The solvent mixture of acetic anhydride and acetic acid could be adjusted (a) to control the acidity of the electrolyte and hence the acids which could be determined, and (b) to control the reaction of hydrogen ions with acetic anhydride which form the slightly dissociated products discussed in part II of this thesis. This latter problem is not serious when the concentration of acetic acid is greater than about 10 mole % and the concentration of strong acid is 10^{-3} VF, or less. If the coulometric titration is performed within 30 min. of mixing, no appreciable loss of hydrogen ions should be observed.

Applications

This method should facilitate the analysis of mixtures of strong acids. The coulometric titration is rapid and does not require any standard solutions or indicators. The potentiometric end point should enable one to obtain accuracies of ± 0.2% in these titrations. The possible accuracies attainable will depend on the difference in acidity of the two acids to be determined. In general, at least 3 or 4 pK units difference is necessary in their dissociation constants. This would be a simple method of determining components of certain binary mixtures of these strong acids:

$HClO_4$, HBF_4, HI, p-$CH_3C_6H_4SO_3H$, HBr and H_2SO_4.

Individual strong acids may also be determined in the presence of weaker acids such as HCl and HNO_3.

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